

Spectroscopy and photodissociative processes of diatomic molecules

Georgi B. Mitev

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
of
University College London.

Department of Physics & Astronomy
University College London

December 11, 2024

I, Georgi B. Mitev, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.

Research Paper Declaration

1. **G. B. Mitev**, S. Taylor, J. Tennyson, S. N. Yurchenko, A. A. Buchachenko, A. V. Stolyarov, 2022;
ExoMol molecular line lists – XLIII. Rovibronic transitions corresponding to the close-lying X $^2\Pi$ and A $^2\Sigma^+$ states of NaO *Mon. Not. Roy. Astron. Soc.* 511, 2349-2355, [10.1093/mnras/stab3357](https://doi.org/10.1093/mnras/stab3357).
Line list adapted for Chapter 3.
2. **G. B. Mitev**, J. Tennyson, S. N. Yurchenko, 2024;
Predissociation dynamics of the hydroxyl radical (OH) based on a five-state spectroscopic model, *J. Chem. Phys.* 160, 144110, [10.1063/5.0198241](https://doi.org/10.1063/5.0198241).
Methodology for predissociation lifetimes adapted for Chapter 5.
3. J. Tennyson, S. N. Yurchenko, J. Zhang, C. A. Bowesman, R. P. Brady, K. L. Chubb, E. R. Guest, C. Hill, A. E. Lynas-Gray, L. K. McKemmish, **G. B. Mitev**, A. Owens, A. N. Perri, M. Pezzella, O. L. Polyanksy, M. Semenov, O. Smola, A. Sokolov, W. Somogyi, A. Upadhyay, S. O. M. Wright., 2024;
The 2024 release of the ExoMol database: molecular line lists for exoplanet and other hot atmospheres. *J. Quant. Spec. Rad. Trans.* 326, 109083, [10.1016/j.jqsrt.2024.109083](https://doi.org/10.1016/j.jqsrt.2024.109083).
4. S. N. Yurchenko, C. A. Bowesman, R. P. Brady, E. R. Guest, K. Kefala, **G. B. Mitev**, A. Owens, A. N. Perri, M. Pezzella, O. Smola, A. Solokov, J. Zhang, J. Tennyson, 2024;
ExoMol line lists – LX. Molecular line list for the ammonia isotopologue $^{15}\text{NH}_3$, *Mon. Not. Roy. Astron. Soc.* [10.1093/mnras/stae1849](https://doi.org/10.1093/mnras/stae1849).

Glossary

Software:

MARVEL: Measured Active Rotational-Vibrational Energy Levels is an algorithm by [Furtenbacher et al. \(2007\)](#) which takes as input assigned experimental transitions and returns self-consistent energy levels. For more details see Section [2.5.1](#).

DUO: A general and parallelised Fortran 2003 code designed to solve the coupled multi-channel Schrödinger equation for diatomics. For more details see Section [2.1.3](#).

EXOCROSS: A general and parallelised Fortran 2003 code designed to produce absorption and emission cross-sections. For more details see [Yurchenko et al. \(2018c\)](#).

PYEXOCROSS: A general and parallelised Python 3 code designed to produce absorption and emission cross-sections. For more details see [Zhang et al. \(2024b\)](#).

LEVEL: A program by [Le Roy \(2017b\)](#) designed to solve the radial Schrödinger equation for $^1\Sigma$ systems.

PGOPHER: A program by [Western \(2017\)](#) used to produce effective Hamiltonian models.

.STATES: File containing all rovibronic levels computed using DUO.

.TRANS: File containing rovibronic transitions between levels in the .STATES file computed using DUO.

.PF: File containing a temperature-dependent partition function. See Sections [3.3.2](#) and [4.6.2](#).

.CONT: File containing continuum absorption cross-sections see Chapter [6](#).

BINSLT: Python 3 code used in conjunction with DUO .STATES files to calculate predissociation lifetimes for diatomic molecules. Available at github.com/exomol.

PYFIT: A Python 3 wrapper for DUO developed to leverage readily available sophisticated non-linear optimization packages, e.g. Dual-Annealing. Available at github.com/gbmitev

Line lists:

MYTHOS: Mitev-Yurchenko-Tennyson-Hydrogen-Oxygen - a high accuracy rovibronic line list for OH in the ExoMol format for use in (hot) exoplanetary and stellar studies. Produced in Chapter [4](#)

NAOUCME: Rovibronic line list for NaO for use in (hot) exoplanetary studies. Pronounced: “Now you see me.” Produced in Chapter [3](#)

Algorithms:

Huber loss Regression: Non-linear regression algorithm which is more resistant to outliers than standard gradient descent ([Huber & Ronchetti, 2009](#)).

Dual-Annealing: Non-linear optimization algorithm building on Simulated Annealing, which uses principles from annealing in metallurgy to approximate the global minimum of a given function ([Xiang et al., 1997](#)).

Telescopes:

ARIEL: Atmospheric Remote-sensing Infrared Exoplanet Large-survey - an upcoming space telescope mission ([Tinetti et al., 2018](#)).

JWST: James Webb Space Telescope - an active space telescope mission ([Gardner et al., 2006](#)).

ELT: Extremely Large Telescope - an upcoming ground-based high resolution telescope ([Brandl et al., 2010](#)).

Astronomical Spectroscopy:

Direct Imaging: A technique whereby a real image of a target object is resolved ([Currie et al., 2023](#))

Transit Spectroscopy: A technique whereby variations in the detected flux from star+planet system during the planet’s transit are leveraged to infer the atmospheric composition of the planet ([Tinetti et al., 2006](#)).

Doppler Shift Spectroscopy: A technique which leverages the Doppler shift of the exoplanetary spectrum to determine the planet’s composition ([Birkby, 2018](#))

Abstract

In the wake of novel high-resolution spectroscopic techniques, the launch of the James Webb Space Telescope, and in preparation for the Atmospheric Remote-sensing Infrared Exoplanet Large-survey (ARIEL) mission, the modelling of exoplanetary atmospheres has increasingly required complete molecular datasets in the form of line lists which meet the high resolution standard.

By applying rigorous quantum mechanical treatments informed by experimental data, line lists are generated for the terrestrially significant radical species sodium monoxide (NaO) and hydroxyl (OH), which has been detected in a wide range of exoplanetary, stellar, and interstellar environments. *Ab initio* electronic structure calculations, spectroscopic model refinement, and a number of post-processing techniques are combined to produce these data. Measured Active Rotational-Vibrational Energy Level (MARVEL) energy levels substitute equivalent levels in the OH line list, with rigorously estimated uncertainties in experimentally dark regions, following the hybridization procedure.

Strong focus is placed on the dissociative processes of OH. Most current photodissociation databases do not consider temperature, which is not suitable for high-resolution studies of hot-exoplanets, motivating techniques to produce temperature dependent photodissociation cross sections and rates. The photodestruction of molecules through photodissociation is of high astrochemical importance in the presence of radiation rich environments, particularly in the evolution of hot exoplanetary atmospheres which experience strong fluxes. Established post-processing methodology is generalised and automated for the efficient production of photodissociation cross sections.

Predissociative effects such as spin-orbit predissociation broadens select transition lines in some species, allowing for detection of such molecules in optically thick regions and leads to a lower threshold for photodissociation. An implementation of the so-called stabilization method for the rigorous computation of predissociation widths of diatomic molecules is presented, with application to OH and SH, reproducing experimental resonances to high fidelity. In light of this, methods are also proposed for a more complete treatment of continuum states in general which are known to have a significant impact on the line positions of bound-bound absorption spectra.

Impact Statement

The line lists and photoabsorption spectra presented in this work aim to serve as high-quality datasets applicable in many fields for the study of many environments, including stars, exoplanets, interstellar molecular clouds, and the terrestrial atmosphere.

The studies on NaO presented here support the understanding of sodium abundances through D-line emissions in the upper atmosphere, the composition of rocky lava planets that are metal-rich, and the composition of certain comets and meteors. NaO is a highly reactive and transient species, however, so its spectra may indeed be used to act as a tracer for other atoms and molecules of importance, particularly sodium and sodium hydroxide (NaOH) through both chemical and photodissociative processes. These species are significant in rocky Super-Earths.

Hydroxyl's importance in a number of astrophysical systems is well established, and is of interest recently through its detection in several ultra hot-Jupiter atmospheres. The line list produced here will hopefully be used for further, more statistically significant detections of OH, especially now that the dataset is extended further into the UV and includes previously disregarded effects, such as temperature dependent photodissociation and predissociation. This allows for the detection of OH in regions of significant radiation, particularly in the UV, and in optically thick environments, where non-predissociated lines may be saturated.

There are also further applications of this work due to the importance of OH in the atmosphere as an oxidizing agent for chlorofluorocarbons (CFCs) and as a source of heat in the upper atmosphere, assisting in the fight against climate change, and as a major component in combustion chemistry, which could be used to produce more efficient combustion, and for the detection of recently launched missiles.

The methods developed to produce self-consistent and reliable temperature dependent photodissociation cross sections and predissociation resonance widths will likely see further development in the coming years. Initial applications will likely focus on application to other diatomic molecules to refine workflows and improve efficiency, before extension to polyatomic molecules. The programs written to produce gaussian smoothed photodissociation cross sections are easily applicable to polyatomics and have been already applied to HCN by M. Pezzella et al.

Complete treatment and refinement of continuum states has not been approached rigorously within the ExoMol group at UCL. However, the current implementation of the predissociation methods returns a technique to do this. The impact that continuum state perturbations have on bound rovibronic levels is established, so a facility to treat them will be important to further increase the accuracy, resolving power, and extrapolation predictability of our data sets.

Acknowledgements

I would like to thank my supervisors Prof. Jonathan Tennyson and Prof. Sergey N. Yurchenko for awarding me their valuable time, expertise, and seemingly endless patience. Without your guidance and encouragement this would have been an impossible enterprise.

I would also like to thank my collaborators Prof. A. V. Stolyarov and Prof. A. A. Buchachenko for their important contributions to the NaO line list project, NaOUCMe; Tibor Furtenbacher, Samuel T. Hegedus, Jonathan Tennyson and Atilla G. Császár for their recent MARVEL network of OH which was used extensively throughout the project; Marco Pezzella and Bridgette Cooper for their invaluable expertise in electronic structure calculations; Ryan Brady and Oleksiy Smola for their efforts in the production of predissociation lifetimes for OH, SH, and SD; Jingxin Zhang for her work on and continued support with PYEXOCROSS, which was used in the predissociation and photodissociation studies; and to Charles Bowesman for his hybridization of the MYTHOS line list.

I extend appreciation to my fellow PhD students and academic colleagues, Tony Lynas-Gray, Marco Pezzella, Bridgette Cooper, Alec Owens, Andrei Sokolov, Oleg Polyansky, Mikhail Semenov, Kyriaki Kefala, Elizabeth Guest, Ryan Brady, Wilfrid Somogyi, Apoorva Upadhyay, Jingxin Zhang, Thomas Mellor, Oleksiy Smola, Armando Perri, and Charles Bowesman for their unwavering support, great ideas, expert programming ability, and their capacity for positivity. You have made this a truly enjoyable experience.

I am thankful to my close friends, Aditya Ramani and Zoltan Kalmar, with whom I began this journey an eye-watering eight years ago as an undergraduate. Thank you for your support, your consistency, and most importantly - your friendship.

I express my eternal gratitude to my partner, Synne Kjelsrud. Thank you for tolerating me as I rambled on endlessly about my research and thesis, for being a constant presence full of love, support, and encouragement, and for making these last few years so much more than just bearable. You have been my rock and I could not have done it without you.

Finally, this could not in a million years have been possible without my dear family, Tanya Krasteva, Bogdan Krastev, and Genka Mihailova. Your support, faith, and guidance has spurred me on and you continue to inspire me to do my best.

This work was supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program through Advance Grant number 883830. I also acknowledge the use of the UCL Myriad High Performance Computing Facility (Myriad@UCL), and associated support services, in the completion of this work.

Contents

1	Introduction	29
1.1	Molecular Databases	30
1.2	Motivation of Theoretical Molecular Spectroscopy	32
1.3	Sodium Oxide Radical - NaO	33
1.4	Hydroxyl Radical - OH	34
1.5	Structure of this Thesis	36
2	Background, Theory, and Software	37
2.1	The Molecular Hamiltonian	37
2.1.1	The Born-Oppenheimer Approximation	38
2.1.2	The Nuclear Motion Problem	39
2.1.3	DUO	41
2.2	Electronic Structure Calculations	46
2.2.1	Hartree-Fock Self-Consistent Field (SCF)	47
2.2.2	Multi-configuration Self-Consistent Field Methods	49
2.2.3	Configuration Interaction (CI)	51
2.2.4	Multi-Reference Configuration Interaction (MRCI)	51
2.3	ExoMol and Line lists	52
2.4	Simulating Absorption Spectra	52
2.5	Energy Levels	54
2.5.1	MARVEL	54
2.5.2	PGOPHER	55
3	Sodium Oxide (NaO) Linelist	57
3.1	Introduction	57
3.1.1	Quantum Number Conversions	57

3.2	Methods	58
3.2.1	Electronic Structure Calculations	58
3.2.2	Fitting Procedure	59
3.3	Results and Discussion	63
3.3.1	Potential energy curves, spin-orbit and L -uncoupling matrix elements	63
3.3.2	Partition Function	64
3.3.3	Final line list and absorption spectra simulation	68
3.3.4	Comparison with the experimental $X \rightarrow A$ spectra	70
3.4	Conclusions	73
3.4.1	Data Availability	73
4	Hydroxyl (OH) Linelist	75
4.1	Introduction	75
4.1.1	Summary of MARVEL energies and quantum number conventions	76
4.2	<i>Ab initio</i> electronic structure calculations	79
4.2.1	Electronic Structure of $X^2\Pi$, $A^2\Sigma^+$ and $1(^2\Sigma^-, ^4\Sigma^-, ^4\Pi)$	79
4.2.2	Electronic Structure of $(B,C)^2\Sigma^+$ and $1^2\Delta$	80
4.3	Spectroscopic Model	84
4.3.1	Global parameters	84
4.3.2	Fitting - $X^2\Pi$ and $A^2\Sigma^+$	86
4.3.3	Fitting - $B^2\Sigma^+$ and $C^2\Sigma^+$	88
4.3.4	Summary of Shape sets and Initial Parameter sets	91
4.4	Bound and unbound rovibronic states	92
4.4.1	Differentiating between bound and unbound states	94
4.5	Simulation of Absorption Spectra	104
4.5.1	Line broadening	105
4.5.2	Voigt line profile	107
4.5.3	Continuum absorption and Photoabsorption Spectra	107
4.6	Results	108
4.6.1	Spectroscopic model of OH	108
4.6.2	Partition function	118
4.6.3	Line list and bound to bound transitions	122
4.6.4	Simulation of absorption spectrum	123

4.7	Conclusions and Future Work	127
4.7.1	Data Availability	127
5	Predissociation of Diatomic Molecules	129
5.1	Introduction	129
5.2	Spin-Orbit Predissociation Lifetimes - General Procedure	132
5.2.1	Leveraging Duo Spectroscopic Models - Stabilization Method . . .	132
5.2.2	Statistical Treatment	134
5.3	Spin-Orbit Predissociation Lifetimes - Numerical Treatment	136
5.3.1	Centring energy profile	136
5.3.2	Initial Parameter values	140
5.3.3	Bin numbers	140
5.3.4	Long lifetimes	141
5.3.5	Skewed Energy profiles	142
5.3.6	Uncertainty estimation	143
5.3.7	Stabilization Fitting	147
5.4	Rotational Predissociation	148
5.5	Results - OH	149
5.5.1	Lifetime Analysis	149
5.5.2	Comparison with Literature	154
5.5.3	Centroids of OH	158
5.6	Preliminary Results - SH/SD	159
5.7	Conclusion and Future work	161
5.7.1	Data Availability	163
6	Direct Photodissociation of OH	165
6.1	Introduction	165
6.2	Methods	166
6.2.1	Leveraging DUO Spectroscopic Models	166
6.2.2	Numerical Treatment	169
6.2.3	Photodissociation Rates	174
6.2.4	Non-LTE Photodissociation Cross-Sections - Preliminary Methods .	176
6.3	Results	179

6.3.1	Photodissociation cross-sections	179
6.3.2	Rates	181
6.4	Conclusion and Future Work	183
6.4.1	Data Availability	184
7	Conclusion	185
7.1	Summary	185
7.2	Future Work	186
	Bibliography	188

List of Figures

2.1	Electronic energy including internuclear repulsion as a function of internuclear separation, R , for a diatomic molecule (Levine, 2013).	39
3.1	<i>ab initio</i> MRCI PECs for the X $^2\Pi$ and A $^2\Sigma^+$ electronic states of NaO. . . .	59
3.2	On-diagonal, $A_{so}(R)$, and off-diagonal, $\xi_{AX}(R)$, spin-orbit coupling curves evaluated by MRCI method for the X-state and A-states (top). $L_{AX}(R)$ is the non-adiabatic matrix element of electron-rotational interaction <i>ab initio</i> calculated between the X-state and A-states (bottom).	60
3.3	Permanent, $d_{XX}(R)$, $d_{AA}(R)$, and transition, $d_{AX}(R)$, dipole moment functions <i>ab initio</i> calculated for the X-state and A-states of NaO molecule. . . .	61
3.4	Empirical EMO (fitted) and original <i>ab initio</i> point-wise potential energy curves obtained for the X $^2\Pi$ and A $^2\Sigma^+$ states of NaO (upper panel); Distance-dependent exponent coefficient for X $^2\Pi$ and A $^2\Sigma^+$ state EMO fits as normalised by $\beta_0 = A_0$ (lower panel).	65
3.5	Diagonal, $A_{SO}(r)$, and off-diagonal, $\xi_{AX}(r)$, spin-orbit coupling curves <i>ab initio</i> calculated for the X-state and A-states.	66
3.6	$L_{AX}(r)$ is the corresponding non-adiabatic matrix element of electron-rotational interaction between the X-state and A-state.	66
3.7	Partition function $Q(T)$ convergence of NaO as dependent on maximum value of rotational quantum number, $J_{\max}$ for temperatures up to 2500 K. . . .	68
3.8	Comparison between, (a): calculated partition function based on Duo states and available data for the partition function of NaO (b): Pickett et al. (1998), (c): Barklem & Collet (2016). Note, $Q(T)$ by Barklem & Collet (2016) has been multiplied by four to account for the convention of including the hyperfine structure degeneration number g_{ns} in the partition function calculation, see Equation 3.14. Upper: Close-up of calculated and reference partition functions for $T \in [0, 300]$ K. Lower: Log scaled representation of calculated and reference partition functions for $T \in [0, 2500]$ K.	69
3.9	Absolute absorption intensity (arbitrary units) spectrum of NaO computed at $T = 400$ K. Black lines represent the experimental transitions containing (from left to right) the observed A $^2\Sigma^+(0, 1) \leftarrow$ X $^2\Pi(0)$ transition bands from Joo et al. (1999). Black vertical lines indicate start and end of the observed band transition regions.	72

3.10	Spectrum of NaO at varying temperatures. Absorption cross-sections were modelled with a Gaussian line profile with HWHM at 1 cm^{-1} with an output on a grid with 1 cm^{-1} spacing.	72
4.1	<i>Ab initio</i> potential energy curves for OH as computed in MOLPRO.	81
4.2	Diagonal and off-diagonal <i>ab initio</i> spin-orbit coupling curves of OH as computed in MOLPRO. The curves here also have an associated factor of $\pm i$	82
4.3	<i>Ab initio</i> L-uncoupling matrix elements for OH as computed in MOLPRO. In the Cartesian coordinate system, there is a factor of $\pm i$	83
4.4	First 8 A_1 symmetry potential energy curves of OH as calculated in MOLPRO using the aug-cc-pV5Z basis set and $6\sigma 2\pi$ active space. The labelling here is [Energy Order].[Symmetry].	84
4.5	<i>Ab initio</i> potential energy curves for the $1^2\Delta$, $B^2\Sigma^+$, and $C^2\Sigma^+$ states of OH.	85
4.6	Example of bound state (upper) and unbound state (lower) wavefunction densities for the $A^2\Sigma^+$ state of OH. The red line is the effective potential $V_{\text{eff}}(R)$ (see Equation 4.38), and the blue line is the unperturbed potential $V(R)$. Baseline of the wavefunction has been placed to sit at level's energy, and the amplitude has been scaled for clarity only.	94
4.7	Effective potential energy curves of OH $X^2\Pi$ state for every J up to 63.5. Black dots indicate $\tilde{D}_e(J)$ at $\tilde{R}(J)$ and black squares indicate $T_e(J)$ at $R_e(J)$	96
4.8	$\int_{R_c-\epsilon}^{R_c} \psi^2(R) dR$ for each MARVEL level of the $X^2\Pi$ and $A^2\Sigma^+$ states of OH.	98
4.9	$\int_{R_c-\epsilon}^{R_c} \psi^2(R) dR$ for each v, J of the $X^2\Pi$ and $A^2\Sigma^+$ states of OH.	99
4.10	Example of a wavefunction where Type C is bound but Type W is unbound. The black lines are the effective and unperturbed PECs for the $A^2\Sigma^+$ state, and the red lines for the $X^2\Pi$ state. The wavefunction has been scaled for visibility and shifted to lie at the correct energy.	101
4.11	Distribution of $\int_{R_c-\epsilon}^{R_c} \psi^2(R) dR$ values for $X^2\Pi$ and $A^2\Sigma^+$ rovibronic levels where the Type C categorization is bound and Type W categorization is unbound.	102
4.12	Ratio of summed intensities between subsets 1 and 2: $\frac{\sum \frac{1}{2}\sigma}{\sum \frac{1}{2}\sigma}$ calculated for $T = [300, 2000, 5000]K$	103
4.13	Example of a wavefunction where Type C is bound but Type W is unbound.	104
4.14	Fitting residual values for the $X^2\Pi$, $A^2\Sigma^+$, $B^2\Sigma^+$ and $C^2\Sigma^+$ states of OH when compared against MARVEL energy levels from Furtenbacher et al. (2022).	110
4.15	PECs used in spectroscopic model of OH. Solid lines: B2B linelist, Dashed lines: Predissociative broadening only, Dotted lines: Continuum absorption only, Dotted+Dashed: Continuum absorption + Predissociative broadening. The area in grey contains all $A^2\Sigma^+$ rovibronic levels with predissociative broadening.	114

4.16	Spin-orbit couplings used in spectroscopic model of OH. Solid lines: B2B linelist, Dashed lines: Predissociative broadening only.	115
4.17	L-uncoupling curve used in spectroscopic model of OH.	116
4.18	Permanent dipole moment curves used in spectroscopic model of OH. These are <i>ab initio</i> , and are taken directly from MOLPRO.	117
4.19	Transition dipole moment curves used in spectroscopic model of OH. These are <i>ab initio</i> , and are taken directly from MOLPRO, x-component only. Solid lines: B2B linelist, Dotted lines: Continuum absorption Only	118
4.20	Comparison of <i>ab initio</i> (T)DMCs from this work (black) and those from (Brooke et al., 2016; van der Loo & Groenenboom, 2005; Yousefi et al., 2018; Langhoff et al., 1982; van Dishoeck et al., 1983; van Dishoeck & Dalgarno, 1983).	119
4.21	Grid point and analytic representations of the X-X permanent dipole moment of OH. Left: This work, Right: Brooke et al. (2016).	119
4.22	Hydroxyl ground-to-ground transitions with different representation of the ground state permanent dipole. Dipoles from sec: 4.2 and Brooke et al. (2016). Numbers represent Δ_v . Red dots are maxima for given Δ_v . Blue line is a fitted through points with $\Delta_v \leq 12$	120
4.23	Convergence of the partition function of OH as a function of $J_{\max}$	121
4.24	Comparison of partition function between this work and Barklem & Collet (2016); Sauval & Tatum (1984), JPL (Pickett et al., 1998), and HITRAN (Gamache et al., 2017)	123
4.25	Comparison of stick spectra produced with $^{16}\text{O}^1\text{H}$ MYTHOS line list and the HITRAN line list (Gordon et al., 2022).	125
4.26	Computed temperature-dependent photoabsorption cross-sections of the transitions of OH for varying temperature.	126
4.27	Comparison between the photoabsorption cross-section of OH computed in this work (black) at 1 K and cross-section given by Leiden database (Hrodmarsson & van Dishoeck, 2023) (magenta).	126
5.1	Toy models describing predissociative mechanisms. Left: Spin-orbit induced predissociation. Right: rotational predissociation.	130
5.2	A toy model of OH consisting of the X $^2\Pi$, A $^2\Sigma^+$, and 1 $^2\Sigma^-$ electronic states. The two green levels, $E(1\ ^2\Sigma^-)_{r_c=3,4\ \text{\AA}}$ are continuum levels in the 1 $^2\Sigma^-$ electronic state with the same quantum numbers, however with different right-side box limits, R_c . This highlights the box size dependence of repulsive state energy levels. The shaded region covers energy levels between D_e^X and D_e^A	133
5.3	The term value of the $ A^2\Sigma^+, J=0.5, v=4, e\rangle$ state as a function of the box length of the calculation in DUO, the variation of the energy is induced by crossings with energy levels in the repulsive states 1 $^2\Sigma^-$, 1 $^4\Sigma^-$, and 1 $^4\Pi$	135

5.4	Term value of the $ A^2\Sigma^+, J = 0.5, v = 2, e\rangle$ state as a function of the box length of the calculation in DUO. The different colors correspond to different spin-orbit contributions.	136
5.5	Term value of the $ A^2\Sigma^+, J = 13.5, v = 1, f\rangle$ state as a function of the box length for a DUO calculation including the $X^2\Pi$ and $A^2\Sigma^+$ states only. The blue markers represent a shift in energy induced by the spin-orbit coupling between the $X^2\Pi$ and $A^2\Sigma^+$ states on the $A^2\Sigma^+$ state level. Energy profile is down shifted by $\langle E \rangle$ (see Equation 5.8) so that it is centered on zero. . . .	137
5.6	Plot of the energy against box length with the fitted histogram of energy points for the $ A^2\Sigma^+, J = 0.5, v = 4, e\rangle$ state.	138
5.7	Example of misassignment in extraction of energy profile term values. Region (a) contains desired values and region (b) contains misassigned values from other local state(s).	139
5.8	Lifetimes calculated using the stabilization method depend on the bin number of the integral normalised histogram, N_b . This relationship is detailed here. The subfigure details the procedure in Section 5.3.3 used to determine Δ_C and recovers the best estimate for the lifetime, μ_τ detailed in the shaded area. The bold red line is μ_τ with Gaussian uncertainty $\Delta_C = \sigma_\tau$	141
5.9	Example of a narrow energy profile resulting in a sparsely populated integral normalised histogram of the term values. This distribution results in an erroneous Lorentzian energy profile and cannot be used.	142
5.10	Example of a skewed energy profile. Distributions like this are harder to fit as information on the topside wings is not present. In cases such as this, an insufficient number of lifetimes are extracted to treat statistically as in Figure 5.8.	143
5.11	Distribution of percentage uncertainties in the lifetime induced by the computational procedure.	145
5.12	The energy profile (subplot) for $ OH, A, 0.5, 4, f\rangle$ is loaded in from left to right starting with $R_c \in [8, 8.2] \text{ \AA}$. The lifetime is recomputed at each step and presented here. The lifetime converged to a $\sim 3\%$ uncertainty against the moving average at 100%.	146
5.13	The energy profile (subplot) for $ OH, A, 17.5, 1, e\rangle$ is loaded in from left to right starting with $r_c \in [8, 8.2] \text{ \AA}$. The lifetime is recomputed at each step and presented here. The lifetime converged to a $\sim 20\%$ uncertainty against the moving average at 100%.	147
5.14	Examples of TP, TP-BF, FP, TN, and FN predissociation energy profiles of OH.	151
5.15	Population of OH predissociation energy profile tag datasets.	152
5.16	Harmonically averaged convergence ratio, $\langle \epsilon \rangle_H$ against order of magnitude of predissociation lifetimes of OH as calculated using the modified stabilization method.	153

5.17	Predissociation lifetimes of OH organized by vibrational and rotational quanta. Top panel: Predissociation lifetimes for rovibronic levels with $E_b < D_e(\text{A})$. Bottom panel: Predissociation lifetimes for rovibronic levels with $E_b \geq D_e(\text{A})$	155
5.18	Distribution of predissociation widths, Γ of the $\text{A } ^2\Sigma^+$ state of OH binned over energy. Solid horizontal lines: Positions of vibrational band centres of the $\text{A } ^2\Sigma^+$ state ($J = 0.5, p = e$). Dotted line: Position of $D_e(\text{X})$	156
5.19	Predissociation lifetimes as calculated in this work compared to experimental values from 05DePoDe (Derro et al., 2005), 78BrErly (Brzozowski et al., 1978), 91GrFa (Gray & Farrow, 1991), 92HeCrJe (Heard et al., 1992), 97SpMeMe (Spaanjaars et al., 1997), and 21SuZhZh (Sun et al., 2021), and theoretical values from 99PaYa (Parlant & Yarkony, 1999).	157
5.20	Centroid shifts of the $\text{A } ^2\Sigma^+$ state of OH averaged over discrete energy regions. Error bars represent minimum and maximum centroid shifts. . . .	159
5.21	Distribution of predissociation widths, Γ of the $\text{A } ^2\Sigma^+$ state of SH binned over energy. Solid horizontal lines: Positions of vibrational band centres of the $\text{A } ^2\Sigma^+$ state ($J = 0.5, p = e$). Dotted line: Position of $D_e(\text{X})$	161
5.22	Centroid shifts of the $\text{A } ^2\Sigma^+$ state of OH averaged over discrete energy regions. Error bars represent minimum and maximum centroid shifts. . . .	162
6.1	<i>Ab initio</i> doublet potential energy curves of OH from van Dishoeck & Dalgarno (1984b)	167
6.2	Initial photodissociation cross-sections calculated for OH using Ex-OCCROSS with $\alpha = 10 \text{ cm}^{-1}$	170
6.3	Dependence of shape of a photodissociation cross-section and its first and second derivatives (with respect to ν) on α in the smoothing procedure. Left column shows the smoothed cross-section, middle column is the first derivative, right column is the second derivative. This calculation is performed for the $1^2\Sigma^- \leftarrow \text{X}^2\Pi$ transition at 300 K	171
6.4	Photodissociation cross-section of the $1^2\Sigma^- \leftarrow \text{X}^2\Pi$ transitions of OH with Gaussian smoothing applied for $\alpha = 400 \text{ cm}^{-1}$ and $\alpha = 1000 \text{ cm}^{-1}$. .	172
6.5	$\Delta\tilde{\nu}_{\nu''}(\nu)$ for the set of transitions, $\text{X } ^2\Pi \rightarrow 1^2\Delta$ of OH. Lower panel displays that the relationship between $\Delta\tilde{\nu}$ and ν can be represented linearly as $\Delta\tilde{\nu} = a\sqrt{\nu} + b$ where a and b are constants.	175
6.6	Photodissociation cross-section of the $1^2\Sigma^- \leftarrow \text{X}^2\Pi$ transitions of OH with Gaussian smoothing applied for $\alpha = 400$ (top panel) and energy-dependent smoothing applied (bottom panel)	176
6.7	Radiation field fluxes for various environments taken from the Leiden database Heays et al. (2017).	177

6.8	Photodissociation cross-section of OH at $T = 300, 1000, 2000, 5000$ K. The black line represents the flat Gaussian smoothed cross-section, the red line is the energy-dependent smoothing cross-section, the magenta line is the Leiden database cross-section Heays et al. (2017), and the other colored lines are the raw cross-sections pre-smoothing, see Figure 6.2.	180
6.9	Comparison between photodissociation cross-section of OH computed in this work at 1 K with $\alpha = \alpha(300 \text{ K})$ from Table 6.2 and cross-section given by Leiden database (Heays et al., 2017).	181
6.10	Comparison of photodissociation rates between those of Hrodmarsson & van Dishoeck (2023) and this work.	182
6.11	Temperature-dependent photodissociation rates of OH for the wavelength region above 125 nm for various standard fluxes from Hrodmarsson & van Dishoeck (2023).	183

List of Tables

3.1	Root-mean squares errors $\Delta(\text{RMS})$ in cm^{-1} comparing the fitted model to Y: Yamada et al. (1989) and J: Joo et al. (1999) rotational transitions.	64
3.2	PEC and morphing parameters obtained for the X $^2\Pi$ and A $^2\Sigma^+$ states of NaO. For the definition of the EMO parameters see Equation (3.5), and for morphing parameters see Equation (3.9).	67
3.3	Comparison of <i>ab initio</i> calculated spin-orbit splitting (A_{so}) and Λ -doubling constants (p, q) of the ground NaO state with their empirical counterparts taken from Yamada et al. (1989). All values are in cm^{-1}	67
3.4	Partition Function, $Q(T)$ as calculated using the Duo computed energies compared to partition functions from JPL database.	68
3.5	Uncertainty estimates (in cm^{-1}) are applied for the rovibronic energy levels of NaO as a function of state quantum numbers.	70
3.6	Extract from .STATES file produced by DUO for NaO. Lifetimes calculated with ExoCross, for uncertainties see Section 3.4 and Table 3.5	71
3.7	Extract from the .TRANS file produced by DUO for NaO.	71
4.1	Summary of all electronic states of OH considered in the $^{16}\text{O}^1\text{H}$ MYTHOS line list and their use case.	76
4.2	Coverage of MARVEL data set Furtenbacher et al. (2022) energy levels for the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH which have been used to refine <i>ab initio</i> PECs, SOCs and coupling constants for the production of a spectroscopic model.	77
4.3	Summary of <i>ab initio</i> electronic structure calculation details. All calculations use aug-cc-pV6Z basis set with the first σ orbital closed. Orbitals correspond to the point group symmetry C_{2v}	80
4.4	Mapping between dipoles and numerical representation of A_1 states in MOLPRO for OH.	82
4.5	Details of MOLPRO calculation for the B $^2\Sigma^+$, C $^2\Sigma^+$, and 1 $^2\Delta$ electronic states of OH.	83
4.6	Parameters, σ_i which best describe <i>ab initio</i> PECs of OH as calculated in Section 4.2.	87

4.7	Shape set for the B $^2\Sigma^+$ state for use in the Morse-Long range potential energy form.	90
4.8	Shape set for the C $^2\Sigma^+$ state for use in the Morse-Long range potential energy form.	92
4.9	Summary of the initial shape sets (see Section 4.3.2.1) for the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH.	92
4.10	Summary of the initial parameter sets (see Section 4.3.2.1) for the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH.	93
4.11	Tabulated comparison between Type C and Type W categorizations of bound vs. unbound states. Type C unbound states are states for which $T_e(J), \tilde{D}_e(J)$ are finite but $E > \tilde{D}_e(J)$, this is distinct from Repulsive, where in the effective potential approximation, all states are unbound as $T_e(J), \tilde{D}_e(J)$ are undefined. Dark states are states where $E < T_e(J)$ and are present likely due to misassignments in the manifold. Calculated with $\varepsilon = 0.5 \text{ \AA}$ and $\delta_I = 10^{-6}$	100
4.12	Tabulated comparison between Type C and Type W categorizations of bound vs. unbound states. Calculated with $\varepsilon = 0.5 \text{ \AA}$ and $\delta_I = 6.7 \times 10^{-4}$	100
4.13	Root-mean square errors for each v , State in the MYTHOS model energies as compared to empirical energy levels from MARVEL dataset by Furtenbacher et al. (2022). Total RMS = 2.67370 cm^{-1}	109
4.14	Fixed parameters for spectroscopic model of OH. Units: $[A_e] = \text{cm}^{-1}$, $[C_n] = \text{cm}^{-1} \text{ \AA}^{-n}$	111
4.15	Summary of the PEC parameters obtained from least squares fitting the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH to MARVEL energy levels from Furtenbacher et al. (2022) in Duo (Yurchenko et al., 2016a). All the figures are kept for the sake of preserving accuracy and reproducibility.	112
4.16	Summary of the <i>morphing</i> and empirical parameters obtained from least squares fitting the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH to MARVEL energy levels and transitions from Furtenbacher et al. (2022) in Duo Yurchenko et al. (2016a).	113
4.17	Comparison between calculated (MYTHOS) line intensities in the X $^2\Pi$ state $v'' \rightarrow v'' = 0 \rightarrow 1$ vibrational band and their HITRAN (Gordon et al., 2022) and measured (Chang et al., 2023) counterparts. Percentage differences are calculated as $\Delta = (I_{\text{MYTHOS}} - I_{\text{Reference}}) / (I_{\text{Reference}}) \times 100$. $\langle \Delta \rangle$ is the average percentage difference.	121
4.18	Sample of the .STATES file produced by DUO for OH. Uncertainties using predicted shifts procedure from Bowesman et al. (2021, 2024b); McKemish et al. (2024). The lifetimes are convolutions of predissociative (Chapter 5) and radiative lifetimes, and Lande-g factors, (g_L) are produced using DUO as per Semenov et al. (2017).	124
4.19	Sample of the .TRANS file produced by DUO for OH.	124

5.1	Conditions for assigning confusion tags for visually assessed energy profile Lorentzian fits. ✓: Condition met, ✗: Condition not met	150
5.2	Rules for assigning uncertainties to predissociation lifetimes of OH as calculated using the modified stabilization method. Δ_C is calculated <i>in situ</i> for each level. $\Delta_{\tau_{so}}$ is calculated as Equation 5.15 with $\Delta_R = \Delta_B = 5\%$	153
5.3	Summary of predissociation lifetime data available from experimental and theoretical sources. Data column: τ_p represents predissociation lifetime, τ_{tot} represents total lifetimes (Equation 5.27), R_p represents predissociation rates.	156
5.4	Summary of comparison between A $^2\Sigma^+$ predissociation lifetimes as calculated in this work and available literature values. Differences are averaged over J for a given v . Only rotationally resolved literature lifetimes are compared here (see Table 5.3).	158
6.1	Transitions of OH included in the photoabsorption spectrum and their associated dissociative properties.	180
6.2	Summary of uniform Gaussian smoothing parameters of direct photodissociation transitions in OH.	180
7.1	Summary of transitions included in each data product.	186

Chapter 1

Introduction

The study of extra-Solar planets has been a rapidly growing topic of study since the discovery of the first exoplanet by [Mayor & Queloz \(1995\)](#), with thousands more having been discovered since, and more still classified as candidates for exoplanets. In order to understand the planets and star within our own Solar System, one can find analogous environments in extra-Solar Systems and infer the evolution of our planets and the Sun. Understanding the chemical composition of these exoplanets is therefore of high importance. [Lapôtre et al. \(2020\)](#) provide several examples of the kinds of problems which are expected to be solved through exoplanetary studies.

Modelling astronomical spectra to derive compositions of atmospheres and to find the abundances of molecules in them is called atmospheric retrieval. Many different approaches can be taken for atmospheric retrieval, with an abundant list of retrieval codes having been produced throughout the years. A summary of the available programs has been compiled by [MacDonald & Batalha \(2023\)](#) with a notable mention to UCL's own τ -REX ([Al-Refaie et al., 2021](#)).

With the recent launch of the James Webb Space Telescope (JWST), and the upcoming Atmospheric Remote-sensing Infrared Exoplanet Large-survey (ARIEL) space telescope and ground-based Extremely Large Telescope (ELT), the rate of data proliferation for exoplanetary studies continues to grow. These telescopes are used in conjunction with several observational techniques to extract information about extra-terrestrial atmospheres.

When an exoplanet transits through the line of sight between telescopes and their mother star or passes behind the star, direct or indirect transits respectively have occurred. During these events, the star + planet system sees a reduction in overall flux detected, and depending on the molecular species present in the planet's atmosphere, the flux reduction magnitude will vary in characteristic wavelength regions ([Tinetti et al., 2006](#)), producing a transit spectrum which can be modelled to predict the composition of the exoplanet's atmosphere.

Another technique by which exoplanet atmospheres may be examined is resolved Direct Imaging (DI), whereby one takes a real image of the target exoplanet. The detection of exoplanets via DI is less common, out of the some 5,000 exoplanets which have been discovered, only 20-25 have been found this way. This technique, until recently, has been largely limited to young, self-luminous gas giants ([Currie et al., 2023](#)). With the JWST, however, more temperate exoplanets can be studied in this fashion, with its first such observation performed on the relatively cold (275 K) Jupiter-sized gas-giant Epsilon Ind A

([Matthews et al., 2024](#)).

Ground-based instruments, such as the aforementioned ELT, can image at a much higher resolution, leading to more robust measurements. However, they must also deal with telluric lines such as those from atmospheric water and OH which obscure the target spectral features. Since the pioneering work of [Snellen \(2014\)](#), High-Resolution (HR) spectroscopic techniques have been used in conjunction with HR instruments and applied in molecule detections in exoplanet atmospheres through cross-correlation / Doppler shift spectroscopy. In this technique, one observes the spectral features of a star+planet system over a period of time. Because the radial velocity of the planet is typically orders of magnitude higher than that of the star, red and blue shifts in its spectrum can be seen, while the telluric and stellar lines remain static over time. Leveraging these Doppler shifts, one can isolate the planetary spectrum from the contaminating lines, and achieve an extremely robust, high- σ detection of target molecules. This does not come without a price, however, and requires that the reference spectra are of very high accuracy, with resolving power, $R = \lambda / \Delta\lambda \geq 100,000$. This is because the Doppler shifts are comparatively small, so would not be resolved at lower resolution. Furthermore the exoplanet's spectrum is obscured by the stellar spectrum, so to achieve a high signal-to-noise ratio, many high accuracy lines are necessary ([Birkby, 2018](#)). In contrast, transit spectroscopy with the JWST can be performed with $R \approx 3,000$ and the upcoming ARIEL mission is expected to require resolving powers of a few hundred ([Tennyson & Yurchenko, 2021](#)).

Doppler shift spectroscopy drives the need for complete and high-accuracy molecular data, informing high-resolution atmospheric retrieval models for significant detections of astrophysically important molecules. Lower resolution datasets with high completeness also remain desirable in the context of transit spectroscopy studies like those done with the JWST. In light of this, many atomic and molecular databases of transitions have been developed over the years.

1.1 Molecular Databases

The ExoMol project began in 2011 with the purpose of providing molecular data for the study of (hot) exoplanetary atmospheres ([Tennyson & Yurchenko, 2012](#)). The primary datasets provided by the ExoMol group are line lists, containing rovibronic levels and the transitions between them with corresponding Einstein-A coefficients, and photoabsorption cross-sections. An emphasis is placed on the temperature-dependence of the latter as higher temperatures are not adequately covered by other databases such as HITRAN ([Gordon et al., 2022](#)). The ExoMol database has established a convention of quadrennial data releases with the first in 2016 ([Tennyson et al., 2016b](#)), followed by 2020 ([Tennyson et al., 2020](#)) and 2024 ([Tennyson et al., 2024](#)). A 10 year review of the ExoMol project was released in 2021 ([Tennyson & Yurchenko, 2021](#)), summarising and reflecting upon the work done by the group.

Up to the 2024 data release, 67 molecules of astrophysical and terrestrial interest have been studied, along with > 150 isotopologues, of which two molecules (NaO and OH) are studied in this thesis. There is a well established balance between completeness and accuracy of a semi-empirical molecular dataset, with high accuracy and full completeness over all quantum numbers being the gold standard. Accounting for continuum and ionic electronic states makes the second criterion infeasible, however, due to their having infinite

possible rovibronic levels. With this in mind, line lists are truncated to some maximum energy and/or set of quantum number values, namely J , and v . These limits are informed by the dissociation limits of the electronic states in the model, and by the required convergence of the partition function.

Wherever possible, ExoMol leverages empirical MARVEL (Measured Active Rotational-Vibrational Energy Level) energy levels (Section 2.5.1), extrapolating upon them using variational models to produce highly complete data sets (McKemmish et al., 2024). Hybrid energy levels are put through the *predicted shifts* methodology by Bowesman et al. (2021, 2024b) which also estimates uncertainty of extrapolated regions through predictive regression modelling of the residuals and interpolates missing energies within regions containing MARVEL energies to ensure experimentally accurate energy levels for as much of the dataset as possible.

Photoabsorption cross-sections are computed using the line list as input, with a convention of providing cross-sections from 100 K to some maximal temperature T_{max} in steps of 100 K. In recent years, line lists have become more and more energetically extended, venturing into the UV range. In these frequency regions, one must consider transitions outside the standard bound-to-bound type. As such, provisions have been made to also cover photodissociation and predissociation. Pezzella et al. (2021) developed a method to compute temperature-dependent continuum absorption cross-sections using methods and tools already within the ExoMol arsenal, with the first ExoMol photodissociation cross-section dataset for HCl and HF being released in 2022 (Pezzella et al., 2022). The methods outlined here are largely a manual and qualitative affair. This conflicts with the convention of computing photoabsorption cross-sections (including continuum absorption) with 100 K intervals for a large range of temperatures because this makes it more difficult to produce self-consistent cross-sections due to variations in individual qualitative assessments. Furthermore, this process is time consuming, especially when many dissociation channels and a large range of temperatures are considered.

The efforts made to automate these processes are covered in Chapter 6. Along with continuum absorption, predissociation processes are necessary for understanding lifetime broadening in certain rovibronic transitions and is covered in Chapter 5. To allow for the addition of these processes, changes to the ExoMol data structure were made in 2023 (Tennyson et al., 2023).

ExoMol has also expanded in its utilization of novel technologies such as machine learning models to predict the rotationally dependent pressure broadening coefficients of different molecules (Guest et al., 2024), extending and supplementing the previously insufficient treatment of such coefficients within the database.

Since the data release in 2020, ExoMol datasets have been used in a vast number of studies covering different environments like sub-Neptunes, Neptune-like exoplanets, warm, hot, and ultra-hot Jupiters, and even for the detection of bio-signatures just to name a few (see Tennyson et al. (2024) and the references therein).

Furthermore, the ExoMol database contains enough data to warrant the creation of further databases, streamlining the experience for users requiring specific data types. Examples of this include the Lifetimes DataBase (LiDB) (Owens et al., 2023a), a database of NASA polynomial fits to specific heats generated from ExoMol data (Wang et al., 2023), a database of high-resolution transitions fit for spectroscopic assignment (Zhang et al., 2024a), and

ExoMolOP, a database of molecular opacities generated from ExoMol data (Chubb et al., 2021).

ExoMol is, of course, not the only reliable source of molecular data. The HITRAN database (Gordon et al., 2022) is well established and contains line lists for 55 molecules and many more isotopologues with data produced for use at 296 K. HITEMP (Rothman et al., 2010) extends the HITRAN database to higher temperatures. This database is not as well populated, however, with only eight molecules available. GEISA (Delahaye et al., 2021) is similarly well established, focusing mainly on molecules important in our Solar System. The Cologne Database for Molecular Spectroscopy (CDMS) (Endres et al., 2016) provides data for around 800 atomic and molecular species but is generally used for lower temperatures with partition functions available up to only 1000 K. The JPL Molecular Spectroscopy database also has an extensive list of transitions and partition functions for a large variety of atoms and molecules suitable for wavelengths longer than 30 μm (Pickett et al., 1998). This catalog is constructed using theoretical least-squares fits to published spectral data. The NASA Ames (Huang et al., 2017) and TheoRets (Rey et al., 2016) projects have provided line lists suitable for high temperatures for a number of important polyatomic molecules, with the latter providing a high-quality line list for methane. The MOLLIST database (Bernath, 2020) works to provide empirical molecular data suitable for high temperatures and has produced datasets for diatomics and polyatomics.

The Leiden database (Hrodmarsson & van Dishoeck, 2023) provide line lists, photoabsorption, and photodissociation cross-sections for atoms, diatomics, triatomics and several larger molecules with datasets constructed from experimental and theoretical published sources. Another major provider of atomic data is the NIST database (Kramida et al., 2021), containing line data for elements with atomic number up to 110.

1.2 Motivation of Theoretical Molecular Spectroscopy

As it pertains to line positions of individual transition lines, advances in experimental techniques have been able to produce extremely accurate measurements. It is clear that experimental measurements are the gold standard for transition frequencies. For example, Lamperti et al. (2023) measured the $|v'' = 0, J'' = 1\rangle \rightarrow |v' = 1, J' = 1\rangle$ line in molecular hydrogen to 10 significant figures making it the most accurate such measurement to date. While accurate theoretical calculations of this line have been performed Komasa et al. (2019), for molecules with more electrons, such accuracy is not feasible.

This raises the question of why one would perform theoretical calculations to begin with, as carefully constructed *ab initio* models, even for small molecules cannot always reproduce the accuracy of experiment, with uncertainties increasing rapidly with the size of the molecule.

One aspect is that of completeness; experiments cannot get a complete, assigned coverage of all rovibronic levels and their transitions simply due to the number of possible transitions and the increasing density of states as one probes higher energies. Theoretical models which have been designed to reproduce available experimental data through semi-empirical techniques, supplementing experimental energy levels where possible, can be used to extrapolate to higher energies and provide a full coverage (McKemmish et al., 2024).

Furthermore, experiments give a discrete picture of the molecular spectrum under specific

conditions, such as a given temperature and pressure. Extrapolating low temperature data to higher temperatures is not possible, and such extrapolations often fail to reproduce highly rotationally excited transitions and hot bands (Tinetti et al., 2013). Accurate intensities over a range of temperatures are difficult to measure and are often sparsely populated and in some cases not available at all.

These factors induce a considerable demand for theoretical modelling of important molecules for use in astronomy and such theory is used to produce extended datasets with accurate line profiles and temperature-dependent intensities. Some good resources on the treatment of diatomic molecules are the textbook by Lefebvre-Brion & Field (2004) and the comprehensive review paper by Tennyson et al. (2016a) (and the references therein).

Theoretical methods include - but are not limited to - two major camps, effective Hamiltonian (EH) / perturbation theory and variational methods, of which the latter are used in the studies making up this thesis. Perturbative methods such as EH rely on expressing the Hamiltonian as a series of functions with associated molecular constants for each vibronic band. One may use a program like PGOPHER (Western, 2017) to model the spectrum of a molecule using this approach by fitting effective Hamiltonians for each vibronic band to produce molecular constants.

When done effectively, this approach can reproduce empirical energy levels with high accuracy and is, in general, better at reproducing experiment than are variational methods. This approach, however, does not extrapolate well, and is not suitable for handling cases like resonances between mutually perturbing states and can lead to misassignments (Polyansky et al., 1997b).

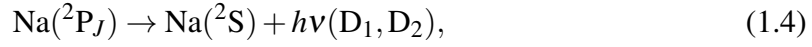
Polyansky et al. (1997a) found that the EH used to describe water does not properly account for these resonances. In cases such as this, one may solve the problem by substituting variational calculations using a spectroscopically determined potential energy surface. Comparison between the two datasets found that the energy levels in the Effective Hamiltonian treatment diverge as much as up to 15 cm^{-1} making it unsuitable for high resolution spectroscopic studies.

Variational method calculations, which are performed using DUO here (Section 2.1), are less suited to reproducing experimental transitions, however extrapolate much better and can produce more complete datasets. The lower reproductive capacity of variational methods can largely be counteracted through the substitution of MARVEL energy levels (Section 2.5.1) which are empirically derived and of very high accuracy, leading to a complete and highly accurate theoretical treatment. This is the so-called hybridization procedure described by Bowesman et al. (2021, 2024b); McKemmish et al. (2024).

1.3 Sodium Oxide Radical - NaO

Sodium Air-glow, sometimes referred to as night-glow, was first reported by Slipher (1929) and has been identified as the emission of Na D-lines. It is proposed that these lines arise from the Chapman mechanism (Chapman, 1939; Sarkhel et al., 2010; Plane et al., 2012) with some modifications suggested in light of modern measurements (Slanger et al., 2005; Sarkhel et al., 2010), as given by





where $k_{1,2}$ are the temperature-dependent rate constants, α is the branching ratio, and $\text{D}_1 \approx 589.6$ nm and $\text{D}_2 \approx 589.0$ nm are the sodium D-line transition frequencies. These arise from the $\text{Na}(^2\text{S}) \leftarrow \text{Na}(^2\text{P}_J)$ emission, where J can be either $\frac{1}{2}$ or $\frac{3}{2}$, corresponding to the D_1 and D_2 lines respectively (Plane et al., 2012).

This mechanism suggests that Na atoms, which are assumed to be ablated from meteors, react with O_3 in the atmosphere to form NaO, re-reacting with atomic oxygen to reform Na. Long lasting visible meteor trails have been attributed to the production of electronically excited Na by in the said reaction chain (Kolb & Elgin, 1976; Joo et al., 1999). In the Chapman mechanism, the rate limiting reaction is the formation of NaO, see Eq. (1.1). As this reaction takes place in the mesosphere, the variation of mesospheric ozone concentration affects Na air-glow intensity. As altitude profiles of ozone are available, ozone concentration variation can be used for deeper study into Sodium air-glow and subsequently NaO. (Plane, 2003; Sarkhel et al., 2010).

Several studies into the electronic structure of NaO have been completed over the years covering the $\text{X } ^2\Pi$ and $\text{A } ^2\Sigma^+$ electronic states (Langhoff et al., 1991; Soldán et al., 1999; Buenker & Liebermann, 2009). The $\text{A } ^2\Sigma^+$ state is very low lying and heavily coupled with the ground state, with a ratio between the ground state dissociation energy and the potential minimum of the $\text{A } ^2\Sigma^+$ state, $D_e(\text{X})/T_e(\text{A}) \approx 10$ (measured relative to the ground state potential minimum). Due to this, electronic transitions largely lie in the infrared, in the 3 to 5 μm region. Due to the symmetries of these two states and the $\text{A } ^2\Sigma^+$ state's low lying nature, the rovibronic levels here are strongly coupled through the corresponding spin-orbit and electronic angular momentum perturbations. The aforementioned studies cover the *ab initio* potential energy curves and permanent dipole moments, however they do not consider the corresponding non-adiabatic coupling curves, which are presented as part of the NaO line list project in Chapter 3.

Experimental spectroscopic data related to NaO is limited, with only two main studies in the literature from Yamada et al. (1989) and Joo et al. (1999) covering microwave rotational and rovibronic transitions respectively. Ground state rovibrational transitions do not appear to have been studied experimentally as of now. These sources are discussed in more detail in Section 3.1.

1.4 Hydroxyl Radical - OH

Similarly to NaO, OH is an important molecule in the context of night-time emission as a reaction product between molecular hydrogen and ozone resulting in the so-called Meinel band night-glow - vibrational transitions in the ground state, $\text{X } ^2\Pi$ (Meinel, 1950; Chen et al., 2021; Unterguggenberger et al., 2016). It is an important source of heat in the mesosphere from the air-glow reaction (Kaufmann et al., 2008; Chen et al., 2021; Brasseur & Offermann, 1986; Franzen et al., 2019).

Hydroxyl is also important in combustion chemistry and due to its role as an oxidizer in the lower atmosphere, causing the destruction of most hydrogen-containing molecules and

the ozone depleting CFCs [Prinn et al. \(1995\)](#). Highly oxygenated aromatic hydrocarbons can be produced through the reaction of both biogenic and anthropogenic aromatics such as benzene and toluene with OH ([Garmash et al., 2020](#)), and understanding OH allows for a better predictive capacity for the concentrations of these molecules in the atmosphere.

Astronomically, OH has seen detection in the atmospheres of Venus ([Piccioni et al., 2008](#)), Mars ([Clancy et al., 2013](#)), ultra-hot Jupiters Wasp-76b ([Landman et al., 2021](#)), Wasp-33b ([Nugroho et al., 2021](#)), in protoplanetary discs between 700K-900K ([Munoz-Romero et al., 2024](#)), in the interstellar medium ([Zannese et al., 2023](#); [Weinreb et al., 1963](#)), diffuse interstellar clouds ([Radenović et al., 2008](#)), M-Dwarfs ([Herbig, 1974](#); [Jones et al., 1988](#)), the red supergiant VY Canis Majoris ([Rosen et al., 1978](#)), sunspots ([Berdyugina & Solanki, 2001](#)), and the Moon ([Schoerghofer et al., 2021](#)).

OH acts as an important tracer for other molecules of astrophysical interest such as molecular hydrogen, CO, and water ([Tang et al., 2021](#); [Wang et al., 2017](#); [Schoerghofer et al., 2021](#)). The latter of which is of particular interest in astrochemistry: OH is heavily involved in the production of water through its reaction with molecular hydrogen, $\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$ and in regions of UV radiation, is a product of water photodissociation ([Wampfler, S. F. et al., 2010](#)). Furthermore, OH can be used to measure oxygen abundances in metal-poor stars ([Melendez et al., 2001](#)) and has been used to report metallicities in GYr-old stars in the Nuclear Star Cluster of the Milky Way ([Thorsbro et al., 2023](#)).

The spectroscopy of OH has seen extensive study since at least the 1970's in both a theoretical and experimental context. Particularly of interest have been its dissociative processes, as OH exhibits direct photodissociation, predissociation through several electronic states, and spontaneous radiative decay.

Much of the early theoretical work was completed by Van Dishoeck and Langhoff et al., computing potential energy curves for many electronic states, their dipoles, transition spectra, predissociation spectra, and photodissociation spectra ([van Dishoeck et al., 1983](#); [Langhoff et al., 1982](#); [van Dishoeck & Dalgarno, 1984b](#); [van Dishoeck & Dalgarno, 1984a](#); [van Dishoeck & Dalgarno, 1983](#); [van Dishoeck et al., 1984](#); [Bauschlicher Jr. & Langhoff, 1987](#)). The studies listed here provide the data for the photoabsorption and photodissociation cross-sections reported by the Leiden database ([Hrodmarsson & van Dishoeck, 2023](#)) (Section 6). Many other groups have studied the *ab initio* structure of OH, most recently by [Srivastava & Sathyamurthy \(2014\)](#); [Qin & Zhang \(2014\)](#) and notably by [van der Loo & Groenenboom \(2005\)](#).

Many experimental and empirical studies on the spectroscopy of OH have been done, including, but not limited to those by [Colin et al. \(2002\)](#); [Bernath & Colin \(2009\)](#); [Brooke et al. \(2016\)](#); [Yousefi et al. \(2018\)](#); [Coxon et al. \(1991\)](#); [Sulakshina & Borkov \(2023\)](#), with those by [Brooke et al. \(2016\)](#) and [Yousefi et al. \(2018\)](#) appearing to make up a majority if not all of the current HITRAN line list ([Gordon et al., 2022](#)). Recently [Furtenbacher et al. \(2022\)](#) released a set of empirically derived energy levels for OH based on the MARVEL procedure. This procedure takes assigned experimental transitions as input and produces self-consistent energy levels with appropriate uncertainties ([Furtenbacher et al., 2007](#)) and is briefly discussed in Section 2.5.1.

The direct photodissociation of OH has not seen much experimental study, however, except for those by [Radenović et al. \(2008, 2003\)](#), despite the importance of this process in regions

of the atmosphere more exposed to high energy radiation.

The predissociative processes of OH have seen many theoretical (Lee, 1995c,b,d,a, 1996; Lee & Freed, 1987; Sink et al., 1980; Yarkony, 1992; Kalyanaraman & Sathyamurthy, 1994; Parlant & Yarkony, 1999; Li & Zhang, 2011; van der Loo & Groenenboom, 2005) and experimental (Derro et al., 2005; Sun et al., 2021, 2020; Brzozowski et al., 1978; Gray & Farrow, 1991; Heard et al., 1992; Spaanjaars et al., 1997; Czarny et al., 1971; Zhou et al., 2003; Goldman et al., 1998) studies, with are discussed in more detail in Chapter 5.

OH has been a constituent of the ExoMol database in the form of the MOLLIST (Bernath, 2020) line list produced by Brooke et al. (2016); Yousefi et al. (2018). In Chapters 4 to 6, OH is studied to produce a new line list which has been given the name MYTHOS (Mitev-Yurchenko-Tennyson-Hydrogen-Oxygen), based on the MARVEL data of Furtenbacher et al. (2022). Further to this, theoretical studies into its predissociation and photodissociation dynamics through the introduction of new methods, such as the stabilization method and extension of methods already in use within ExoMol, such as the Gaussian smoothing of photodissociation cross-sections.

1.5 Structure of this Thesis

This thesis is organized into several chapters, which are, for the most part, self-contained. Chapter 2 covers the basic theoretical background needed to understand the remaining chapters. Certain theoretical concepts such as dissociative processes and the details of forming spectroscopic models are not discussed in great detail here, however, and are elaborated upon ad hoc in the relevant methods and discussion sections of the following chapters. In general, four separate projects were undertaken as part of this thesis, these being the production of NaO and OH line lists, the study of diatomic predissociation, and optimal smoothing of photodissociation cross-sections. The methods implemented to complete the projects do not overlap significantly bar a few exceptions. As such, an all containing methodology chapter has been forgone in favour of dedicated methodology sections within each relevant chapter. Chapter 3 examines the formation of a new line list for the sodium oxide radical.

Chapter 4, similarly to the previous, covers the formation of a line list, this time for the hydroxyl radical. Here, we introduce several more considerations, such as prefitting in Section 4.3.2.1, bound-state classification in Section 4.4, *ab initio* calculation of electronic structure 4.2, and a more detailed calculation of photoabsorption spectra with line broadening in Section 4.5.1.

Chapters 4-6 are not entirely independent of each other in that the work done in Chapters 5 and 6 rely on the spectroscopic model produced in Chapter 4. The lifetime line broadening parameters referenced in Section 4.5.1 are computed in Chapter 5 by treating the A $^2\Sigma^+$ states spin-orbit predissociation dynamics through the implementation of a novel method based on the stabilization procedure, and the continuum absorption sections of the photoabsorption spectrum produced are computed in Chapter 6 by building on the work of Pezzella et al. (2021, 2022).

The final Chapter (7) summarises all the work completed as part of this thesis and discusses some potential future projects which may be undertaken by other researchers.

Chapter 2

Background, Theory, and Software

2.1 The Molecular Hamiltonian

The theoretical framework for modelling the spectra of molecules is based on solving a formulation of the time-independent Schrödinger equation,

$$\hat{H}\psi = E\psi, \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian operator, E is the energy eigenvalue of the system, and ψ is the system's wavefunction. The Hamiltonian operator of a single particle in a potential V , is expressed as,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V, \quad (2.2)$$

where the first term is the kinetic energy operator and the second is the potential energy, V . To find the energies of a molecular system, one must solve the Schrödinger equation with the molecular Hamiltonian. The most general non-relativistic form of the molecular Hamiltonian is the Coulomb Hamiltonian,

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e}\sum_i\nabla_i^2 + \sum_{\alpha}\sum_{\beta>\alpha}\frac{Z_{\alpha}Z_{\beta}e^2}{4\pi\epsilon_0r_{\alpha\beta}} \quad (2.3)$$

$$\begin{aligned} & -\sum_{\alpha}\sum_i\frac{Z_{\alpha}e^2}{4\pi\epsilon_0r_{i\alpha}} + \sum_j\sum_{i>j}\frac{e^2}{4\pi\epsilon_0r_{ij}} \\ & = \hat{T}_Z + \hat{T}_e + \hat{V}_Z + \hat{V}_{Z,e} + \hat{V}_e, \end{aligned} \quad (2.4)$$

with energies,

$$\hat{H}\psi(\mathbf{q}, \mathbf{Q}) = E\psi(\mathbf{q}, \mathbf{Q}), \quad (2.5)$$

where $\hbar$ is the reduced Planck's constant, m is the mass of the particle, ϵ_0 is the permittivity of free space, and r_{ab} is the distance between two particles a and b . Here the notation of [Levine \(2013\)](#) is taken where nuclear particle labels are signified by α, β and electrons are signified by i, j along with the majority of the derivations. The terms in Equation 2.4 are, respectively, the nuclear kinetic energy, the electronic kinetic energy, the repulsive potential between nuclei, the attractive potential between nuclei and electrons, and the repulsive potential between electrons. $\mathbf{q}$ and $\mathbf{Q}$ in equation 2.5 represent generalized coordinates for

the electrons and nuclei respectively.

Solving this Hamiltonian scales in complexity very quickly with the number of particles considered and so far has only been pursued for very small atoms and diatomics (Sutcliffe & Woolley, 2005; Cafiero et al., 2003; Kozłowski & Adamowicz, 1993). For larger diatomics, like the OH and NaO radicals considered in this thesis, one must make approximations to the system. Most solutions for the molecular problem are performed using the so-called Born and Oppenheimer approximation.

2.1.1 The Born-Oppenheimer Approximation

The key assumptions made in the Born-Oppenheimer approximation is that the nuclear and electron motions can be treated separately resulting in the clamped nuclei Hamiltonian $\hat{H}_{\text{cn}}$,

$$\hat{H}_{\text{cn}}(\mathbf{Q}) = \hat{T}_{\text{e}} + \hat{V}_{\text{Z,e}}|\mathbf{Q} + \hat{V}_{\text{e}} + \hat{V}_{\text{Z}}|\mathbf{Q}. \quad (2.6)$$

This form of the Hamiltonian is dependent on the positions of the nuclei, $\mathbf{Q}$, only parametrically and so its form is computed given a specific configuration of the nuclei. This assumption is made because the electrons move much faster than the nuclei as,

$$m_{\alpha} \gg m_e. \quad (2.7)$$

This can be rewritten as a sum of the electronic Hamiltonian and nuclear repulsion potential for a given set of nuclear coordinates,

$$\hat{H}_{\text{cn}}(\mathbf{Q}) = \hat{H}_{\text{el}} + \hat{V}_{\text{Z}}|\mathbf{Q} \quad (2.8)$$

$$= \hat{H}_{\text{el}} + V_{\text{Z}}. \quad (2.9)$$

Omitting the nuclear repulsion potential one can write the electronic energy as,

$$\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}}, \quad (2.10)$$

and the total electronic energy given a nuclear configuration as,

$$\hat{H}_{\text{cn}}\psi_{\text{el}} = (\hat{H}_{\text{el}} + V_{\text{Z}})\psi_{\text{el}} = (E_{\text{el}} + V_{\text{Z}})\psi_{\text{el}} = U\psi_{\text{el}}. \quad (2.11)$$

Since $V_{\text{Z}} = V_{\text{Z}}(\mathbf{Q})$, the above equation is parametrically dependent on $\mathbf{Q}$ as,

$$\hat{H}_{\text{cn}}(\mathbf{Q})\psi_{\text{el},n}(\mathbf{q};\mathbf{Q}) = U(\mathbf{Q})\psi_{\text{el},n}(\mathbf{q};\mathbf{Q}), \quad (2.12)$$

which returns the electronic wavefunction for a given nuclear configuration, $\psi_{\text{el},n}(\mathbf{q};\mathbf{Q})$ and the total electronic energy as dependent on the nuclear configuration, $U(\mathbf{Q})$. This term is known as the potential energy surface of the molecule in the nuclear motion problem. Considering a diatomic molecule, $\mathbf{Q}$ becomes the internuclear separation R ; computing $U(R)$ for range of separations returns the potential energy curve as dependent on internuclear distance. An example of a PEC is given in Figure 2.1. The electronic potential, $U(R)$ has three main features. At $R = 0$, the internuclear repulsion causes the potential to become singular.

The internuclear separation which minimises $U(R)$ is called the equilibrium bond length, R_{e} . Asymptotically, the limit of $U(R \rightarrow \infty)$ tends to a value, D_{e} relative to the potential minimum, which is known as the dissociation energy. This is not, however, the dissoci-

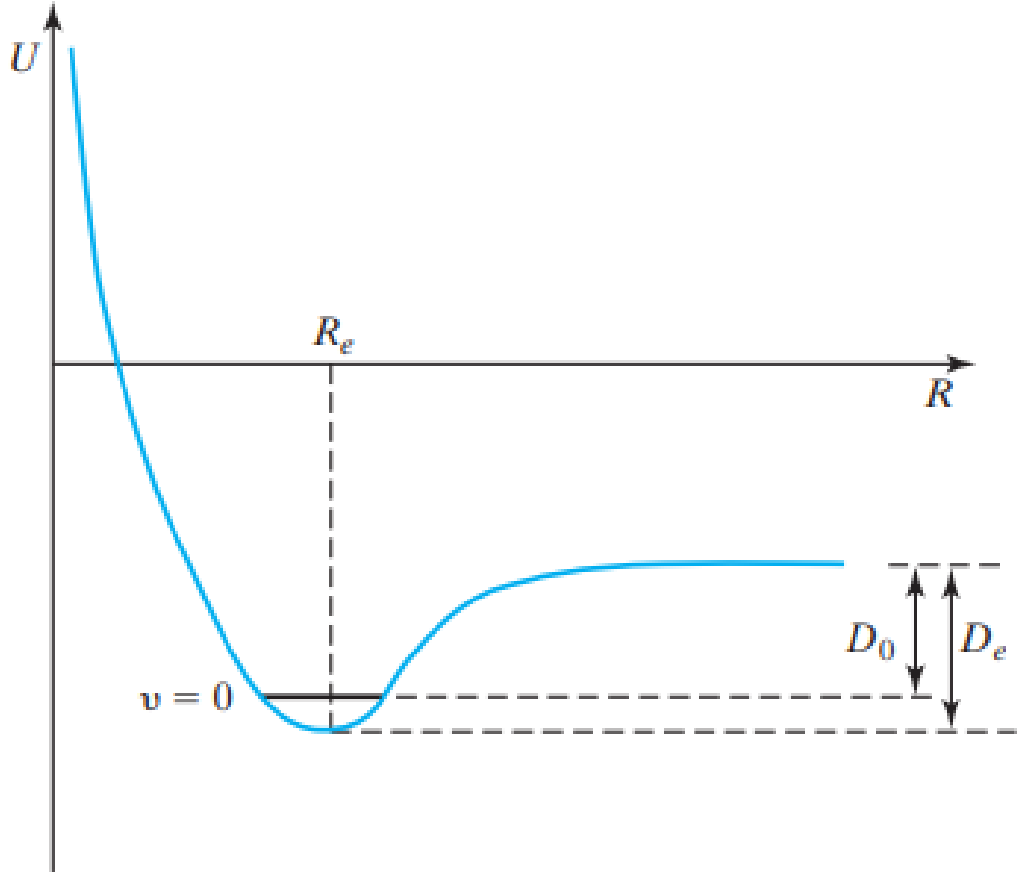


Figure 2.1: Electronic energy including internuclear repulsion as a function of internuclear separation, R , for a diatomic molecule (Levine, 2013).

ation energy which an experiment would observe, as this does not include treatment of the nuclear motion, only the electronic motion. When considering nuclear motion, the observed dissociation energy is not measured from the minimum of the potential, rather from the lowest vibrational eigenenergy which is found by solving the nuclear motion problem. This dissociation limit is referred to as D_0 and the zero-point energy, E_{ZPE} , can be evaluated as $E_{\text{ZPE}} = D_e - D_0$.

2.1.2 The Nuclear Motion Problem

The goal of the nuclear motion problem is to find the total wavefunction of the system, not just the electronic part. The nuclear motion Hamiltonian, $\hat{H}_N$ is,

$$\hat{H}_N = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 + U(\mathbf{Q}), \quad (2.13)$$

with energies,

$$\hat{H}_N \psi_N = E \psi_N. \quad (2.14)$$

ψ_N is the nuclear motion wavefunction and E is the total energy on the molecule as the nuclear motion Hamiltonian already contains the electronic energy in the form of the potential, $U(R)$. This treatment also implies that the total wavefunction of the system, $\Psi(\mathbf{q}, \mathbf{Q})$,

is adequately represented by,

$$\Psi(\mathbf{q}, \mathbf{Q}) = \psi_{\text{el}}(\mathbf{q}; \mathbf{Q}) \psi_N(\mathbf{Q}), \quad (2.15)$$

where ψ_{el} is the electronic wavefunction and ψ_N is the nuclear wavefunction. This wavefunction corresponds to a solution to the Schrödinger equation where couplings between the motions of electrons and nuclei are ignored (Lefebvre-Brion & Field, 2004).

2.1.2.1 The diatomic nuclear motion problem

In a diatomic molecule, one can rewrite Equation 2.14 as,

$$\left[-\frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_\beta} \nabla_\beta^2 + U(R) \right] \psi_N = \hat{H}_{\text{Diatom}} \psi_N = E \psi_N, \quad (2.16)$$

where α, β are the nuclei and $\psi_N = \psi_N(q_\alpha, q_\beta)$ for $q = a\hat{x} + b\hat{y} + c\hat{z}$. $U(R)$ is only a function of the internuclear distance, however, we refrain from writing $\psi_N(R)$ because this implies the lack of any translational energy. In reality, the total energy of this Hamiltonian is represented by the sum of the translational and internal motion energies,

$$E = E_{\text{trans}} + E_{\text{internal}} \text{ for } \psi_N = \psi_{N,\text{trans}} \psi_{N,\text{internal}}. \quad (2.17)$$

For now we will ignore modelling the translational motion and focus only on the internal motion of the nuclei relative to each other, hence changing the coordinate system to one in R in the center of mass frame, we rewrite $\hat{H}_{\text{Diatom}}$ as,

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + U(R) \right] \psi_{N,\text{internal}} = E_{\text{internal}} \psi_{N,\text{internal}}, \quad (2.18)$$

where μ is the reduced mass of the molecule defined as,

$$\frac{1}{\mu} = \sum_{\alpha} \frac{1}{m_\alpha}. \quad (2.19)$$

As the potential energy in this problem depends only on the internuclear separation, one can separate out the radial and angular properties of the wavefunction,

$$\psi_{N,\text{internal}} = P_J(R) Y_J^M(\theta_N, \phi_N), \quad J \in \mathbb{N}, \quad M \in [-J, -J+1, \dots, J], \quad (2.20)$$

where Y_J^M are the spherical harmonics with quantum numbers, J , and M and angular coordinates, θ_N , ϕ_N . It can be shown that, by taking the substitution $F_J(R) = RP_J(R)$ (Levine, 2013) we can arrive at,

$$-\frac{\hbar^2}{2\mu} \frac{\partial}{\partial R^2} F_J(R) + [U(R) + J(J+1)B] F_J(R) = E_{\text{internal}}^J F_J(R), \quad (2.21)$$

where $B = \frac{\hbar^2}{2\mu R^2}$, hence the effective potential in this calculation is $V_{\text{eff}} = U(R) + J(J+1)B$.

The solution to Equation 2.21 returns the familiar rovibrational solutions. One can solve

this equation by first solving the electronic structure problem (Section 2.2) to return $U(R)$ and then substituting this into Equation 2.21 before solving numerically. Solutions for $F(R)$ are calculated for a given J and are further characterised by the vibrational quantum number v , hence the internal energies are found as the rovibrational energies, $E_{\text{internal}} = E_{v,J}$. The explicit step-by-step solution to this equation is not covered here¹, however, there are many nuclear motion codes available, notably, DUO (Yurchenko et al., 2016a) and LEVEL (Le Roy, 2017b), with their own methods of solution. DUO is used to perform such nuclear motion calculations in the coupled, multichannel regime, covering many electronic states. The principles of how DUO is used is covered in Section 2.1.3. Unlike LEVEL, DUO allows for the inclusion of states with symmetry other than $^1\Sigma$ and Mizus et al. (2022) found that DUO converges to an accurate solution much faster than does LEVEL, making it more general, with the capacity to deal with heavier diatomics accurately.

2.1.3 DUO

DUO (Yurchenko et al., 2016a) is a general purpose variational (open access²) code that solves the rovibronic Schrödinger equation for diatomic molecules. The nuclear motion Hamiltonian described in Section 2.1.2.1 considers the non-relativistic, uncoupled, single channel case, which is insufficient for effective modelling of diatomic molecules with spectroscopic accuracy. Including multiple states, and perturbations induced by electronically diagonal and off-diagonal couplings requires the formulation of a more comprehensive Hamiltonian. Within the center-of-mass frame, a body-fixed set of Cartesian axis are introduced with the nuclear separation set in the direction of z-axis, the DUO non-relativistic nuclear Hamiltonian, $\hat{H}_{\text{nr}}$ is as follows,

$$\hat{H}_{\text{nr}} = \hat{H}_{\text{e}} + \hat{H}_{\mu} + \hat{H}_{\text{vib}} + \hat{H}_{\text{rot}}, \quad (2.22)$$

where

$$\hat{H}_{\text{e}} = -\frac{\hbar^2}{2m_e} \sum_i^{N_e} \nabla_i^2 + V_C(R, q_i) \quad (2.23)$$

is the electronic Hamiltonian with an electron mass, m_e , number of electrons N_e , and V_C is the Coulomb interaction potential for internuclear separation R and electronic coordinates $\mathbf{q}$;

$$\hat{H}_{\mu} = -\frac{\hbar^2}{2m_Z} \sum_{i=1}^{N_e} \sum_{j=1}^{N_e} \nabla_i \cdot \nabla_j \quad (2.24)$$

is the mass-polarization term for a total nuclear mass, m_Z ;

$$\hat{H}_{\text{vib}} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \quad (2.25)$$

¹Example solutions to the above equation in the uncoupled, single channel nuclear motion problem is given in pages 348-351 in Levine (2013).

²DUO is available for download at www.github.com/exomol

is the vibrational kinetic energy operator for a molecular reduced mass μ , and;

$$\hat{H}_{\text{rot}} = \frac{\hbar^2}{2\mu R^2} \hat{\mathbf{R}}^2 = \frac{\hbar^2}{2\mu R^2} (\hat{\mathbf{J}} - \hat{\mathbf{L}} - \hat{\mathbf{S}})^2 \quad (2.26)$$

is the body-fixed (Islampour & Miralinaghi, 2015; Hougen & Wiersma, 2001) rotational angular momentum term, where $\hat{\mathbf{R}}$, is the rotational angular momentum for a total angular momentum, $\hat{\mathbf{J}}$, electron orbital angular momentum, $\hat{\mathbf{L}}$ and spin angular momentum, $\hat{\mathbf{S}}$. DUO introduces the following ladder operators to rewrite the above form (in body-fixed coordinates),

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y, \quad (2.27)$$

$$\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y, \quad (2.28)$$

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y, \quad (2.29)$$

leading to,

$$\begin{aligned} \hat{H}_{\text{rot}} = & \frac{\hbar^2}{2\mu R^2} [(\hat{J}^2 - \hat{J}_z^2) + (\hat{L}^2 - \hat{L}_z^2) + (\hat{S}^2 - \hat{S}_z^2) \\ & + (\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+) - (\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+) + (\hat{S}_+\hat{L}_- + \hat{S}_-\hat{L}_+)] . \end{aligned} \quad (2.30)$$

The terms $\hat{J}_{\pm}\hat{S}_{\mp}$, $\hat{J}_{\pm}\hat{L}_{\mp}$, and $\hat{S}_{\pm}\hat{L}_{\mp}$, are the S -uncoupling, L -uncoupling, and spin-electronic terms respectively. Here we arrive at the first coupling curve which sees use in this work.

The matrix elements of the orbital angular momentum operators averaged over electronic wave functions give rise to R -dependent electronic angular momentum coupling curves (EAMCs). DUO accepts the $\langle \text{state}', R | \hat{L}_x | \text{state}'', R \rangle$ matrix elements for off-diagonal angular momentum coupling, inferring the ladder operators in Equation 2.30. $\text{state}', ''$ refers to two different electronic states. These matrix elements are non-zero for the selection rules, $\Delta S = 0$, $\Delta \Lambda = \pm 1$, $\Delta \Sigma = 0$, and are used in Chapters 3 and 4 to describe the angular momentum coupling between the X $^2\Pi$ and A $^2\Sigma^+$ states, which meet the non-zero matrix element selection rules. In this context, this curve has the effect of controlling the magnitude of the splitting in parity. When inputting the $\hat{L}_x$ matrix elements, DUO also requires information on the $\hat{L}_z$ matrix elements of the individual states in order to convert to the appropriate coordinate system as required in DUO. For example, for the EAMC between the X $^2\Pi$ and A $^2\Sigma^+$ states of NaO and OH, the $\langle X | \hat{L}_z | X \rangle$ and $\langle A | \hat{L}_z | A \rangle$ are required which are uniform for all R .

Further splittings can be considered by introducing relativistic considerations such as spin-orbit, $\hat{H}_{\text{SO}}$, spin-rotation, $\hat{H}_{\text{SR}}$, and the Λ -doubling terms, α_{opq} , α_{p2q} , and q to the Hamiltonian in Equation 2.22.

The spin-orbit splitting is determined by the matrix elements of the Breit-Pauli spin-orbit operator, $\hat{H}_{\text{SO}}$ (Dmitri G. Fedorov & Gordon, 2003) and similarly to the EAMCs, obey certain selection rules. Matrix elements are non-zero for cases where the two states spin-orbit coupled obey, $\Delta S = 0, \pm 1$, $\Delta \Lambda = 0, \pm 1$, $\Delta \Omega = 0$. If $\Delta S = 0$ and $\Sigma' = \Sigma'' = 0$, then the matrix element is zero, meaning singlet-to-singlet matrix elements are zero. However, coupling between a Σ^+ and Σ^- state may be non-zero, but is always zero for coupling

between $\Sigma^\pm$ and $\Sigma^\pm$.

So in the case of the NaO and OH X $^2\Pi$ and A $^2\Sigma^+$ states, we expect that the $\langle X_{\Omega=\pm\frac{1}{2}} | \hat{H}_{SO} | A_{\Omega=\pm\frac{1}{2}} \rangle$ and $\langle X | \hat{H}_{SO} | X \rangle$ matrix elements are non-zero. Again, these matrix elements are given as R -dependent curves, and DUO similarly accepts the x -components, with the conversion to the appropriate coordinate system occurring *in situ* using the $\hat{L}_z$ matrix elements from before. For diagonal spin-orbit couplings, one can use the z -component, without the need for the conversion. These spin-orbit coupling curves control the magnitude of the splitting in Ω .

The spin-rotation coupling, $\hat{H}_{SR}$ concerns the relativistic interaction between the electronic spin and the rotational motion of the molecule and is, except for light molecules, a much smaller contribution than the spin-orbit (Lefebvre-Brion & Field, 2004).

The Λ -doubling terms are non-zero for electronic states with $\Lambda \neq 0$, which have a minimum of a double degeneracy in their rovibrational levels caused by a positive or negative projection of the angular momentum in the internuclear axis, informed by the parity. These constants hence control the magnitude of the energy splitting in parity and are described by the terms α_{opq} , α_{p2q} , and q (Brown et al., 1987). One example of this is the X $^2\Pi$ states in NaO and OH, which have non-zero terms as $\Lambda_\Pi = \pm 1$.

DUO allows an arbitrary number of couplings between various electronic states defining the so-called spectroscopic model. One usually has solved the electronic motion Schrödinger equation *a priori* in order to obtain PECs, SOCs, EAMCs, (T)DMCs etc. for the electronic states involved. It is common for quantum chemistry packages such as MOLPRO (Sections 2.2 and 4.2) to compute these property curves in the Born-Oppenheimer approximation. These curves can be supplied to the program as either a grid of *ab initio* points which are mapped onto the DUO grid using cubic splines, or in an analytical form.

First DUO solves the uncoupled one-dimensional vibrational Schrödinger equation with $J = 0$,

$$-\frac{\hbar^2}{2\mu} \frac{d}{dR^2} \psi_v(R) + V(R) \psi_v(R) = E_v \psi_v(R), \quad (2.31)$$

using the sinc-DVR (discrete variable representation) method (Guardiola & Ros, 1982; Lund & Riley, 1984), which returns a set of vibrational energies, E_v and vibrational wavefunctions ψ_v , a subset of which is selected to form the basis set of rovibronic basis functions (more details are available in Yurchenko et al. (2016a)). DUO uses this basis set to solve the complete problem given by Equation 2.22. In doing so, we obtain eigenstates and energies for the good quantum numbers J (total angular momentum), and τ (parity); other quantum numbers are assigned on the basis of the largest coefficient in the basis set. The vibrational quantum numbering scheme can be done this way, however recently, the standard has become to assign the vibrational quanta by counting up in energy within a given J, τ symmetry block for a given electronic state. This counteracts a problem where states with a higher vibrational quanta are sometimes lower in energy than states with lower vibrational quanta. This is not a perfect solution, however, as misassignments in regions where many electronic states overlap can still occur.

A complete spectroscopy for the system in question is then obtained by use of the eigenfunctions to compute transition line strengths and Einstein-A coefficients using the *ab initio* (T)DMCs (Section 2.1.3.1). All computed rovibronic states are outputted into a .STATES

file which contains an enumerator, n (acting as a unique key), quantum numbers, term values, and other metadata such as lifetimes and Landé g factors (Semenov et al., 2017). The computed transitions are provided as a .TRANS file which contains the upper and lower states of the transition given by enumerators n_i (initial) and n_f (final), the Einstein-A coefficient, and transition frequency ν (Tennyson et al., 2013).

To compute rovibronic energies and wavefunctions one requires a set of boundary conditions upon which the nuclear motion Schrödinger equation is solved, usually the setting of eigenstate wavefunctions and their derivative with respect to bond length, R , to zero at the simulation border. This is achieved in DUO by introducing a potential barrier of infinite height at the long-range (large R) side of the simulation region at bond length, R_c - the so-called particle in a box problem. Whilst this methodology is fully defined for solving bound rovibronic states which come as solutions to the nuclear motion inside potential wells, it does not provide a complete solution to the continuum region where states are unbound. Since we introduce a finite simulation box size, the continuum is truncated to the solutions which satisfy the boundary conditions, consequently the continuum is effectively discretized. If one could solve the nuclear motion for an infinite simulation box size, i.e. $R_c \rightarrow \infty$, then the infinite rovibronic solutions are reconstructed. Such a solution is necessary to completely model continuum processes such as predissociation and photodissociation, so efficient and accurate approximate methods to extend DUO's capacity for modelling the continuum are developed in Chapters 5 and 6, respectively.

2.1.3.1 Intensities

The Einstein-A coefficients (A_{fi} , in s^{-1}) in the .TRANS files are used to model the intensity of transitions, these are computed in DUO through the following relationship (Yurchenko et al., 2016a),

$$A_{fi} = \frac{64 \times 10^{-36} \pi^4}{3h} (2J_i + 1) \nu^3 \sum_{t=-1,0,1} \left| \sum_{n_i, n_f} \left(C_{\lambda_f, n_f}^{J_f, \tau_f} \right)^* C_{\lambda_i, n_i}^{J_i, \tau_i} (-1)^{\Omega_i} \begin{pmatrix} J_i & 1 & J_f \\ \Omega_i & t & -\Omega_f \end{pmatrix} \langle v_f | \bar{\mu}_t^{f,i}(R) | v_i \rangle \right|^2, \quad (2.32)$$

where ν is the transition frequency in cm^{-1} and $\bar{\mu}_t$ are the electronically averaged body-fixed electronic dipole moment components in Debye, with,

$$\bar{\mu}_0 = \bar{\mu}_z, \quad (2.33)$$

$$\bar{\mu}_{\pm 1} = \mp \frac{1}{\sqrt{2}} (\bar{\mu}_x \pm i \bar{\mu}_y), \quad (2.34)$$

and the vibrationally averaged dipole moments $\langle v_f | \bar{\mu}_t^{f,i}(R) | v_i \rangle$ are calculated using the vibrational wavefunctions, $v_{f,i}$. The indices, $n_{f,i}$ are enumerators uniquely identifying each rovibronic state.

$$\begin{pmatrix} J_i & 1 & J_f \\ \Omega_i & t & -\Omega_f \end{pmatrix}$$

is the 3-J symbol (Zare, 1988) for the given transition with initial J_i, Ω_i and final J_f, Ω_f .

The nuclear motion wavefunctions, $\phi_\lambda^{J,\tau}$ are written in the expanded form,

$$\phi_\lambda^{J,\tau} = \sum_n C_{\lambda,n}^{J,\tau} |n\rangle, \quad (2.35)$$

where λ is a counting index, and J, τ are the good quantum numbers for rotation and parity, and $|n\rangle$ is shorthand index for the basis set labels,

$$|n\rangle = |state, J, \Omega, \Lambda, S, \Sigma, v\rangle, \quad (2.36)$$

hence the same coefficients in Equation 2.32 are the coefficients from this basis set expansion. The Einstein-A coefficients are used in the simulation of absorption spectra as described in Section 2.4.

2.1.3.2 Curve refinement

The aforementioned set of *ab initio* curves can be used to solve the nuclear motion problem to obtain rovibrational energies and transitions. However, the results here are typically not in line with experimental data, even in cases where the level of electronic structure theory is very sophisticated. This is because experimental energy levels include all possible potential energy curves and couplings implicitly. In principle, one should be able to produce spectroscopically accurate rovibrational solutions using only *ab initio* curves by simply computing an increasing number of curves with a high level of theory. In practise this is not always the case, especially when many continuum electronic states are present, which are difficult to treat as previously mentioned. Additionally, *ab initio* methods, even at a high level of theory, are not always able to produce sufficiently accurate curves to begin with. Instead, whatever effect these curves may have on the positions of the energy levels is rerouted through refining the available potential energy curves and coupling curves.

Three flavours of curve refinement are available in DUO;

- Parameter variation of analytic representations (hereafter referred to simply as parameter variation),
- Morphing (Skokov et al., 1999; Meuwly & Hutson, 1999; Patrascu et al., 2014),
- Variation of individual points in the grid-point representation.

Irrelevant of the type of refinement, the curves are iteratively modified by solving the nuclear motion problem and comparing the rovibronic levels or transitions with experimentally derived values. These are often given in the form of MARVEL datasets (Section 2.5.1) or in the form of molecular constants which are then converted to energy levels using an effective Hamiltonian code such as PGOPHER (see Western (2017) and Section 2.5.2). At each iteration, a conjugate gradient descent algorithm (Yurchenko et al., 2016a) is applied to compute new curve shapes until a weighted least-squares solution to the nuclear motion problem is found. In this thesis, parameter variation and morphing are used extensively to model NaO and OH and are described briefly as follows.

Parameter variation works by first assigning an analytic form to the curve in question and then varying the parameters through the procedure described above. For potential energy

curves, the analytic forms used in these studies include the Morse potential (Morse, 1929), Extended Morse Potential (Sections 3.2.2 and 4.3.2) (Lee et al., 1999; Le Roy et al., 2006), and the Morse Long-Range potential (Section 4.3.3 (Le Roy et al., 2006; Le Roy & Henderson, 2007; Le Roy et al., 2009; Robert J. Le Roy & Li, 2011)). Common between them are the parameters which describe the features discussed in Figure 2.1, those being the position of the potential minimum, henceforth referred to as T_e , the asymptotic energy limit, or dissociation limit, D_e , and the equilibrium bond length, R_e . The remaining parameters further refine the shape of the potential, making it narrower, wider, or adjusting the shape of the long-range region at internuclear separations greater than R_e . This type of refinement is typically only performed on PECs as it is necessary to know R_e , T_e , and D_e when comparing to literature and coupling curves do not have a standard set of analytic forms which are easy to implement.

In the case of couplings, morphing is more applicable. Morphing is similar to parameter variation fitting with one degree of separation. Instead of modifying the target curve's analytic form, one modifies a morphing function, f_m , to minimise the least squares. f_m acts on the *ab initio* grid points as,

$$f_{\text{Morphed}} = f_m f_{\text{ab initio}}. \quad (2.37)$$

This is not typically applied when refining PECs as it then becomes difficult or impossible to arrive at an accurate measurement of the equilibrium bond length, R_e , directly from the morphing form, which is a parameter of interest. A further reason that morphing is not applied to PECs is that, should the electronic state in question be the ground state, the potential minimum, T_e , has zero energy and so the position of this minimum cannot be refined through a multiplicative factor like f_m .

2.2 Electronic Structure Calculations

Electronic structure theory attempts to recover the electronic potential energy $U(R)$ from Equation 2.12 to substitute into the nuclear motion equation 2.21. This is a much studied problem with many techniques having been developed to treat atomic and molecular systems to varying degrees of complexity. Despite the simplification due to Born and Oppenheimer, the clamped nuclei Hamiltonian is not easy to solve and analytic solutions are not available. As such this problem must be solved numerically. This section will briefly cover some techniques for obtaining $U(R)$. This is not an exhaustive list of methods, and will only go as far to introduce the methods used in Section 4.2 for the calculation of the OH radical's curves. A good introductory textbook for these topics is Levine (2013). The review paper by Lodi & Tennyson (2010) also provides good context to a broad range of methods and recommends many other useful resources.

Fundamentally, the methods used here are based on the variation theorem, which states that for a system with a time-independent Hamiltonian, and with a lowest energy eigenstate with energy, E_0 , and a wavefunction, ϕ , which satisfies the boundary conditions, the integral in Equation 2.38 is always an upper bound for the energy,

$$\langle \phi | \hat{H} | \phi \rangle \geq E_0. \quad (2.38)$$

While the molecules studied in this thesis, NaO and OH, are both open-shell systems, in

this section we consider only closed-shell systems. This section is written to serve as a brief and high-level introduction to electronic structure theory and the mathematics required to treat open-shell systems is significantly more complex than that for closed-shell systems.

2.2.1 Hartree-Fock Self-Consistent Field (SCF)

The Hartree-Fock method, often referred to simply as the self-consistent field method (SCF) is based on minimising the variation integral. Taking the electronic Hamiltonian, $\hat{H}_{el}$ from Equations 2.6 to 2.12, we write the Hartree-Fock (HF) energy as,

$$E_{HF} = \langle D | \hat{H}_{el} + V_Z | D \rangle, \quad (2.39)$$

where D is the Slater determinant of molecular orbitals. The HF energy of a closed-shell diatomic molecule is rewritten as,

$$E_{HF} = 2 \sum_{i=1}^{n/2} H_{ii}^{core} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_Z, \quad (2.40)$$

where the summation limits represent molecular orbitals. As all orbitals are doubly occupied, we have n electrons in $n/2$ orbitals. H_{ii}^{core} is the diagonal matrix element of the one electron core Hamiltonian, $\hat{H}^{core}$, defined as,

$$\hat{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}}, \quad (2.41)$$

again, with α representing nuclear terms, hence,

$$H_{ii}^{core} = \langle \phi_i | \hat{H}^{core}(1) | \phi_i \rangle, \quad (2.42)$$

and J_{ij} and K_{ij} being the Coulomb and exchange integrals respectively,

$$J_{ij} = \langle \phi_i(1)\phi_j(2) | \hat{g}_{ij} | \phi_i(1)\phi_j(2) \rangle, \quad (2.43)$$

$$K_{ij} = \langle \phi_i(1)\phi_j(2) | \hat{g}_{ij} | \phi_j(1)\phi_i(2) \rangle, \quad (2.44)$$

$$\hat{g}_{ij} = \frac{1}{r_{ij}}. \quad (2.45)$$

For a set of orthonormal molecular orbitals ϕ_i , we find ϕ_i such that Equation 2.40 is minimised as per Equation 2.38. One finds that ϕ_i satisfy,

$$\hat{F}(1)\phi_i(1) = \epsilon_i\phi_i(1), \quad (2.46)$$

$$\hat{F}(1) = \hat{H}^{core}(1) + \sum_{j=1}^{n/2} (2\hat{J}_j(1) - \hat{K}_j(1)), \quad (2.47)$$

where $\hat{F}$ is the Fock operator and the Coulomb and exchange operators are defined by the following integrals,

$$\hat{J}_j(1)f(1) = f(1) \int |\phi_j(2)|^2 \frac{1}{r_{12}} dv_2, \quad (2.48)$$

$$\hat{K}_j(1)f(1) = \phi_j(1) \int \frac{\phi_j^*(2)f(2)}{r_{12}} dv_2 \quad (2.49)$$

for an arbitrary function, f , integrated over all space. To find the molecular energy, ϵ_i , we multiply Equation 2.47 by ϕ_i^* ,

$$\epsilon_i = H_{ii}^{\text{core}} + \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}), \quad (2.50)$$

where J_{ij} and K_{ij} are from Equations 2.43 to 2.45, hence summing over all orbital energies,

$$E_{\text{HF}} = 2 \sum_{i=1}^{n/2} \epsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_Z. \quad (2.51)$$

Now expanding the molecular orbitals in terms of a set of one-electron basis functions, χ_s ,

$$\phi_i = \sum_{s=1}^b c_{si} \chi_s, \quad (2.52)$$

where b is the size of the basis set, and c_{si} are the expansion coefficients. To exactly represent ϕ_i , $b \rightarrow \infty$, however in practise, one uses a finite b , however if b is large enough, and the basis functions, χ_s are well chosen, this is a very good approximation to ϕ_i . By substituting this expansion into Equation 2.47, then multiplying by χ_r^* we arrive at,

$$\sum_{s=1}^b c_{si} (F_{rs} - \epsilon_i S_{rs}) = 0 \quad r \in 1, 2, \dots, b, \quad (2.53)$$

$$F_{rs} = \langle \chi_r | \hat{F} | \chi_s \rangle, \quad (2.54)$$

$$S_{rs} = \langle \chi_r | \chi_s \rangle, \quad (2.55)$$

forming a set of b simultaneous equations with b unknowns, c_{si} , for $s \in 1, 2, \dots, b$, that describe the molecular orbitals in Equation 2.52. Non-trivial solutions must satisfy,

$$\det(\mathbf{F} - \epsilon_i \mathbf{S}) = 0. \quad (2.56)$$

These equations are known as the Roothaan equations and must be solved iteratively, as the Fock operator matrix elements depend on ϕ_i which in turn depend on the expansion coefficients c_{si} . In general, the procedure is as follows.

1. Guess initial values for the expansion coefficients of the ϕ_i orbitals, c_{si} ,
2. Compute the form of the Fock operator as per Equation 2.47,
3. Compute the values for the integrals, F_{rs} and S_{rs} ,

4. Solve the Roothaan Equation 2.56 for an initial value of ϵ_i ,
5. Use the ϵ_i from 4. to solve the expanded form of Equation 2.46, to obtain improved coefficients,
6. Use the improved coefficients to repeat the process until the value of ϵ_i converges.

Pages 410-414 of Levine (2013) give an explicit example of this procedure.

There are several different flavours of the Hartree-Fock method described, depending on the type of system being solved. For closed-shell systems like the one above, one uses Restricted Hartree-Fock (RHF). RHF is characterised by a system of equations such that spin-paired electrons are given the same spatial orbitals. For open-shell systems, one can use Restricted Open-Shell Hartree-Fock (ROHF) or Unrestricted Hartree-Fock (UHF). In ROHF, electrons which are paired with each other are given the same spatial orbitals, otherwise, one can use different spatial orbitals. An atomic example which can be used analogously given in Levine (2013) is that of the ground state of Li whereby the electron configuration is $|1s1\bar{s}2s|$. The two $1s$ electrons are paired and are given the same spatial orbital, whereas the $2s$ can be given a different orbital. The problem with this is that the $2s$ electron with spin α will interact differently with the $1s$ electron with spin α/β than with the $1\bar{s}$ electron with spin β/α . As such the $1s$ and $1\bar{s}$ electrons are given different spatial orbitals, this is the UHF regime. UHF does, in general return a lower energy solution to the variation problem, however, the wavefunctions calculated are not eigenfunctions of the $\hat{S}^2$ operator, and so are not spin-pure. When using UHF, if the value of $\langle \hat{S}^2 \rangle$ is very different from $S(S+1)\hbar^2$, then the wavefunction must be treated with some caution. The ROHF wavefunction is a true eigenfunction of the $\hat{S}^2$ operator but doesn't return as low energies as the UHF wavefunctions.

2.2.2 Multi-configuration Self-Consistent Field Methods

While the HF methods described are often a good approximation of the ground-state energies of some molecular systems. HF fails to account for instantaneous correlations between motions of electrons (dynamic correlation) and at large R , HF energies do not behave properly and so give inaccurate dissociation energies. This can be remedied by introducing Multi-configuration Self-Consistent Field (MCSCF) methods.

Consider another atomic example of the excited state of He, $|1s2s|$. One can write several different spin configurations for this electronic configuration. For example, the spins of the $1s$ and $2s$ electrons can both be α or both be β , or they can be opposite, each such many electron function, Φ_i is a configuration state function (CSF), which is normally anti-symmetric in spin. An analogous treatment can be performed for the molecular orbitals (MOs) and form the molecular CSF. Each such CSF is a Slater determinant or a linear combination of Slater determinants, for simplicity, we will consider the former.

We shall take as an example some arbitrary configuration state function as,

$$\Phi_i = |\phi_i \bar{\phi}_i|, \quad (2.57)$$

where ϕ_i is an MO. The total wavefunction, considering these CSFs is written as their linear combination,

$$\Psi = \sum_i c_i \Phi_i. \quad (2.58)$$

Recalling Equation 2.52, that the MOs are rewritten in their expanded form, leading to two sets of coefficients which can be optimized: The c_i coefficients above to modify the weights of the CSFs making up the wavefunction and the c_{si} coefficients from Equation 2.52 to modify the orbitals themselves. One can then arrive at the following equation, bearing resemblance to Equation 2.56,

$$\det(\mathbf{H} - E\mathbf{S}) = 0, \quad (2.59)$$

where,

$$H_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle, \quad (2.60)$$

$$S_{ij} = \langle \Phi_i | \Phi_j \rangle, \quad (2.61)$$

which is solved variationally for the set of CSFs with the target symmetry and spin multiplicity, e.g. $^2\Sigma_g^+$, $^4\Pi$ to arrive at the best expansion coefficients, c_i , and c_{si} .

A common MCSCF method, Complete Active Space Self-Consistent Field (CAS-SCF) is used in electronic structure calculations in this thesis which contains the added concept of an active space. One divides the CSFs into active and inactive orbitals (commonly referred to as open and closed orbitals). Inactive orbitals are always kept doubly occupied. Active orbitals contain electrons which are free to move to other active orbitals, this defines the active space. One writes the wave function of the system as a linear combination of all CSFs that can be formed by distributing the active electrons among the active orbitals in all possible ways given the spin and symmetry values of the state in question. Then performs the above calculation, optimizing c_i and c_{si} as before.

Within the MCSCF method, there is the added concept of state-averaging, whereby MCSCF orbitals are optimized for states of more than one symmetry and spin multiplicity, allowing one to get a single set of optimized orbitals which work for all states considered. For example, consider a system with a ground state, X $^2\Pi$ and first excited state A $^2\Sigma^+$. One can form MCSCF orbitals which are optimized for both states and can extract potential energy curves simultaneously and also allows for the computation of coupling curves. The downside to this, however, is that this state-averaging negatively impacts the calculation of the ground state potential energy curve. The produced orbitals are no longer optimized for the ground state, which would produce the best results, but rather for the entire system. This leads to a reduction in accuracy (McKemmish et al., 2016).

In the CAS-SCF calculations performed in Section 4.2, several state averaging schemes are used depending on the electronic state calculated. Transition dipole moments and coupling curves between two electronic states are calculated for states which share optimized CAS-SCF orbitals. The final state averagings are heavily based on the “recipe” provided by van der Loo & Groenenboom (2005), which covers which states to include in the state-averaging and appropriate active spaces.

2.2.3 Configuration Interaction (CI)

Similarly to MCSCF methods, the CI family of methods deals with an optimization of the total wavefunction expressed as an expansion of CSFs. Going back to the atomic Helium example, when calculating the ground state, $|1s^2|$, corrections to the wavefunction arise from contributions of higher energy configurations like $|2s^2|$ and $|2p^2|$. Considering these contributions is the so-called CI method. These CI calculations are called singly, doubly, triply,... excited depending on how many electrons are excited from the ground state configuration, leading to a hierarchy of models of varying complexity (Lodi & Tennyson, 2010).

The most common way to perform this calculation - again - uses the variation principle. We choose a basis set (of size b) one-electron function, χ_s , as in Equation 2.52, obtaining b molecular orbitals. These orbitals can be obtained using an SCF calculation. The lowest energy orbitals are occupied orbitals (OO) for the ground state, the remaining unoccupied orbitals are called virtual orbitals (VO). Using the set of OOs and VOs, one can form the set of many-electron functions, $\{\Phi_i\}$ that have different occupancies - the CSFs. After writing the total wavefunction as a linear combination of these CSFs, one optimizes the expansion coefficients c_i variationally by minimizing Equation 2.59. The number of CSFs possible increases very rapidly with the number of electrons, n , and the number of basis functions, b , roughly scaling as,

$$|\{\Phi_i\}| \approx b^n. \quad (2.62)$$

If a CI calculation is solved for all possible CSFs for a given symmetry and spin, this is called a **full CI** calculation which is prohibitively expensive for large n due to the rapidly increasing number of CSFs. Vogiatzis et al. (2017) were able to achieve a single full CI iteration for the chromium tetramer. This required the calculation of almost one trillion Slater determinants and was the largest such calculation attempted to date with $n = 24$.

In practice, CI is typically truncated by including only excitations from valence shell electrons. In other words, the inner (core) electrons are always kept doubly occupied. This is the so-called **frozen core** (FC) approximation.

2.2.4 Multi-Reference Configuration Interaction (MRCI)

Combining MCSCF and CI leads to the MRCI method. The principle behind this method is to take the already optimized CSFs from a successful MCSCF calculation and then apply the CI method on top of this. One effectively moves electrons out of OOs in the set of m MCSCF CSFs, $\Phi_i^{\text{MCSCF}}, \dots, \Phi_m^{\text{MCSCF}}$ and produces more excited CSFs leading to n total CSFs, $\Phi_i^{\text{MCSCF}}, \dots, \Phi_m^{\text{MCSCF}}, \Phi_{m+1}, \dots, \Phi_n$. Again defining the wavefunction as in Equation 2.58, one optimizes the expansion coefficients to produce lower energies and more accurate state wavefunctions. MRCI is a very computationally expensive method if applied directly as is described above. As such many further approximations have been proposed, namely internally contracted MRCI (icMRCI) which is the method implemented in the MOLPRO quantum chemistry package used here with descriptions available by Werner et al. (2012) and the references therein. The MOLPRO quantum chemistry package has been used here to produce potential energy curves, coupling curves, and (transition) dipole moment curves for the OH radical. The calculation set up used is heavily based on the recipe produced by van der Loo & Groenenboom (2005) and details are available in Section 4.2.

The coupling curves used in Section 2.1.3 can be calculated *ab initio* using MOLPRO. Leveraging the above computed optimal MRCI electronic wavefunctions, one uses them

as an input to calculate the matrix elements of the appropriate operator to calculate the corresponding coupling curve. For example, the electronic wavefunctions can be used in conjunction with the Breit-Pauli spin-orbit operator, $\hat{H}_{SO}$, to compute the spin-orbit coupling term between two electronic states, or the orbital angular momentum operator $\hat{L}_{x,y,z}$ to calculate the EAMCs.

The spin-rotation, $\gamma_{A,B}$ and Λ -doubling terms are not calculable in MOLPRO, and for use in DUO are typically found semi-empirically by referencing effective Hamiltonian studies or by the curve refinement process in Section 2.1.3.2.

Similarly, one computes the (transition) dipole moment curves by computing the matrix elements of the electronic dipole moment operator, $\hat{\mu}$ in the same fashion, allowing for the calculation of line intensities as in Section 2.1.3.1³.

2.3 ExoMol and Line lists

The ExoMol project has been producing molecular data such as line lists and absorption cross-sections for modelling exoplanetary atmospheres since 2011 with a strong focus on temperature-dependence of the absorption cross-sections. Datasets are released every four years with the latest release being Tennyson et al. (2024). The primary data product, line lists, consist of two file types, .STATES, and .TRANS files. These contain lists of rovibronic states and the transitions between them respectively. .STATES files contain information about individual states such as their energy, quantum numbers, total lifetimes, uncertainties, and Landé g factors (Semenov et al., 2017) as per the latest ExoMol standard (Tennyson et al., 2023). Each state has a unique key n , effectively a counting number which relates to the .TRANS file which is organised as the unique keys of the upper state and the lower state, the Einstein-A coefficient, and the transition frequency in cm^{-1} . Samples of these files can be found in Tables 3.6, 3.7 for NaO and 4.18, 4.19 for OH.

These line lists can be formed in several ways. The previous OH linelist is based on the effective Hamiltonian computations of Brooke et al. (2016) and Yousefi et al. (2018), whereas the current line list, MYTHOS, is based the nuclear motion model described in Section 4. MARVEL datasets (Section 2.5.1) can also be used to form linelists directly from experimental data, however these tend to be more limited than the variational approach which is performed in Chapters 3 and 4. While experimental energy levels are very accurate, they are not always sufficiently complete in quantum number coverage.

2.4 Simulating Absorption Spectra

The simulation of molecular absorption spectra is done using the EXOCROSS (Yurchenko et al., 2018c) and PYEXOCROSS (Zhang et al., 2024b) packages. EXOCROSS is a Fortran 2003 code and PYEXOCROSS is a more recent, Python code. These take the line list (.STATES and .TRANS) files as input, and produce a photoabsorption spectrum for a given temperature, T . Transition intensities, I , are calculated as,

$$I(f \leftarrow i) = \frac{g_f^{\text{tot}} A_{fi}}{8\pi c \nu_{fi}^2} \frac{e^{-c_2 E_i/T} (1 - e^{-c_2 \nu_{fi}/T})}{Q(T)}, \quad (2.63)$$

³For more information on MOLPRO calculations: www.molpro.net/manual/doku.php

where the partition function $Q(T)$ is defined as:

$$Q(T) = \sum_n g_n^{\text{tot}} e^{-c_2 E_n / T}, \quad (2.64)$$

Where the total degeneracy, $g_n^{\text{tot}} = g_n^{\text{ns}}(2J_n + 1)$ for the nuclear-spin statistic g_n^{ns} . $c_2 = 1/k_b$ is the second radiation constant in cm K and T is the temperature in K. ν_{fi} is the transition frequency, A_{fi} is the transition Einstein-A coefficient, and c is the speed of light in cm s⁻¹.

In reality, transition lines are not seen purely as discrete transitions with infinitesimal width and must be broadened using an appropriate line profile. The selection of a line profile depends on the type of broadening effects considered which can include Doppler broadening, lifetime broadening, and pressure broadening. Section 4.5.1 discusses the specifics of this when it comes to selecting line profiles for OH. The simplest form of broadening one can use is Gaussian broadening, whereby a Gaussian line profile with a line width, α_G , is applied for all transitions, accounting for the Doppler effect. This is used in the case of NaO in Section 3.3.3, with a more complete version described for OH in Section 4.5.1. The Gaussian line profile is defined as,

$$G(\nu; \sigma_G) = \frac{1}{\sigma_D \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{\nu - \nu_{fi}}{\sigma_G} \right)^2}, \quad (2.65)$$

where σ_G is the Gaussian profile's standard deviation defined as;

$$\sigma_G = \frac{\alpha_G}{2\sqrt{2 \ln 2}}. \quad (2.66)$$

For an arbitrary line profile, $P(\nu)$, we expect that the transition intensity for a specific line centered on ν_{fi} , $I(\nu_{fi})$, and the integral of cross-section of that line, $\int_0^\infty \sigma_{fi}(\nu) d\nu$, should be the same. Line profiles are normalised, so one defines the cross-section as;

$$\sigma(\nu) = P(\nu) \times I(\nu_{fi}). \quad (2.67)$$

Cross-sections are produced on a grid of finite resolution. Consider the grid-represented wavenumber range, ν (between $\nu_{\min}$ and $\nu_{\max}$ with grid spacing $\delta\nu$) and the infinite set of all possible wavenumber values, $\tilde{\nu}$ (between 0 and ∞ with grid spacing approaching 0). It is clear that one cannot simply produce a cross-section with a wavenumber grid, ν without losing information because this will omit intensity in regions where $\nu_{fi} \in \tilde{\nu}$ but $\nu_{fi} \notin \nu$. EXOCROSS and PYEXOCROSS do indeed account for this. The methods by which they do this are given by Yurchenko et al. (2018c) and Zhang et al. (2024b) respectively.

Cross-sections are also used in the computation of photodissociation rates k , whereby the photodissociative transitions' cross-section is isolated from the total photoabsorption cross-section and is integrated over a flux of photons, $F(\nu)$, between two wavelengths as such,

$$k = \int_{\nu_1}^{\nu_2} F(\nu) \sigma(\nu) d\nu. \quad (2.68)$$

This is discussed in more detail in Section 6.2.3 when computing these rates for photodissociative transitions in OH.

2.5 Energy Levels

2.5.1 MARVEL

Measured Active Rotational-Vibrational Energy Levels (MARVEL) is an algorithm produced by [Furtenbacher et al. \(2007\)](#) to compute a set of self-consistent energy levels from a data set of experimental transitions (line positions) and transition uncertainties. It does this by employing a transition inversion algorithm to arrive at a set of energy levels with associated uncertainties. The energy levels produced by MARVEL are self-consistent in their transitions, quantum numbers, and uncertainties, such that as many experimental sources as possible are appropriately accounted for. The set of energy levels produced are modelled as a graph of nodes representing the levels, and connectors representing transitions between levels - the so-called spectroscopic network. This is a robust method for producing energy levels empirically, and has seen extensive use within the ExoMol group, recently having produced high quality line lists for methane [Kefala et al. \(2024\)](#), VO ([Bowesman et al., 2024b](#)), and ozone ([Upadhyay et al., 2024](#)) to name a few.

These datasets are often used in the curve refinement procedure from Section 2.1.3.2 by providing the reference energy levels. Each MARVEL energy level's uncertainty, Δ_E is paired with a number, N_C , representing the number of connectors to a given energy level. An energy level with more connectors is more rigorously defined relative to other transitions, and so can be treated with more confidence. The uncertainty and number of connectors is often used to inform the weighting in the least-squares algorithm by some function, $f_\Delta(\Delta_E, N_C)$, which increases the weighting as N_C increases, and decreases the weighting as the uncertainty increases. Formally,

$$\lim_{N_C \rightarrow \infty} (f_\Delta) \rightarrow 1, \quad (2.69)$$

$$\lim_{\Delta_E \rightarrow \infty} (f_\Delta) \rightarrow 0. \quad (2.70)$$

The form of f_Δ is dependent on how much weight is to be put on N_C and Δ_E , and is sometimes adjusted to scale with J or v in some manner as to not punish higher energy states for a lower number of connections. Some examples of weighting functions are,

$$f_\Delta(\Delta_E, N_C) = \frac{1}{\Delta_E} N_C, \quad (2.71)$$

$$\tilde{f}_\Delta(\Delta_E, N_C) = \log_{10} \left(\frac{1}{\Delta_E} \right) N_C, \quad (2.72)$$

$$(2.73)$$

the second of which is used in Chapter 4 after being normalised such that $\sum_i f_{\Delta_i} = 1$.

2.5.2 PGOPHER

PGOPHER ([Western, 2017](#)) is a general purpose program for simulating and fitting molecular spectra with the effective Hamiltonian method. This program has seen wide use in other groups for producing effective Hamiltonian models of several molecules, including the MolLIST model of OH ([Brooke et al., 2016](#); [Yousefi et al., 2018](#)) which makes up a considerable portion of the recent MARVEL dataset of OH ([Furtenbacher et al., 2022](#)).

It was used in this work to simulate the rotational levels of the $\nu = 0$ band of NaO using the molecular constants from [Yamada et al. \(1989\)](#) for preliminary studies in forming the spectroscopic model, but was forsaken in favour of directly using experimental transitions and is not discussed further.⁴

⁴For more details on the PGOPHER linear molecule Hamiltonian, documentation is available at pgopher.chm.bris.ac.uk/Help/linham.htm.

Chapter 3

Sodium Oxide (NaO) Linelist

3.1 Introduction

The experimental spectroscopic data related to optical transitions of the gas-phase NaO molecule is very sparse. [Yamada et al. \(1989\)](#) provide comprehensive microwave data on the pure rotational transitions of the ground $X^2\Pi$ electronic state for the lowest vibrational $v'' = 0, 1, 2, 3$ levels. However, no experimental data on ro-vibrational transitions are available, and hence, the separations between vibrational levels are not yet experimentally determined. Some information is available on the $B^2\Pi \rightarrow X^2\Pi$ emission spectrum. However, this is minimal, unassigned, and with no characterisation of the B state ([Pfeifer & Gole, 1984](#); [Pugh et al., 1996](#)), which sometimes is assigned as the C $^2\Pi$ state ([Langhoff et al., 1991](#)). The only experimental observation of the lowest excited A $^2\Sigma^+$ state is due to [Joo et al. \(1999\)](#) who could assign a handful of the low rotational levels $J \in [4.5, 19.5]$ belonging to the rovibronic A $^2\Sigma^+(v' = 0) \leftarrow X^2\Pi(v'' = 0)$ transitions, however, the majority remain unassigned.

3.1.1 Quantum Number Conversions

[Joo et al. \(1999\)](#) provided transition frequencies for A $^2\Sigma^+ \leftarrow X^2\Pi$ for $J \in [4.5, 19.5]$. These data were represented using the quantum labels F_1 and F_2 , representing spin components $J = N + \frac{1}{2}$ and $J = N - \frac{1}{2}$, respectively. For Hund's Case (a) as is the case for the $X^2\Pi$ state in the limit of low J , for a given vibrational level, a rotational level (aside from those split by Λ doubling) can be given by:

$$B[(J+S)^2 - \Lambda^2] \pm \frac{1}{2}(A - 2B) \quad (3.1)$$

Where B is the rotational constant and $A = A_{SO}$ is the spin-orbit constant. If the second term in Equation 3.1 is positive, this corresponds to F_2 states, and F_1 if it is negative. Since $A < 0$ and $B > 0$, $E_{F_1} < E_{F_2}$ and this corresponds to the $^2\Pi_{|\Omega|=\frac{1}{2}}$ and $^2\Pi_{|\Omega|=\frac{3}{2}}$ states respectively. For the A $^2\Sigma^+$ state, Hund's case (b) applies and the splitting is given by:

$$BN(N+1) + E_{sr}, \quad (3.2)$$

where E_{sr} is the spin-rotation term. This term is given by

$$E_{sr} = \begin{cases} \frac{1}{2}\gamma N & \text{for } F_1 \\ -\frac{1}{2}\gamma(N+1) & \text{for } F_2 \end{cases}, \quad (3.3)$$

where γ is the spin-rotation constant, and,

$$N = \begin{cases} J - \frac{1}{2} & \text{for } F_1 \\ J + \frac{1}{2} & \text{for } F_2 \end{cases}. \quad (3.4)$$

In the case for NaO, [Joo et al. \(1999\)](#) give the nominal estimate of $\gamma \approx 0.01$, so $\gamma \ll B$. From this, we can see that $E_{F_1} < E_{F_2} \forall J$. As is this is the only splitting in the A $^2\Sigma^+$ state, this labelling is redundant and they can be assigned as e and f states respectively ([Wang et al., 2020](#)). Only the relative energy needs to be considered when converting between schemes. This was done by matching energy levels from DUO ([Yurchenko et al., 2016a](#)) to the given transitions from [Joo et al. \(1999\)](#) and checking which parity returns the higher energy level; this one is assigned the F_2 label ($E_e < E_f \forall J$).

3.2 Methods

3.2.1 Electronic Structure Calculations

Electronic structure calculations were performed by collaborators, Prof. Alexei Buchachenko and Prof. Andrei Stolyarov. The initial set of required potential energy curves (PECs), permanent and transition dipole moments for the ground $X^2\Pi$ and near-lying excited $A^2\Sigma^+$ states of NaO were obtained in the framework of *ab initio* electronic structure calculations which were accompanied by the evaluation of the relevant non-adiabatic matrix elements for the spin-orbit and Coriolis (electron-rotational) coupling. Scalar relativistic effects are introduced by means of the second-order Douglas-Kroll Hamiltonian ([Reiher & Wolf, 2004](#)). All calculations were performed in the range of internuclear distance $R \in [1.0, 5.0]$ Å using the MOLPRO program suite ([Werner et al., 2010, 2015, 2020](#)).

For both Na and O atoms, aug-cc-pVQZ all electrons basis sets was used. The optimized molecular orbitals (MO's) were generated using the state-averaged self-consistent field (SA-CASSCF) method ([Werner & Knowles, 1985](#)), taking the lowest doublet (1-3) Π , (1) Σ^+ , (1) Σ^- , and (1) Δ states with equal weights. Internally-contracted multi-reference configuration interaction (MR-CISD) calculations ([Knowles & Werner, 1992](#)) followed, in which impact of higher excitation on the correlation energy was taken into account implicitly using the Davidson correction ([Langhoff & Davidson, 1974](#)). For both SA-CASSCF and MR-CISD steps the active space consisted of $7a_1$, $3b_1$ and $3b_2$ orbitals corresponding to the point group symmetry C_{2v} , while the lowest two a_1 orbitals were kept to be doubly occupied.

The full counterpoise correction ([Boys & Bernardi, 1970](#)) was accounted for each state individually with the residual size-consistency error eliminated at $R = 20$ Å. Both permanent and transition dipole moments as well as non-adiabatic L -uncoupling matrix elements (electronic angular momentum coupling) were computed using the MR-CISD wave functions. The same wave functions and the full Breit-Pauli operator were used to compute the SOCs ([Berning et al., 2000](#)). Figures 3.1, 3.2, and 3.3 outline the calculated curves that

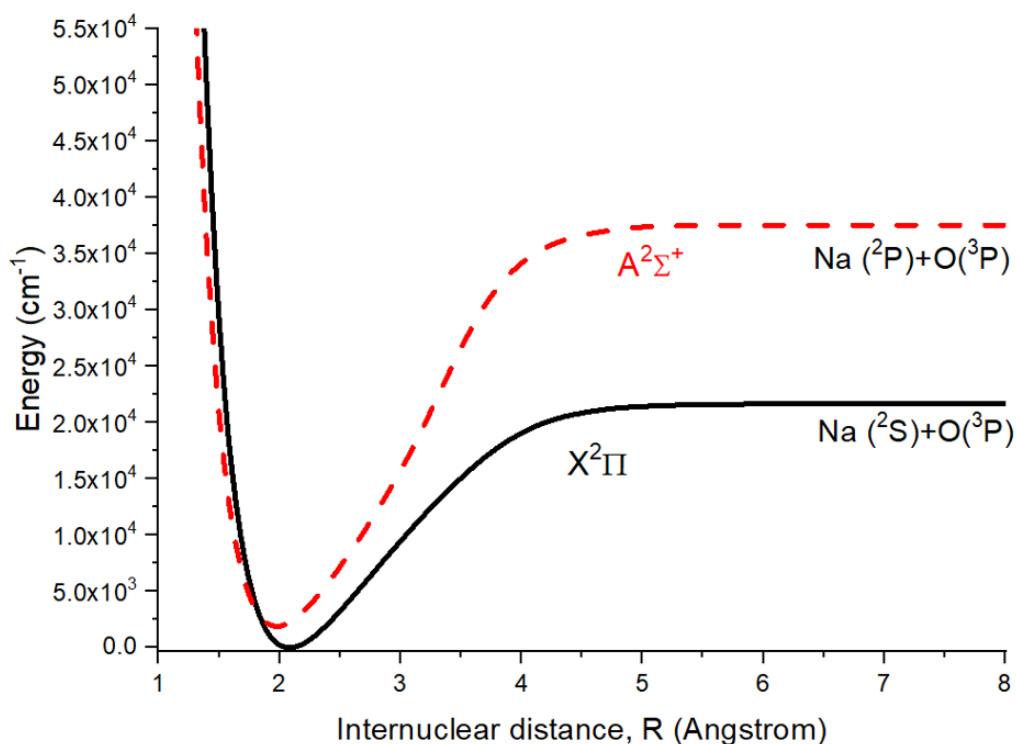


Figure 3.1: *ab initio* MRCI PECs for the $X^2\Pi$ and $A^2\Sigma^+$ electronic states of NaO.

have been used in this study.

The present dipole moments are in a good agreement with their previous theoretical counterparts computed by [Langhoff et al. \(1991\)](#).

According to the expected ion-pair character of the interatomic bond, the permanent dipole moments of both A and X states are rapidly increasing linear functions of R while the corresponding A–X electronic transition dipole moment is small, but not negligible (see Figure 3.3). The maximal values of the present A–X transition moment are about 0.1–0.15 D which agree well with the estimate $|d_{AX}| < 0.2$ D given in [Joo et al. \(1999\)](#). At $R > 3.5$ Å, the ground state permanent dipole decreases due to the avoided crossing effect with the excited $C^2\Pi$ state. An even more abrupt drop in the permanent dipole is observed for the A-state but at larger internuclear distances, presumably also due to an avoided crossing.

[O’Hare & Wahl \(1972\)](#) give an equilibrium dipole moment for the $X^2\Pi$ state of 8.71 D which was adopted by the JPL Molecular Spectroscopy Database ([Pickett et al., 1998](#)) to provide transition intensities. The *ab initio* equilibrium value is $|d_{XX}(R_e)| = 8.43$ D, while the vibrationally averaged dipole moment extracted from the DUO the matrix element $|\langle v_X = 0 | d_{XX} | v_X = 0 \rangle|$ is 8.44 D, which is very similar to the equilibrium dipole moment. These results suggest that JPL predicted transitions are slightly (about 6%) too strong.

3.2.2 Fitting Procedure

The *ab initio* PECs, spin-orbit coupling (SOC) and electronic angular momentum coupling curves calculated above in Section 3.2.1 are combined to form the spectroscopic model. This is then used to evaluate non-adiabatic rovibronic term values and corresponding multi-channel wavefunctions for the mutually perturbed $X^2\Pi$ and $A^2\Sigma^+$ states of NaO. However,

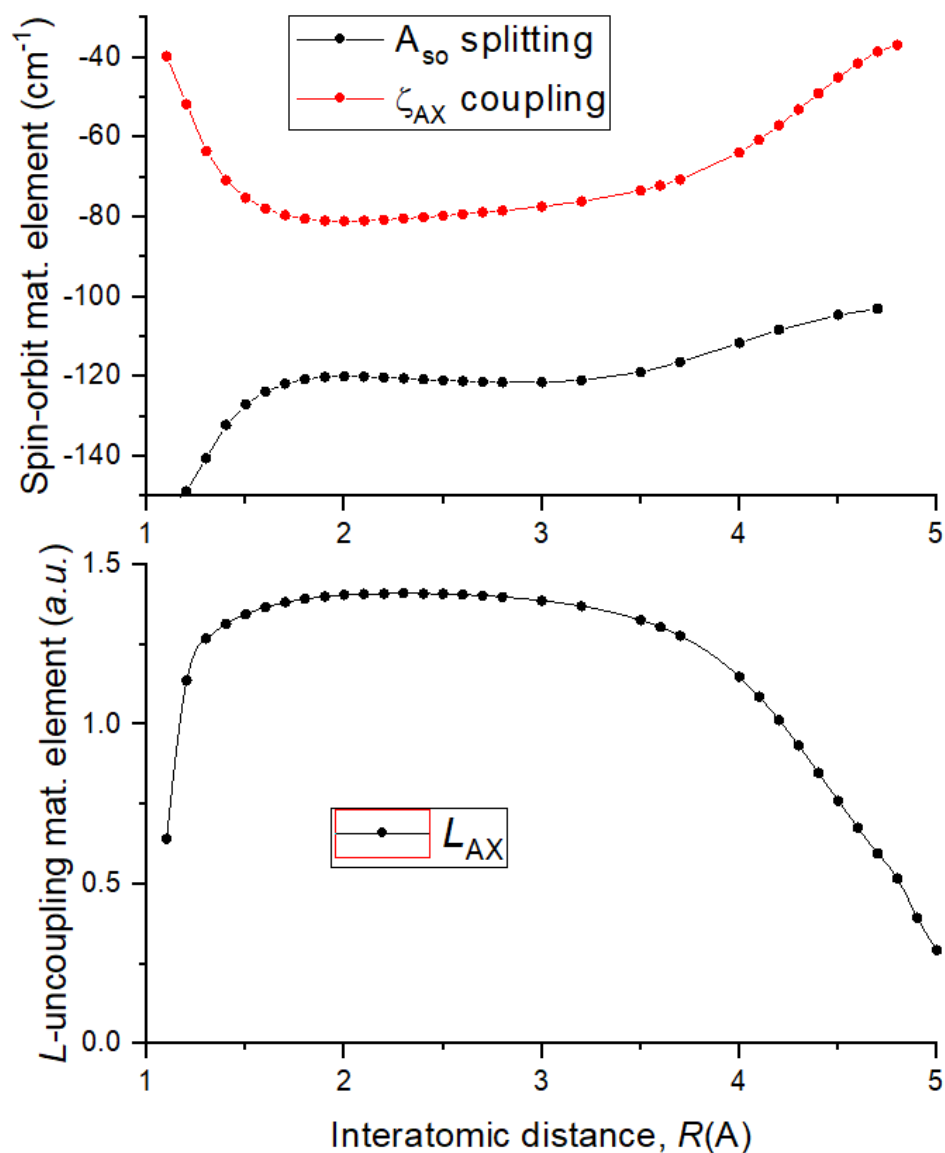


Figure 3.2: On-diagonal, $A_{so}(R)$, and off-diagonal, $\zeta_{AX}(R)$, spin-orbit coupling curves evaluated by MRCI method for the X-state and A-states (top). $L_{AX}(R)$ is the non-adiabatic matrix element of electron-rotational interaction *ab initio* calculated between the X-state and A-states (bottom).

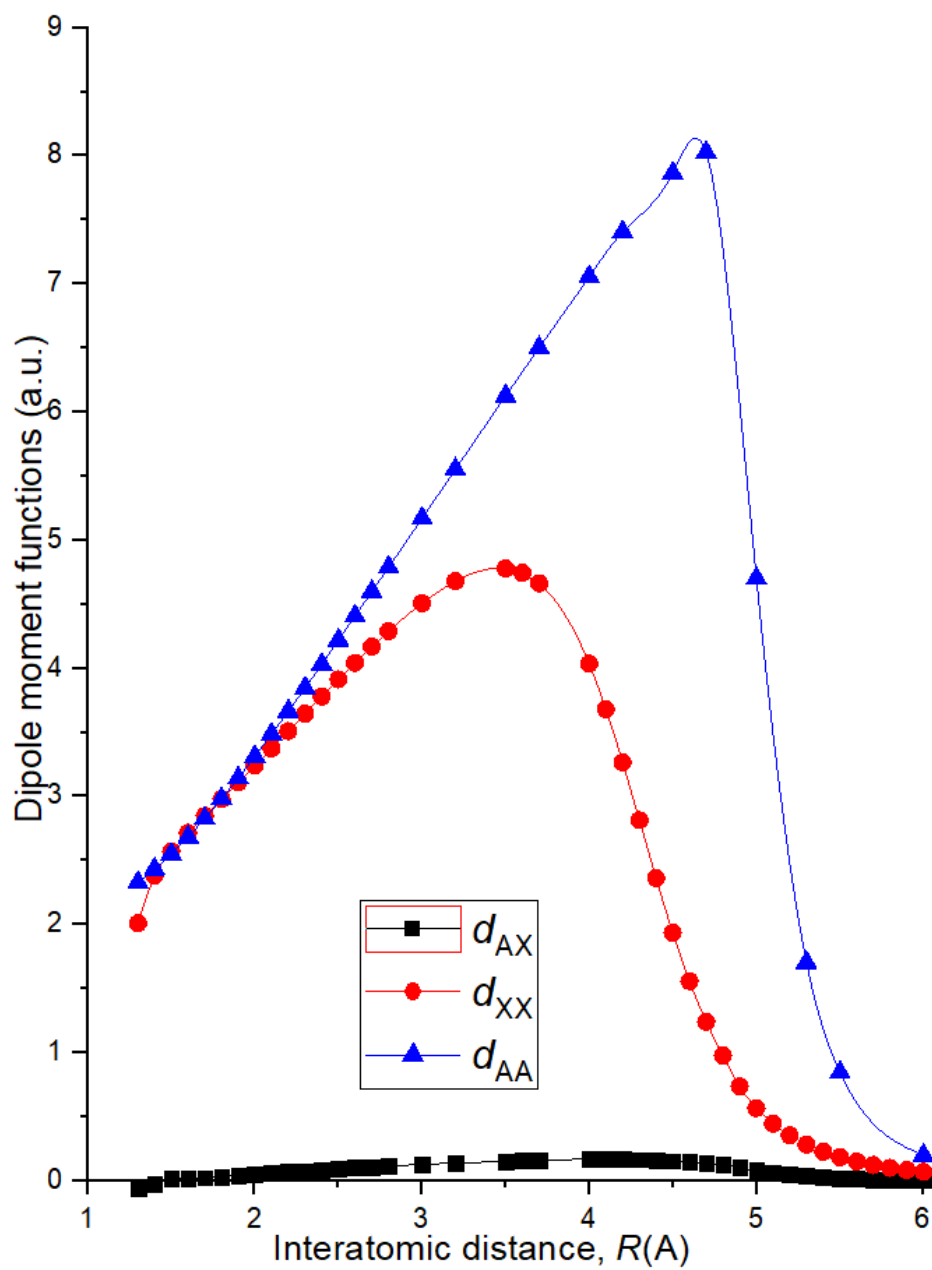


Figure 3.3: Permanent, $d_{XX}(R)$, $d_{AA}(R)$, and transition, $d_{AX}(R)$, dipole moment functions *ab initio* calculated for the X-state and A-states of NaO molecule.

the pure *ab initio* estimates are *a priori* and are not accurate enough to predict the rovibronic energy with the spectroscopic accuracy required. For better agreement between predicted and observed transitions, PECs and coupling curves are refined by making constrained adjustments to the parameters which describe them. This is done by a least-squares fitting to experimental data and is performed in DUO (Yurchenko et al., 2016a).

The input set of the experimental data taken from (Yamada et al., 1989) consisted of pure rotational transition frequencies (with $\Delta v_X = 0$ and $v_X = 0, 1, 2, 3$) for $J'' \leq 16.5$. Joo et al. (1999) provided rovibronic frequencies for the A – X (0,0) band for $J'' \leq 15.5$ together with relative absorption intensities. Joo et al. (1999) also observed the $v' - v'' = 1$ band suggesting an A $^2\Sigma^+$ state vibrational spacing of 498.9 cm^{-1} in agreement with - at the time - unpublished results by S. R. Langhoff. This spacing was included in the fit using an artificial $A(v' = 1) - A(v'' = 0)$ line for $J' = J'' = 0.5$.

The *ab initio* point-wise PECs of both states treated were approximated using the fully analytical Extended Morse Oscillator (EMO) form (Lee et al., 1999; Yurchenko et al., 2016a; Le Roy, 2017a):

$$V_{\text{EMO}}(R) = T_e + D_e \left[1 - e^{-\beta(R)(R-R_e)} \right]^2, \quad (3.5)$$

where T_e is the potential minimum, D_e is the dissociation energy and R_e is the equilibrium distance. In contrast to the conventional Morse potential, the R -dependent exponent coefficient $\beta(R)$ in Equation (3.5) is defined as the polynomial series;

$$\beta(R) = \sum_{i=0}^N \beta_i [y_p(R)]^i; \quad N = \begin{cases} N_R & \text{for } R > R_e \\ N_L & \text{for } R \leq R_e \end{cases} \quad (3.6)$$

with respect to the reduced coordinate

$$y_p(R) = \frac{R^p - R_e^p}{R^p + R_e^p}, \quad (3.7)$$

which was first introduced by Šurkus et al. (1984).

At the first step, the EMO potentials (3.5) were least-squares-fitted to the *ab initio* PECs using a gradient descent algorithm to minimise the least-squares residuals to provide an initial analytic form of the potentials. The electronic energy of the ground state was fixed to zero, and both PECs were fit to fourth order in the $\beta(R)$ polynomial expansion (3.6). The parameter p in Equation(3.7) was fixed to 6 and 4 for the ground and excited state, respectively.

At the second step, the resulting *ab initio* EMO PECs were refined by adjusting to the experimental transition frequencies (Joo et al., 1999; Yamada et al., 1989) where the $\beta_0(X, A)$, $T_e(A)$, $R_e(X)$ and $R_e(A)$ fitting parameters were varied.

Furthermore, both diagonal, $A_{\text{SO}}(R)$, and off-diagonal, $\xi_{\text{AX}}(R)$, spin-orbit coupling (SOCs) functions as well as the L -uncoupling function, $L_{\text{AX}}(R)$, between A $^2\Sigma^+$ and X $^2\Pi$ states were also fitted simultaneously with the trial EMO PECs above. This was done using the

facility in DUO to adjust curves using a *morphing* function, f_m :

$$f_C^{\text{morphed}}(R) = f_m(R)f_C^{ab}(R), \quad (3.8)$$

where C is the coupling curve in question. $f_C^{ab}(R)$ are the *ab initio* point-wise functions. The morphing function, $f_m(R)$, in Equation 3.8, was modeled by the following truncated form of the *polynomial decay* function (Equation 4.20);

$$f_C(r) = B_0(1 - y_p(r)) + y_p(r)B_\infty \quad (3.9)$$

of the Šurkus-like variable, $y_p(R)$, (see Equation (3.7)), where the equilibrium distance R_e is substituted for the fixed parameter $R_0 = 2.053 \text{ \AA}$. The parameter $p = 6$ and $B_\infty = 1$ are also fixed for all morphing functions while only the B_0 parameter is kept to be variable. B_∞ is set to unity to maintain the asymptotic behaviours of the *ab initio* curves.

Morphing was used as it avoids the need for an analytical representation of the *ab initio* point-wise coupling curves by refining their original shapes directly. This approach is, however, not normally applied for PECs for the reason of difficulty to control the equilibrium parameter R_e , which is a value of interest not explicitly derivable from this morphing form. It should be noted that if the grid-point represented curves have roots, then the positions of these roots cannot be changed. This property of morphing has not been explored further as part of this thesis as these types of curves did not see consideration. However, one may consider forming an analytic representation should in this case and using a highly constrained parameter variation instead for increased flexibility.

3.3 Results and Discussion

3.3.1 Potential energy curves, spin-orbit and L -uncoupling matrix elements

The resulting *ab initio* adiabatic PECs obtained for the X- and A-states of NaO are depicted in Figure 3.4 together with their empirical (adjusted) counterparts. The fitted parameters of the EMO potentials (Equation (3.5)) for the both states treated are collected in Table 3.2. The corresponding *ab initio* diagonal spin-orbit function, $A_{SO}(R)$, of the ground X-state as well as the off-diagonal SOC, $\xi_{AX}(R)$, and the L -uncoupling, $L_{AX}(R)$, functions are shown in Figures 3.5 and 3.6 respectively. It is clear that the morphing procedure has significantly distorted these functions, especially the L -uncoupling term which has a sign change introduced at short range. This is unlikely to be an accurate representation of this curve but was used anyway as this form best reproduced the experimental energy levels. In retrospect, this warranted further investigation and should have been corrected. Due to time constraints, however, this task has been left as future work. The relevant morphing parameters for these functions are given in Table 3.2.

The fitted EMO PECs and coupling functions reproduce the input experimental data with an overall root-mean-squares (RMS) error of $\approx 0.086 \text{ cm}^{-1}$. This RMS is deceptively large due to the pronounced discrepancy of the A $^2\Sigma^+$ artificial line, skewing the mean RMS, see Table 3.1. Indeed, for the ground X $^2\Pi$ state, there is agreement with the experiment on order of $\sim 0.006 \text{ cm}^{-1}$ and for the A($v' = 0$) $\leftarrow$ X($v'' = 0$) case there is agreement on order $\sim 0.02 \text{ cm}^{-1}$.

Table 3.1: Root-mean squares errors $\Delta(\text{RMS})$ in cm^{-1} comparing the fitted model to Y: Yamada et al. (1989) and J: Joo et al. (1999) rotational transitions.

v	Δ^Y	Δ^J
0	0.002664	0.022501
1	0.002846	0.679901 ^a
2	0.002758	
3	0.017115	
Ave.	0.006345	0.351201

^a: artificial line, see Section 3.2.2.

The *ab initio* $L_{AX}(r)$ function obeys Van Vleck's hypothesis (Mulliken & Christy, 1931) of *pure precession* in the interval $r \in [1.3, 3.7]$ Å:

$$L_{AX}(r) \approx \sqrt{L(L+1) - |\Lambda|(|\Lambda| \pm 1)} = \sqrt{2}, \quad (3.10)$$

where the total electronic angular momentum of molecule L is equal to 1 while its projection on the internuclear axis is zero. Moreover, the relationship

$$\xi_{AX}(r) \approx A_{SO}(r)L_{AX}(r)/2 \approx A_{SO}(r)/\sqrt{2} \quad (3.11)$$

between diagonal and off-diagonal spin-orbit functions is valid as well.

The *ab initio* SO splitting of the ground X-state is found to be close to the empirical A_{SO} value determined by Yamada et al. (1989) (see Table 3.3). The reliability of the *ab initio* off-diagonal spin-orbit and L -uncoupling functions is indirectly confirmed by a good agreement of the Λ -doubling constants (p , q) empirically obtained for the regular perturbed levels of the ground state by Yamada et al. (1989). Their theoretical counterparts are roughly estimated for the lowest vibrational levels, v_X , according to the relations (Lefebvre-Brion & Field, 2004; Pazyuk et al., 1994):

$$p = 2\langle v_X | B\xi_{AX}L_{AX}/\Delta U_{XA} | v_X \rangle \quad (3.12)$$

$$q = 2\langle v_X | [BL_{AX}]^2/\Delta U_{XA} | v_X \rangle, \quad (3.13)$$

where $B = 1/2\mu R^2$, μ is the reduced molecular mass, $\Delta U_{XA} = U_X - U_A$ is the difference of the PECs, while $|v_X\rangle_R$ are the vibrational wavefunctions of the ground state.

3.3.2 Partition Function

The temperature-dependent partition function for NaO molecule was calculated as the sum:

$$Q(T) = \sum_i g_i e^{\frac{-E_i}{k_B T}}, \quad (3.14)$$

where $g_i = g_{\text{ns}}(2J+1)$ is the total degeneracy of the state, g_{ns} is the nuclear statistical weight factor, and k_B is the Boltzmann constant. As $Q(T)$ sums over J , the value of $Q(T)$ at some T depends on the value of J_{max} used in the sum. To ensure completeness of the line list, it is a requirement that, up to a given temperature, in the case of this study, 2500 K, the value of $Q(2500)$ converges with J_{max} . Should J_{max} not be large enough, $Q(T)$ would not

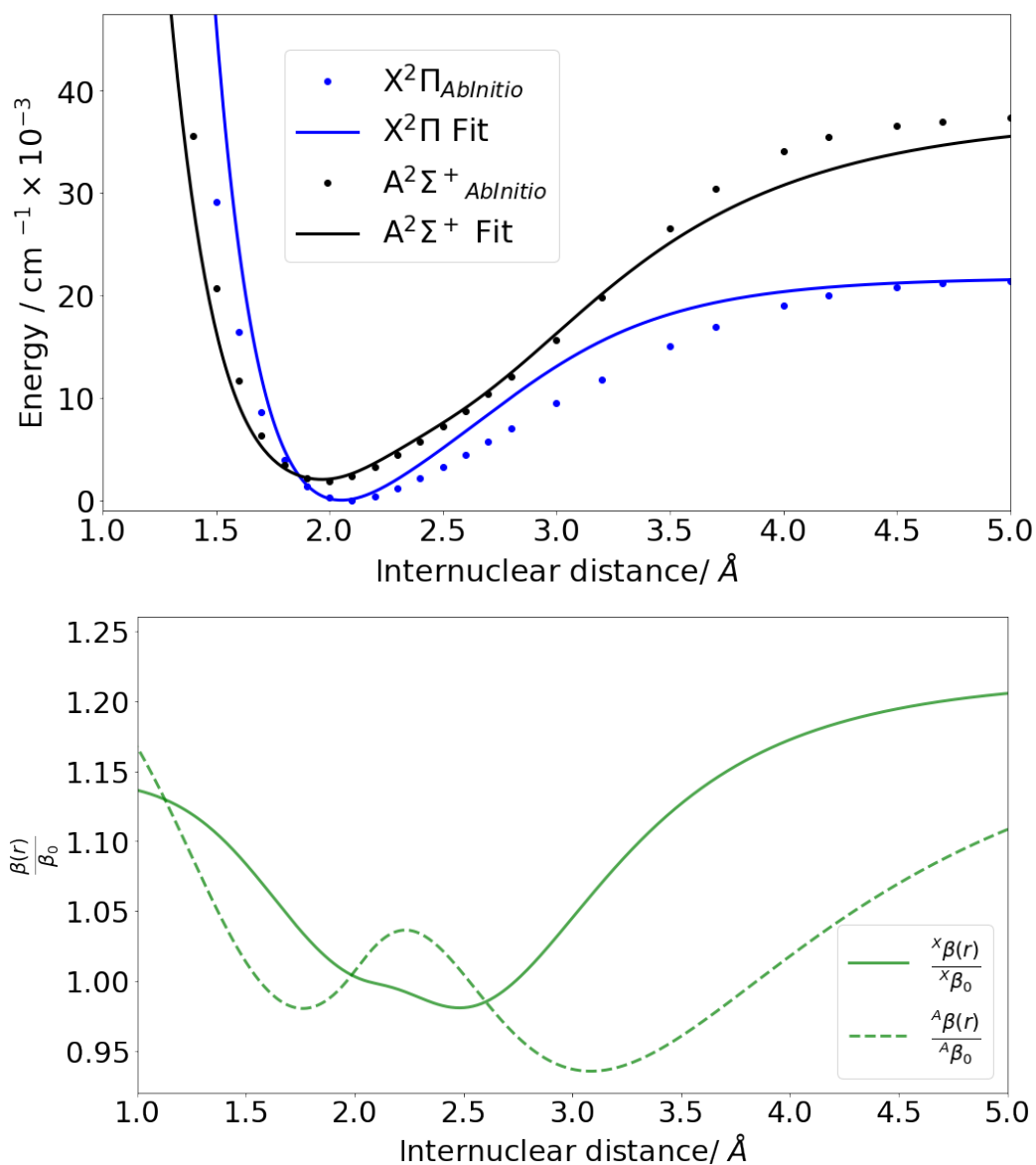


Figure 3.4: Empirical EMO (fitted) and original *ab initio* point-wise potential energy curves obtained for the X ²Π and A ²Σ⁺ states of NaO (upper panel); Distance-dependent exponent coefficient for X ²Π and A ²Σ⁺ state EMO fits as normalised by β₀ = A₀ (lower panel).

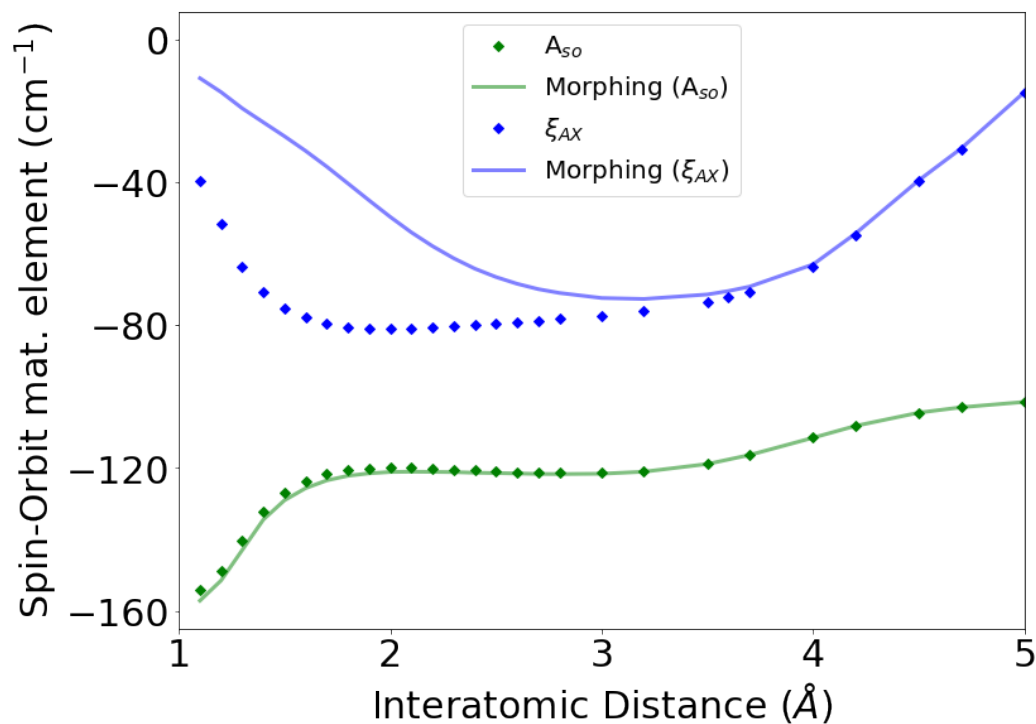


Figure 3.5: Diagonal, $A_{SO}(r)$, and off-diagonal, $\xi_{AX}(r)$, spin-orbit coupling curves *ab initio* calculated for the X-state and A-states.

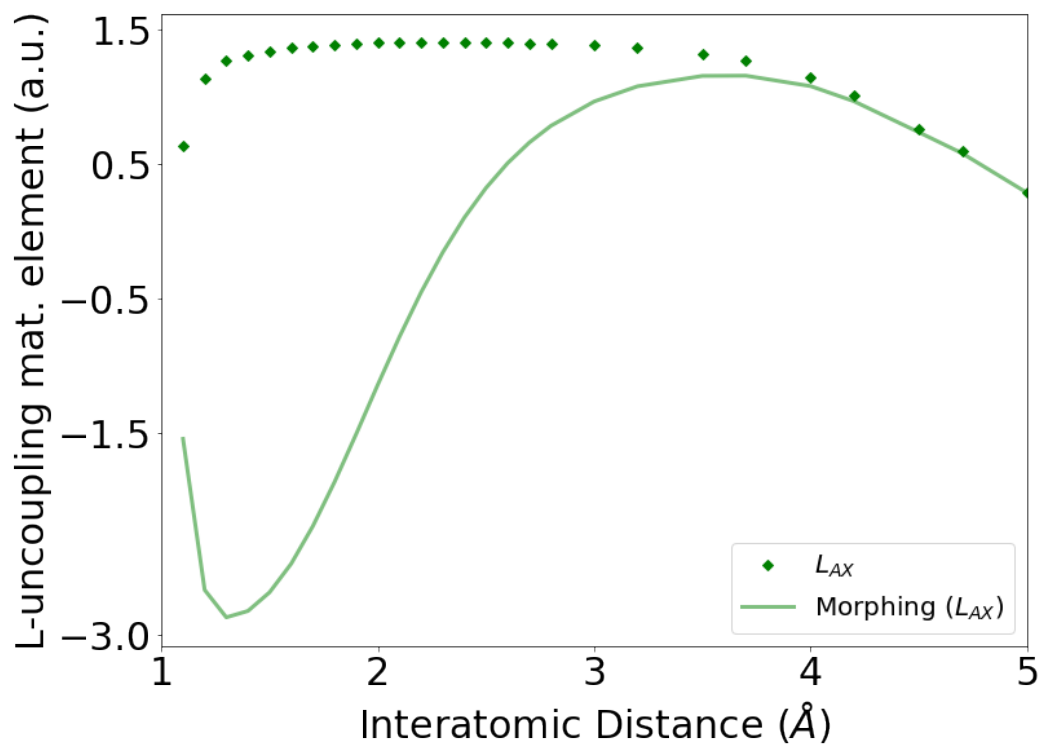


Figure 3.6: $L_{AX}(r)$ is the corresponding non-adiabatic matrix element of electron-rotational interaction between the X-state and A-state.

Table 3.2: PEC and morphing parameters obtained for the X $^2\Pi$ and A $^2\Sigma^+$ states of NaO. For the definition of the EMO parameters see Equation (3.5), and for morphing parameters see Equation (3.9).

PEC Parameterisation		
EMO Param.	X $^2\Pi$	A $^2\Sigma^+$
T_e	0	2029.147 ^a
r_e	2.05189 ^a	1.96723 ^a
D_e	21735.7	35496.4
p	6	4
N_L	2	2
N_R	4	4
β_0	1.50708327083484 ^a	0.989061691136872 ^a
β_1	-0.04809897091909	0.181504940347642
β_2	0.16743487156786	0.424100841906937
β_3	-0.95627676523677	-2.926458322108940
β_4	1.16624139895144	2.522897112151440
B_0^a parameters used for morphed coupling functions ^b		
Function	B_0	
A_{so}	1.0098	
ξ_{AX}	0.6277	
L_{AX}	-0.7455	

^a: value achieved via varying in Duo. All others were fixed.

^b:For Morphing parameters: As per Sec 3.2.2, $r_0 = 2.05 \text{ \AA}$, $p = 6$, $B_\infty = 1$ (standard when using Morphing) for all three f_C .

Table 3.3: Comparison of *ab initio* calculated spin-orbit splitting (A_{so}) and Λ -doubling constants (p, q) of the ground NaO state with their empirical counterparts taken from Yamada et al. (1989). All values are in cm^{-1} .

Parameter	Empirical	<i>Ab initio</i>
A_{so}	-107	-120
p	+0.044	+0.04
q	+0.0003	+0.0003

converge. As shown in Figure 3.7, with $J_{\max} = 200.5$, Q converges up to $T = 2500 \text{ K}$.

The JPL database (Pickett et al., 1998) provides partition function values up to $T=300 \text{ K}$. Barklem & Collet (2016) provide numerical values for the partition functions of NaO up to 10,000 K which we multiply by four to account for the convention of including the Na nuclear spin degeneracy (g_{ns}) in the partition function. We (and JPL) include $g_{ns} = 2I_{Na} + 1 = 4$ (which is appropriate for $I_{Na} = \frac{3}{2}$) in $Q(T)$, while Barklem & Collet (2016) does not. A comparison between these partition functions is given in Figure 3.8. The JPL values agree well with ours (see Table 3.4), with the level of agreement decreasing as temperature goes up which is likely due to a lack of higher vibrational levels in the JPL partition sum. However, there is poor coincidence with Barklem & Collet (2016) at low temperature with agreement improving for higher temperature. The reason for the low temperature disagreement between Barklem & Collet (2016) and the results of JPL and

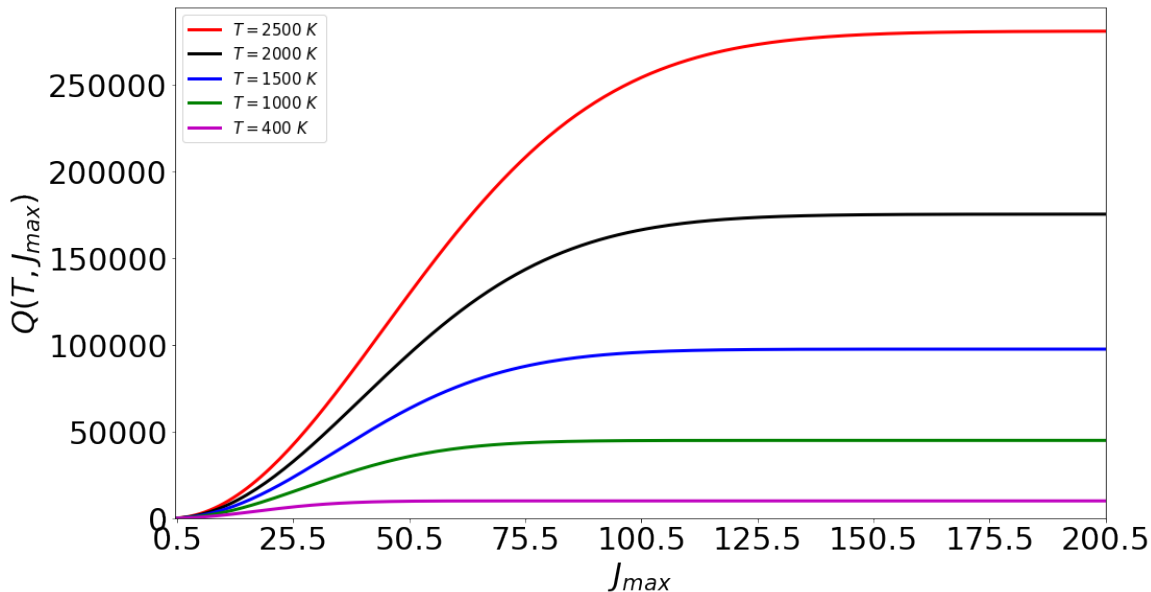


Figure 3.7: Partition function $Q(T)$ convergence of NaO as dependent on maximum value of rotational quantum number, $J_{\max}$ for temperatures up to 2500 K.

Table 3.4: Partition Function, $Q(T)$ as calculated using the Duo computed energies compared to partition functions from JPL database.

T / K	Q_{Duo}	Q_{JPL}	$\Delta / \%$
300	7027.4727	6633.1886	5.61
225	4694.9814	4491.5223	4.33
150	2734.0243	2645.0047	3.26
75	1134.4648	1109.3245	2.22
37.5	518.8865	516.1226	0.53
18.75	262.9106	262.9886	-0.030
9.375	139.2536	139.3226	-0.050

our own is unclear but we believe our values are correct in this region. This is because our energy levels are semi-empirical, whereas the data from [Barklem & Collet \(2016\)](#) is based on calculated rather than experimental molecular constants taken from [Huber & Herzberg \(1979\)](#)

3.3.3 Final line list and absorption spectra simulation

The DUO package was used to produce a NaO line list which we call NaOUCMe. This line list is given in ExoMol format ([Tennyson et al., 2014, 2020](#)) as .STATES file containing term values for the lowest 36,120 rovibronic levels of the $A \sim X$ complex up to $J = 200.5$ and $v_X = 29$ and a .TRANS file consisting of the corresponding Einstein coefficients and frequencies for 4,726,137 dipole-allowed $X - X$, $A - A$ and $X - A$ transitions. In line with the ExoMol standard ([Tennyson et al., 2020](#)), the .STATES file also provides values for; the radiative lifetime of each energy level, the Landé g -factor (which informs the magnitude of the Zeeman splitting in the presence of a magnetic field ([Semenov et al., 2017](#))), and approximate uncertainties for the energies which allow the accuracy with which we predict the frequency of each transition to be estimated.

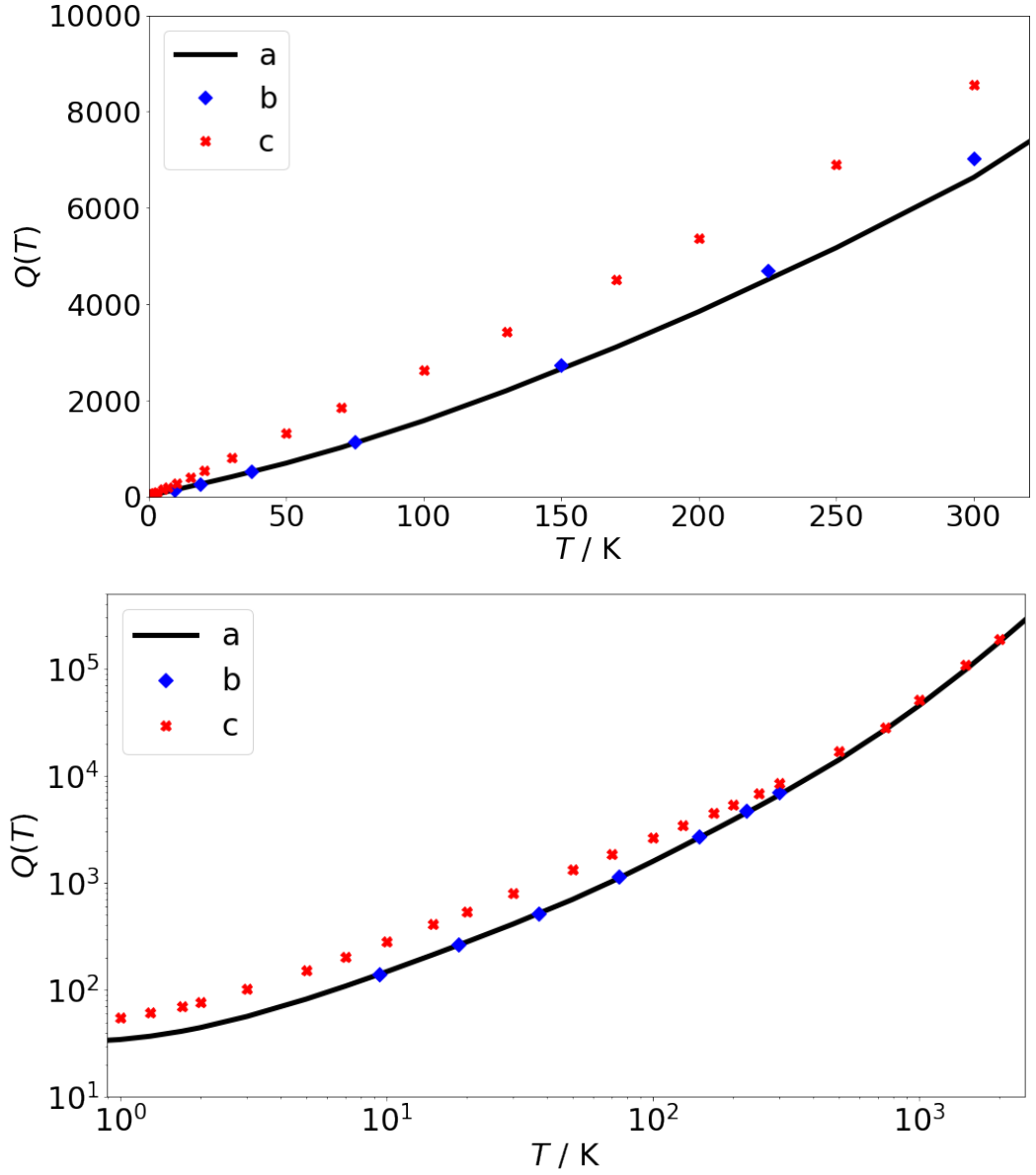


Figure 3.8: Comparison between, (a): calculated partition function based on Duo states and available data for the partition function of NaO (b): [Pickett et al. \(1998\)](#), (c): [Barklem & Collet \(2016\)](#). Note, $Q(T)$ by [Barklem & Collet \(2016\)](#) has been multiplied by four to account for the convention of including the hyperfine structure degeneration number g_{ns} in the partition function calculation, see Equation 3.14. Upper: Close-up of calculated and reference partition functions for $T \in [0, 300]$ K. Lower: Log scaled representation of calculated and reference partition functions for $T \in [0, 2500]$ K.

Table 3.5: Uncertainty estimates (in cm^{-1}) are applied for the rovibronic energy levels of NaO as a function of state quantum numbers.

State	X $^2\Pi$			A $^2\Sigma^+$
Case	$J_X < 16.5, v_X = 0$	$J_X > 16.5, v_X = 0$	$v_X > 0$	all v_A and J levels
Uncertainty	0.003	$0.001J_X^2 + 0.01J_X + 0.01$	20-40	10-30

For fitted regions, transition uncertainties equal to those in Table 3.1 are recommended. For the ground electronic state, for the case where $J < 16.5$ and $v_X = 0$, an uncertainty of 0.003 cm^{-1} is recommended. Typically, energy level uncertainties scale with J quadratically and the following rule-of-thumb functional form for $J > 15.5$ is recommended: $\delta E \approx 0.001J^2 - 0.01J + 0.01$. For all other (extrapolated) cases in the X state, the *ab initio* vibrational uncertainty takes precedence at $20\text{-}40 \text{ cm}^{-1}$.

The vibrational spacing between the $v_A = 0$ and $v_A = 1$ states were fit to a satisfactory level of agreement (*artificial line* from Section 3.2.2). However, it is recommended that this line list only be used for high resolution observational studies at long wavelengths covering pure rotational transitions. Overall energy level uncertainties are summarised in Table 3.5.

Samples from the .STATES and .TRANS files are given in Tables 3.6 and 3.7. These were processed in EXOCROSS (Yurchenko et al., 2018c) to produce Figure 3.9, an absolute absorption spectrum for the region studied by Joo et al. (1999), and Figure 3.10, the absorbance cross-section for NaO as a function of temperature computed at a resolution of 1 cm^{-1} with a half-width at half-maximum (HWHM) of 1 cm^{-1} .

3.3.4 Comparison with the experimental X $\rightarrow$ A spectra

The experimental A $^2\Sigma^+(0,1) \leftarrow$ X $^2\Pi(0)$ absorption bands were observed by Joo et al. (1999) but their measurements were only sensitive in the very narrow spectral regions: $2015\text{--}2095 \text{ cm}^{-1}$ and $2646\text{--}2697 \text{ cm}^{-1}$. The lines in these regions were assigned to the $\Delta v = 0$ and $\Delta v = +1$ bands respectively. An absolute intensity absorption spectrum was calculated as a stick spectrum to compare to this, see Figure 3.9. The calculated absorption lines result in a line profile significantly broader than those visible from measurements of Joo et al. (1999). The observed spectrum (relative intensities) has been scaled by matching the intensity of the strongest line [A ($J' = 7.5, v' = 0$) $\leftarrow$ X ($J'' = 7.5, v'' = 0, \Omega'' = -1.5$)] from experiment to that of its conjugate calculated line; it can be seen that the observed $\Delta v = +1$ transitions lie on the tail end, *R*-branch of the calculated absorption spectrum with a matching downward slope.

We note that Joo et al. (1999) used their measurements to determine the vibronic term value for the A(0)–X(0) band, $T_0(\text{A})$, of 1992.905 cm^{-1} . Using approximate $J = 0$ zero-point energies (ZPEs) generated by DUO, and $T_0(\text{A}) = T_e(\text{A}) - \text{ZPE}(\text{X}) + \text{ZPE}(\text{A})$ shows that our $T_0(\text{A})$ from this model is 1982.3 cm^{-1} , which is less than that of Joo et al. (1999) by 10 cm^{-1} . An attempt was made to reproduce the experimental $T_0(\text{A})$ value above by manually adjusting $T_e(\text{A})$ and refitting. However, this results in significantly worse fits in the transitions (around an order of magnitude).

Table 3.6: Extract from .STATES file produced by DUO for NaO. Lifetimes calculated with ExoCross, for uncertainties see Section 3.4 and Table 3.5

NN	Energy	gtot	J	uncertainty	lifetime	Landé	τ	e/f	State	ν	Λ	Σ	Ω
1	118.305521	8	0.5	0.003000	5.1528E+03	0.001493	+	e	X2Pi	0	1	-0.5	0.5
2	704.551592	8	0.5	30.000000	2.8981E+00	0.001932	+	e	X2Pi	1	1	-0.5	0.5
3	1282.294758	8	0.5	30.000000	1.4807E+00	0.002994	+	e	X2Pi	2	1	-0.5	0.5
4	1850.69127	8	0.5	30.000000	1.0028E+00	0.012246	+	e	X2Pi	3	1	-0.5	0.5
5	2045.653545	8	0.5	20.000000	1.0894E-01	1.988261	+	e	A2Sigma	0	0	0.5	0.5
6	2409.940124	8	0.5	30.000000	6.5698E-01	0.041505	+	e	X2Pi	4	1	-0.5	0.5
7	2544.609918	8	0.5	20.000000	6.4721E-02	1.957978	+	e	A2Sigma	1	0	0.5	0.5
8	2960.425378	8	0.5	30.000000	3.7063E-01	0.112844	+	e	X2Pi	5	1	-0.5	0.5
9	3042.140902	8	0.5	20.000000	4.9272E-02	1.887345	+	e	A2Sigma	2	0	0.5	0.5
10	3501.549396	8	0.5	30.000000	1.4379E-01	0.388061	+	e	X2Pi	6	1	-0.5	0.5

NN: State counting number,

Energy: State energy in cm^{-1} ,

gtot: Total degeneracy of the state,

J : Angular momentum quantum number,

uncertainty: Energy level uncertainty in cm^{-1} ,

lifetime: Lifetime of the state in seconds,

Landé: Landé g factor (Semenov et al., 2017),

τ : Parity,

e/f: Rotationless parity,

State: Electronic state, given as X2Pi or A2Sigma+ for $X^2\Pi$ and $A^2\Sigma^+$ states respectively

ν : Vibrational quantum number,

Λ : Projection of electronic angular momentum,

Σ : Projection of electronic spin,

Ω : $\Lambda + \Sigma$ (Projection of total electron angular momentum).

Table 3.7: Extract from the .TRANS file produced by DUO for NaO.

n_f	n_i	A_{fi}	ν_{fi}
2097	2007	7.7832E-17	0.001009
843	933	2.4392E-16	0.001035
1799	1889	9.3118E-17	0.001043
1883	1793	9.4292E-17	0.001055
1219	1309	1.6125E-16	0.001066
3848	3758	2.7618E-17	0.001137
1520	1430	1.7928E-16	0.001148
1595	1685	1.3851E-16	0.001153
3146	3056	4.9277E-17	0.001177
1688	1598	1.5019E-16	0.001179
766	676	5.6326E-16	0.001185

n_f : Lower state counting number

n_i : Upper state counting number

A_{fi} : Einstein A-coefficient in s^{-1}

ν_{fi} : Transition wavenumber in cm^{-1}

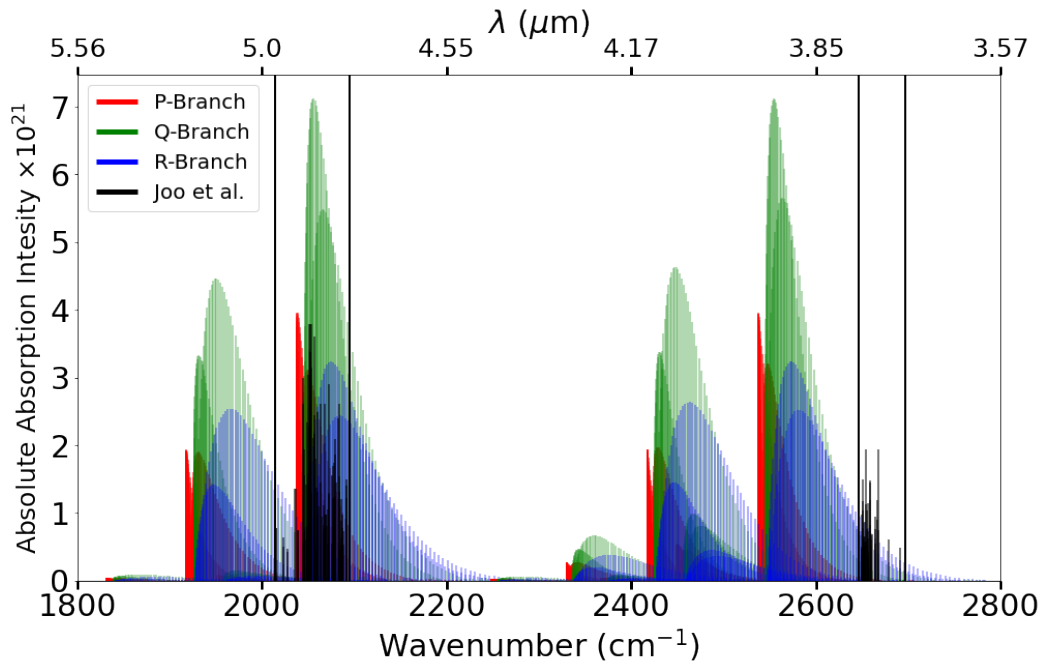


Figure 3.9: Absolute absorption intensity (arbitrary units) spectrum of NaO computed at $T = 400$ K. Black lines represent the experimental transitions containing (from left to right) the observed $A\ ^2\Sigma^+(0,1) \leftarrow X\ ^2\Pi(0)$ transition bands from [Joo et al. \(1999\)](#). Black vertical lines indicate start and end of the observed band transition regions.

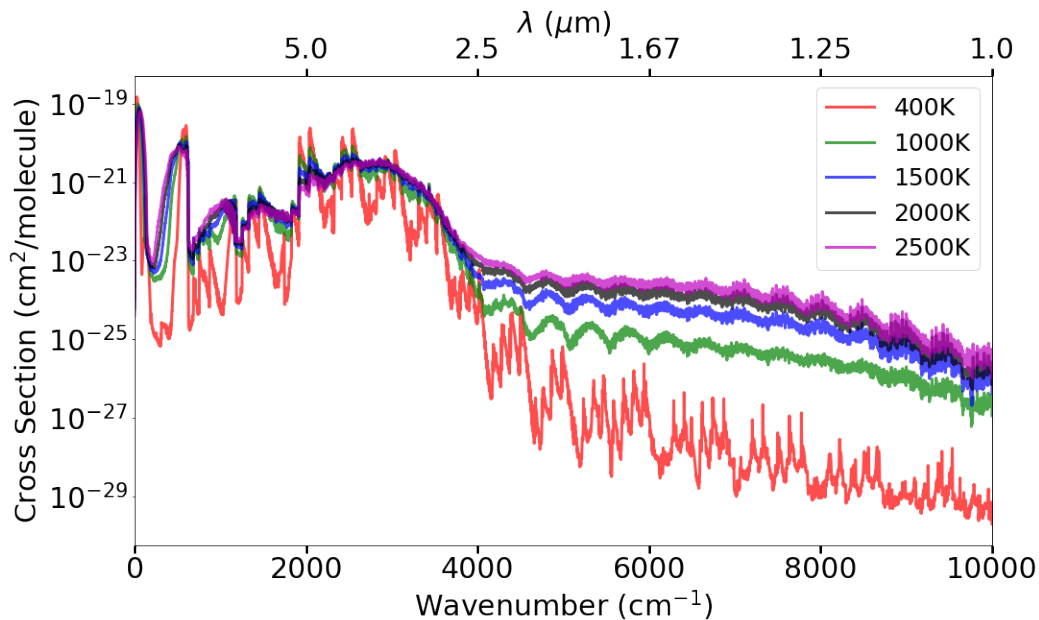


Figure 3.10: Spectrum of NaO at varying temperatures. Absorption cross-sections were modelled with a Gaussian line profile with HWHM at 1 cm^{-1} with an output on a grid with 1 cm^{-1} spacing.

3.4 Conclusions

An optical line list called NaOUCMe is presented for the alkali monoxide radical, NaO covering transitions up to $J = 200.5$ and $v_X = 29$ with applicability up to the equilibrium temperature $T = 2500$ K. The experimental lines for pure rotational transitions in the ground electronic state (Yamada et al., 1989) and rovibronic $A\ ^2\Sigma^+(0,1) \leftarrow X\ ^2\Pi(0)$ transitions (Joo et al., 1999) were used to refine the deperturbation model applied. An average RMS of $\sim 0.006\text{ cm}^{-1}$ was achieved for the $X\ ^2\Pi$ state rotational transitions and 0.35 cm^{-1} for the $A\ ^2\Sigma^+ \leftarrow X\ ^2\Pi$ transitions, with $\sim 0.023\text{ cm}^{-1}$ RMS for the $A(v' = 0) \leftarrow X(v'' = 0)$ transitions and $\sim 0.680\text{ cm}^{-1}$ RMS for the $A(v' = 1, J' = 0.5) \leftarrow A(v'' = 0, J'' = 0.5)$ artificial line (see Section 3.2.2). Uncertainties of the reproduced and predicted lines rapidly increase as the vibrational and rotational quantum numbers increase for both electronic states, and, hence, further experimental data on higher excited transitions is required to create a more robust line list.

The use of the CaO line list (Yurchenko et al., 2016b) in a spectrum assignment of a meteor at 29 km above the Earth's surface by Berezhnoy et al. (2018) is indicative of potential importance of s-block metal monoxides like NaO. NaO similarly is a molecule that can be studied in a terrestrial environment at approximately 90 km above the Earth's surface (Slanger et al., 2005) and has been recently studied as a transient species in airglow by Sarkhel et al. (2009, 2010) and Plane et al. (2012).

While the line list is in good agreement with experimental data, the scarcity of such data is a limiting factor on the quality of this line list. Given that new data is produced, an update on this line list is warranted. This also allows for an opportunity to remedy the highly distorted coupling curves mentioned in Section 3.3.1, which have likely resulted in a model which is over-fit to the experimental data, reducing its predictive capacity. Given enough new experimental data, a MARVEL project may be warranted as well. Another limiting factor is the quality of the *ab initio* potentials and coupling curves, which have influenced the rovibrational structure of this model significantly as much of the structure had to be constrained to the *ab initio* curves; the same applying to the line intensities, as they are dictated entirely by the *ab initio* (T)DMCs. Along with improving the quality of the present electronic structure calculations by, for example, using a larger basis set, one can also attempt to characterise the (B,C) $^2\Pi$ states which have been explored tenuously by Pfeifer & Gole (1984); Pugh et al. (1996) and Langhoff et al. (1991).

3.4.1 Data Availability

The DUO model, including potential energy curves, spin-orbit coupling curves, electronic angular momentum coupling curves, and (transition) dipole moment curves; the NaOUCMe line list .STATES and .TRANS files; and the computed partition function are available at www.exomol.com/.

Chapter 4

Hydroxyl (OH) Linelist

4.1 Introduction

The hydroxyl radical, OH, is a molecule of high importance in terrestrial atmospheric chemistry in several contexts, including Meinel band night-glow ([Meinel, 1950](#); [Chen et al., 2021](#)), which is an important source of heat in the upper atmosphere ([Kaufmann et al., 2008](#); [Chen et al., 2021](#); [Brasseur & Offermann, 1986](#); [Franzen et al., 2019](#)); due to its role in the lower atmosphere as an oxidizer, especially in reactions with ozone depleting chlorofluorocarbons (CFCs) ([Prinn et al., 1995](#)), and for its interactions with aromatic molecules such as benzene and toluene ([Garmash et al., 2020](#)). Astrochemically, OH is of interest due to its relationship with water. Water can be formed efficiently at high temperatures through the reaction between the hydroxyl radical and molecular hydrogen ($\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$). Moreover, in the presence of UV radiation, water photodissociates and forms OH ($\text{H}_2\text{O} + \gamma_{\text{UV}} \rightarrow \text{OH} + \text{H}$) ([Wampfler, S. F. et al., 2010](#)).

OH has been detected in many planets and exoplanets including Venus ([Piccioni et al., 2008](#)), Mars ([Clancy et al., 2013](#)), ultra-hot Jupiters Wasp-76b ([Landman et al., 2021](#)) and Wasp-33b ([Nugroho et al., 2021](#)). Further detections have been made in the ISM ([Zanese et al., 2023](#); [Weinreb et al., 1963](#)), in protoplanetary discs at moderate temperatures ([Munoz-Romero et al., 2024](#)), and in stellar environments such as M-dwarfs ([Herbig, 1974](#); [Jones et al., 1988](#)) and sunspots ([Berdyugina & Solanki, 2001](#)).

Many of the early theoretical studies of hydroxyl spectroscopy were done by Van Dishoeck and Langhoff (see Section 1.4) which form the base of the photoabsorption spectrum given by the Leiden database ([Hrodmarsson & van Dishoeck, 2023](#)). Recent theoretical studies into the electronic structure of OH have been performed by [Srivastava & Sathyamurthy \(2014\)](#); [Qin & Zhang \(2014\)](#) and most notably by [van der Loo & Groenenboom \(2005\)](#), which inform most of the electronic structure calculations performed in this chapter.

This chapter covers the formation of a replacement to the current ExoMol line list for OH. The current line list is based on the works by [Brooke et al. \(2016\)](#) and [Yousefi et al. \(2018\)](#) (MOLLIST), similar to the current HITRAN line list. The motivation behind improving the line list, in addition to the general atmospheric and astrophysical interest in OH, is that the MOLLIST dataset does not currently consider the dissociative processes, predissociation (Chapter 5) and continuum absorption (Chapter 6), which are very important sources of opacity in many astrophysical environments. Furthermore, the MOLLIST line list's intensities in the Meinel bands have recently seen criticism by [Medvedev et al. \(2024\)](#), as

Table 4.1: Summary of all electronic states of OH considered in the $^{16}\text{O}^1\text{H}$ MYTHOS line list and their use case.

State	Linelist	Predissociation Widths	Continuum Absorption
X $^2\Pi$	✓		✓
A $^2\Sigma^+$	✓	✓	✓
$^a\text{B } ^2\Sigma^+$	✓	✓	✓
$^a\text{C } ^2\Sigma^+$	✓	✓	
1 $^2\Sigma^-$		✓	✓
1 $^4\Sigma^-$		✓	
1 $^4\Pi$		✓	
1 $^2\Delta$			✓

^a Predissociation widths are not rigorously calculated for these states, however they are assumed to be dissociative due to crossings with local repulsive states, as such, are included in line list with only their natural width considered.

intensities appear to be unphysical past $\Delta v = 5$. Lastly, this update gives the opportunity to leverage the new MARVEL dataset to extend the line list to include two additional bound electronic states, B $^2\Sigma^+$ and C $^2\Sigma^+$, whereas MOLLIST contains only X $^2\Pi$ and A $^2\Sigma^+$. This new line list is named MYTHOS (Mitev-Yurchenko-Tennyson-Hydrogen-Oxygen).

A summary of all electronic states and their associated use in the development of the line list is tabulated in Table 4.1

This project started with the computation of new *ab initio* PECs and their corresponding diagonal and off-diagonal coupling curves for the electronic states mentioned in Table 4.1. These calculations are very much based on the work by van der Loo & Groenenboom (2005) and are described in Section 4.2. The process of further refining these curves and forming the spectroscopic model used to produce the bound-bound line list is discussed in Section 4.3, with further discussion into the isolation of bound-bound transitions in Section 4.4. A detailed description of the simulation of the absorption spectra of OH is given in Section 4.5. This section also includes brief introductions to the methodologies of the chapters on predissociation (Chapter 5) and continuum absorption (Chapter 6). Final results can be found in Section 4.6.

4.1.1 Summary of MARVEL energies and quantum number conventions

Furtenbacher et al. (2022) collected 15,938 rovibronic transitions from 45 sources and produced values for 1619 empirical rovibronic energy levels for the system of electronic states, X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, C $^2\Sigma^+$. Table 4.2 presents the coverage of the MARVEL energy levels used in this study.

The complete set of quantum numbers used to characterise the MARVEL energy levels are the state label (X $^2\Pi$, A $^2\Sigma^+$, 1 $^2\Sigma^-$, ...) total angular momentum, J , the vibrational quantum number, v , the rotationless parity, e/f and the projection of the total angular momentum on the molecular axis, $\Omega = \Sigma + \Lambda$, where, Σ and Λ are projections of the spin and orbital angular momenta on the molecular axis, respectively.

In line with the Hund's case (a) conventions used in DUO, the following quantum numbers

Table 4.2: Coverage of MARVEL data set [Furtenbacher et al. \(2022\)](#) energy levels for the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH which have been used to refine *ab initio* PECs, SOCs and coupling constants for the production of a spectroscopic model.

ν	$J_{\min}$	$J_{\max}$	Number of Levels
X $^2\Pi$			
0	0.5	49.5	196
1	0.5	42.5	154
2	0.5	41.5	152
3	0.5	36.5	131
4	0.5	19.5	77
5	0.5	19.5	76
6	0.5	18.5	74
7	0.5	18.5	74
8	0.5	18.5	74
9	0.5	18.5	74
10	0.5	11.5	42
11	0.5	8.5	23
12	0.5	7.5	28
13	0.5	7.5	27
Total	0.5	49.5	1202
A $^2\Sigma^+$			
0	0.5	36.5	73
1	0.5	28.5	58
2	0.5	19.5	40
3	0.5	26.5	54
4	0.5	19.5	40
5	0.5	7.5	15
6	0.5	8.5	17
7	0.5	7.5	16
8	0.5	9.5	19
9	0.5	8.5	17
Total	0.5	36.5	349
B $^2\Sigma^+$			
0	0.5	10.5	21
1	0.5	8.5	17
Total	0.5	10.5	38
C $^2\Sigma^+$			
0	0.5	7.5	15
1	0.5	7.5	15
Total	0.5	7.5	30
Grand Total	0.5	49.5	1619

are used to characterize the rovibronic states, $|J, v, \tau, \Sigma, \Lambda, \Omega, \text{state}\rangle$ where state is a counting number associated with the electronic states as ordered by potential minima, T_e and τ is the state parity $+/-$ (see [Tennyson et al. \(2016a\)](#) for conversion between e/f and τ), which can be directly related to the MARVEL data set.

Instead of using the the Hund's case (a) convention, many data sets on the rovibronic state of OH in the literature opt for the rotational quantum number N and the fine structure components, F_1 and F_2 (Hund's case (b)). In order to correlate these data with our MARVEL data set, their representations have been converted to the rigorous quantum labels $J, e/f$ using the following relations.

For the $^2\Sigma^+$ states:

$$J = \begin{cases} N + \frac{1}{2} & \text{for } F_1 \\ N - \frac{1}{2} & \text{for } F_2 \end{cases}, \quad (4.1)$$

$$e/f = \begin{cases} f & \text{for } F_1 \\ e & \text{for } F_2 \end{cases}. \quad (4.2)$$

These relations arise, in particular, as the (A, B, C) $^2\Sigma^+$ state levels are generally presented using Hund's case (b), hence the relation between J and N , Equation (4.1) and due to the common approximation,

$$E_{F_1} = BN(N+1) + \frac{1}{2}\gamma N, \quad (4.3)$$

$$E_{F_2} = BN(N+1) - \frac{1}{2}\gamma(N+1). \quad (4.4)$$

Therefore, because $\gamma \ll B$, [Brooke et al. \(2016\)](#) where B is the rotational constant and γ is the spin-rotation constant,

$$E_{F_1} > E_{F_2} \quad \forall \quad N, J. \quad (4.5)$$

Since the $^2\Sigma^+$ states have only parity splitting as $\Lambda^{2\Sigma^+} = 0$, the F_1 and F_2 components correspond directly to f and e parities respectively ([Herzberg, 1989](#)).

For the X $^2\Pi$ state the relevant Hund's case (a) approximation is:

$$E_{F_1} = B[(J+S)^2 - \Lambda^2] - \frac{1}{2}(A - 2B), \quad (4.6)$$

$$E_{F_2} = B[(J+S)^2 - \Lambda^2] + \frac{1}{2}(A - 2B), \quad (4.7)$$

where A is the diagonal spin-orbit coupling. This is applied for a given parity and correlates with the following relation ([Herzberg, 1989](#)):

$$E_{F_1} = E\left(\Omega = \frac{3}{2}\right) < E_{F_2}, \quad (4.8)$$

$$E_{F_2} = E\left(\Omega = \frac{1}{2}\right) > E_{F_1}. \quad (4.9)$$

The quantum number correlations for the $1 (^4\Sigma^-, ^4\Pi, ^2\Delta)$ states have not been considered here as there are no experimental data which will require transformation.

4.2 *Ab initio* electronic structure calculations

Initially, the electronic structure calculations were performed only for the $X ^2\Pi$, $A ^2\Sigma^+$, and $1 (^2\Sigma^-, ^4\Sigma^-, ^4\Pi)$ electronic states as these were all that was required for the computation of the photodissociative transition $1^2\Sigma^- \leftarrow X^2\Pi$ and the calculation of predissociation lifetimes of the $A ^2\Sigma^+$ state. As such this section is separated into two subsections, Section 4.2.1 covers the *ab initio* electronic structure calculations of the curves relevant to the $X ^2\Pi$ and $A ^2\Sigma^+$ electronic states and 4.2.2 builds on this and covers the treatment for the $B ^2\Sigma^+$, $C ^2\Sigma^+$, and $1 ^2\Delta$ electronic states.

4.2.1 Electronic Structure of $X ^2\Pi$, $A ^2\Sigma^+$ and $1 (^2\Sigma^-, ^4\Sigma^-, ^4\Pi)$

The initial potential energy curves (PECs), spin-orbit coupling curves (SOCs) and angular momentum coupling curves (AMCs) were computed using the MOLPRO quantum chemistry program (Werner et al., 2010, 2012, 2020). Following van der Loo & Groenenboom (2005), optimal molecular orbitals were computed using carefully selected combinations of state-averaged complete active space self-consistent field (SA-CASSCF) (Werner & Knowles, 1985) calculations: details of which are given in Table 4.3. These orbitals provide the input to multi-reference configuration interaction (MRCI) calculations which included a Davidson correction (Langhoff & Davidson, 1974) to the energies. Final results were computed using an aug-cc-pV6Z basis set. The calculations were performed over internuclear distances ranging from 1 to 10 a_0 with a greater density of points around the equilibrium bond length. We ensured that no $^2\Delta$ states were obfuscating the presence of the desired $^2\Sigma^\pm$ states by calculating PECs for both A_1 and A_2 irreducible representations of C_{2v} and selecting the appropriate symmetries. There are two linearly independent spin components in the $^4\Pi$ state giving rise to the same value of $|\Omega| = \frac{1}{2}$: $|1' ^4\Pi\rangle \rightarrow \Lambda = -1, \Sigma = \frac{3}{2}$ and $|1 ^4\Pi\rangle \rightarrow \Lambda = 1, \Sigma = -\frac{1}{2}$.

The spin-orbit coupling between the $A ^2\Sigma^+$ and $1 ^4\Pi$ states has the relationship,

$$\langle 1 ^4\Pi | \hat{H}_{SO} | A ^2\Sigma^+ \rangle = -\sqrt{3} \langle 1' ^4\Pi | \hat{H}_{SO} | A ^2\Sigma^+ \rangle, \quad (4.10)$$

which is derived from the application of the Wigner-Eckart theorem (Parlant & Yarkony, 1999; Yarkony, 1992). In DUO, for spin-orbit matrix elements it is sufficient to specify only one of these combinations with the correct Λ and Σ , the other is generated using the Wigner-Eckart theorem. Here we select $1 ^4\Pi$, where $\Sigma = -\frac{1}{2}$, $\Lambda = 1$ as is done by Parlant & Yarkony (1999). One should note it does not matter which coupling is chosen, as long as the correct Λ , Σ combination is given in Duo.

MOLPRO produces coupling curves and dipoles with an arbitrary phase factor of ± 1 or $\pm i$ which is not guaranteed to be consistent between geometries. This uncertainty in phase leads to discontinuities in the curves and hence requires post-processing. Within an MRCI calculation informed by a set of SA-CASSCF orbitals, the phase may not be consistent between geometries, however it is consistent over all curves computed with those orbitals for a given geometry; any discontinuities will appear in the same places for all curves (Patrascu et al., 2014). The coupling curves in this study, however, were not all computed with one set of orbitals and instead were split up as shown in the SA-CASSCF column in

Table 4.3: Summary of *ab initio* electronic structure calculation details. All calculations use aug-cc-pV6Z basis set with the first σ orbital closed. Orbitals correspond to the point group symmetry C_{2v} .

Curve	SA-CASSCF	Space
PECs		
X $^2\Pi$	X $^2\Pi_x$, X $^2\Pi_y$	$5\sigma 2\pi$
A $^2\Sigma^+$, 1 $^2\Sigma^-$	A $^2\Sigma^+$, 1 $^2\Sigma^-$	$5\sigma 2\pi$
1 $^4\Sigma^-$	A $^2\Sigma^+$, 1 $^2\Sigma^-$, 1 $^4\Sigma^-$	$5\sigma 2\pi$
1 $^4\Pi$	1 $^4\Pi_x$, 1 $^4\Pi_y$, A $^2\Sigma^+$	$6\sigma 2\pi$
Coupling Curves		
$\langle X ^2\Pi \hat{H}_{SO} A ^2\Sigma^+ \rangle$	X $^2\Pi_x$, X $^2\Pi_y$, A $^2\Sigma^+$	$5\sigma 2\pi$
$\langle X ^2\Pi \hat{L}_x A ^2\Sigma^+ \rangle$	X $^2\Pi_x$, X $^2\Pi_y$, A $^2\Sigma^+$	$5\sigma 2\pi$
$\langle X ^2\Pi \hat{H}_{SO} X ^2\Pi \rangle$	X $^2\Pi_x$, X $^2\Pi_y$	$5\sigma 2\pi$
$\langle A ^2\Sigma^+ \hat{H}_{SO} 1 ^2\Sigma^- \rangle$	A $^2\Sigma^+$, 1 $^2\Sigma^-$	$5\sigma 2\pi$
$\langle A ^2\Sigma^+ \hat{H}_{SO} 1 ^4\Sigma^- \rangle$	A $^2\Sigma^+$, 1 $^2\Sigma^-$, 1 $^4\Sigma^-$	$5\sigma 2\pi$
$\langle A ^2\Sigma^+ \hat{H}_{SO} 1 ^4\Pi \rangle$	1 $^4\Pi_x$, 1 $^4\Pi_y$, A $^2\Sigma^+$	$6\sigma 2\pi$
(Transition) Dipole Moments		
$\langle X ^2\Pi \hat{\mu}_z X ^2\Pi \rangle$	X $^2\Pi_x$, X $^2\Pi_y$	$5\sigma 2\pi$
$\langle A ^2\Sigma^+ \hat{\mu}_z A ^2\Sigma^+ \rangle$	A $^2\Sigma^+$, 1 $^2\Sigma^-$	$5\sigma 2\pi$
$\langle X ^2\Pi \hat{\mu}_x A ^2\Sigma^+ \rangle$	X $^2\Pi_x$, X $^2\Pi_y$, A $^2\Sigma^+$	$5\sigma 2\pi$
$\langle X ^2\Pi \hat{\mu}_x 1 ^2\Sigma^- \rangle$	X $^2\Pi_x$, X $^2\Pi_y$, A $^2\Sigma^+$, 1 $^2\Sigma^-$	$5\sigma 2\pi$

Table 4.3. Inter-SA-CASSCF phase consistency was ensured by first smoothing all curves with an arbitrary global phase and comparing to a set of reference curves. These were produced by performing an aug-cc-pVTZ calculation with all states present in the SA-CASSCF, ensuring phase consistency between all relevant curves.

The reference curve calculation covers all curves initially computed with the aug-cc-pV6Z basis set. As all curves in the 3Z calculation are computed with the same SA-CASSCF, they are phase consistent with each other for a given geometry. In principle, these curves would still require smoothing to remove discontinuities, and if this is to be done, it must be ensured that all phase changes are applied consistently. In the case of this work, all curves came out smooth from MOLPRO and no such smoothing was required. After this calculation, the 6Z curves' phases are matched to that of the reference curves to retrieve the final results. Visual representations of these curves can be seen in Figures 4.1, 4.2, and 4.3. Discussion on the (transition) dipole moment curves can be found in Section 4.6.1.3.

4.2.2 Electronic Structure of (B,C) $^2\Sigma^+$ and 1 $^2\Delta$

The curves pertaining to the B $^2\Sigma^+$, C $^2\Sigma^+$, and 1 $^2\Delta$ states were computed similarly as the others as described above. These states are in the A_1 irreducible representation in the C_{2v} point symmetry group.

The 1 $^2\Delta$ state has the degenerate A_2 representation. To identify this state, calculations including both representations were performed. The PEC corresponding to the 1 $^2\Delta$ state was found to be degenerate in these representations, as expected, and so could be identified. Results were compared with the curves of [van der Loo & Groenenboom \(2005\)](#) to verify the shape and asymptotic energy of the potential.

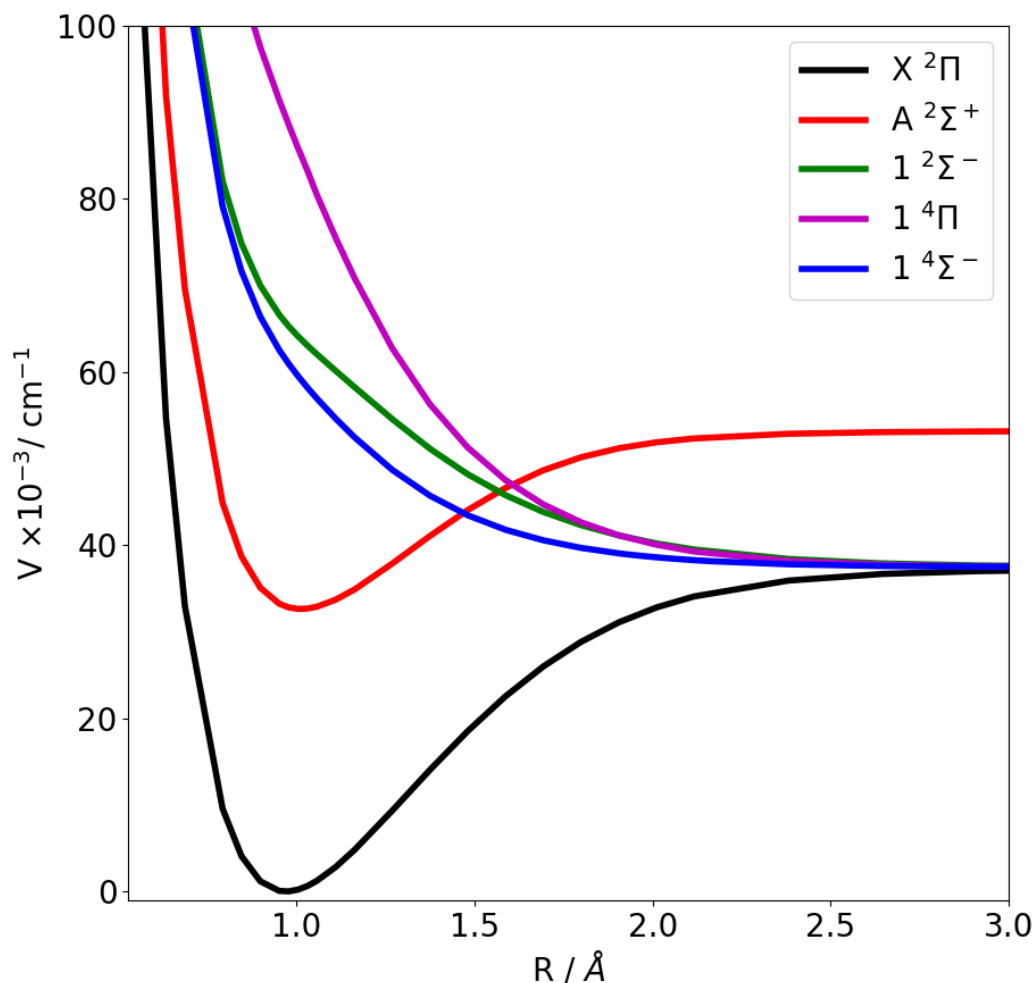


Figure 4.1: *Ab initio* potential energy curves for OH as computed in MOLPRO.

$B\ ^2\Sigma^+$ was identified similarly by checking against the asymptotic limits. It is expected that the energy gap between the $A\ ^2\Sigma^+$ and $B\ ^2\Sigma^+$ asymptotic limits should be on the order of $18,000\text{ cm}^{-1}$ (Kramida et al., 2021) as the $A\ ^2\Sigma^+$ state tends to the $O(^1D) + H(^2S)$ limit and the $B\ ^2\Sigma^+$ state tends to the $O(^1S) + H(^2S)$ limit. This was found to be the case and the shape of the curve was again verified against van der Loo & Groenenboom (2005).

A difficulty in this calculation was identifying the $C\ ^2\Sigma^+$ state, especially since many states were required in the SA-CASSCF to achieve convergence. In this calculation, the $A\ ^2\Sigma^+$, $1\ ^2\Delta$, $B\ ^2\Sigma^+$, and $C\ ^2\Sigma^+$ states were present, along with a further 4 A_1 states, which have not been used in the production of the spectroscopic model. The $C\ ^2\Sigma^+$ state exhibited orbital swapping with the other local states. This is visible in Figure 4.4. This state was identified by its characteristically high equilibrium bond length at $\sim 3.8\ a_0$ as was shown by Langhoff et al. (1982).

From this it is visible that, the third and fourth PEC correspond to $B\ ^2\Sigma^+$ and $C\ ^2\Sigma^+$ electronic states. The $C\ ^2\Sigma^+$ *ab initio* PEC is not particularly useful, however, as the short-range potential energy curve is tangled with high-energy Rydberg states at $R < 2.6\ \text{\AA}$. Untangling the swapped orbitals and dealing with avoided crossings was deemed impractical and unproductive. Instead this PEC was used to extract a rough guide for the potential minimum, T_e .

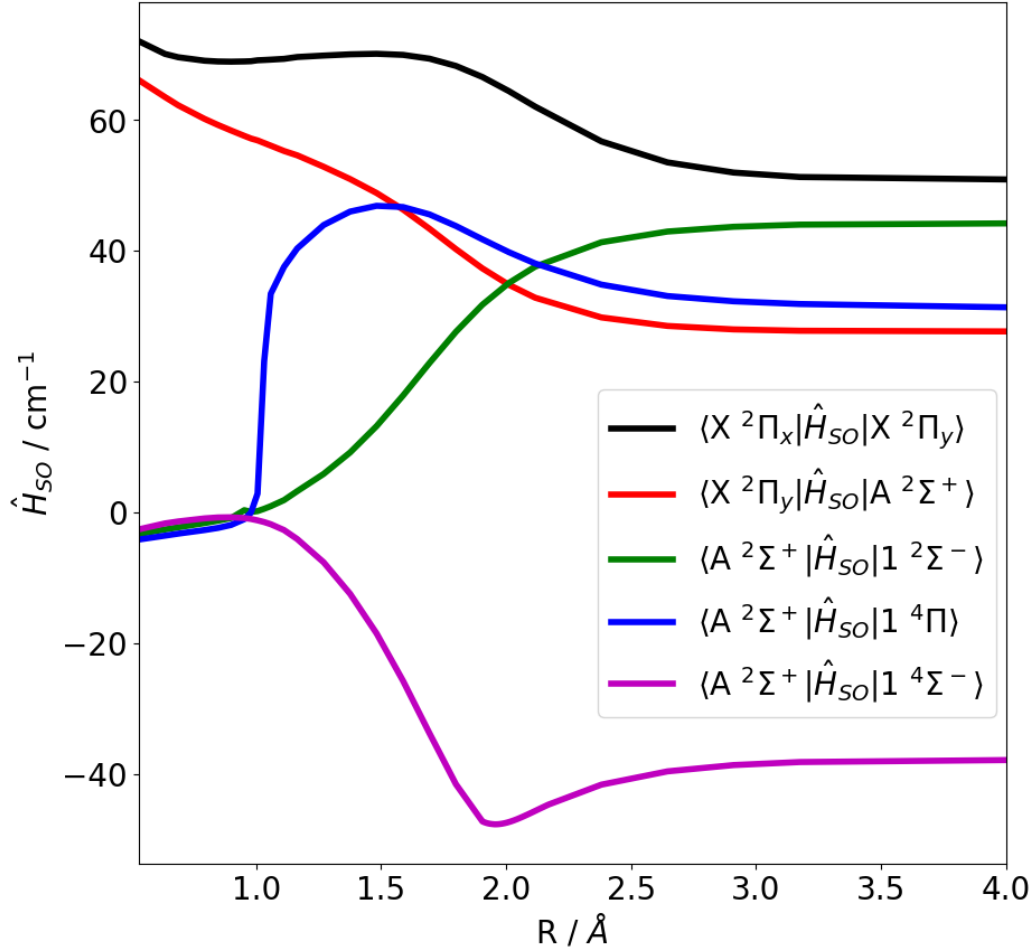


Figure 4.2: Diagonal and off-diagonal *ab initio* spin-orbit coupling curves of OH as computed in MOLPRO. The curves here also have an associated factor of $\pm i$.

Table 4.4: Mapping between dipoles and numerical representation of A_1 states in MOLPRO for OH.

Dipole	Numerical Representation
$\langle X^2\Pi \hat{\mu}_x 1^2\Delta \rangle$	$\langle 1.2 \hat{\mu}_x 2.1 \rangle$
$\langle X^2\Pi \hat{\mu}_x B^2\Sigma^+ \rangle$	$\langle 1.2 \hat{\mu}_x 3.1 \rangle$
$\langle X^2\Pi \hat{\mu}_x C^2\Sigma^+ \rangle$	$\langle 1.2 \hat{\mu}_x 4.1 \rangle$

We find from Figure 4.4 that the relevant dipoles correspond to the numerical symmetry representations from MOLPRO as in Table 4.4. These mappings were used when calculating the (transition) dipole moment curves for these electronic states. Details of these calculations are given in Table 4.5.

A picture containing these *ab initio* potential energy curves is available in Figure 4.5.

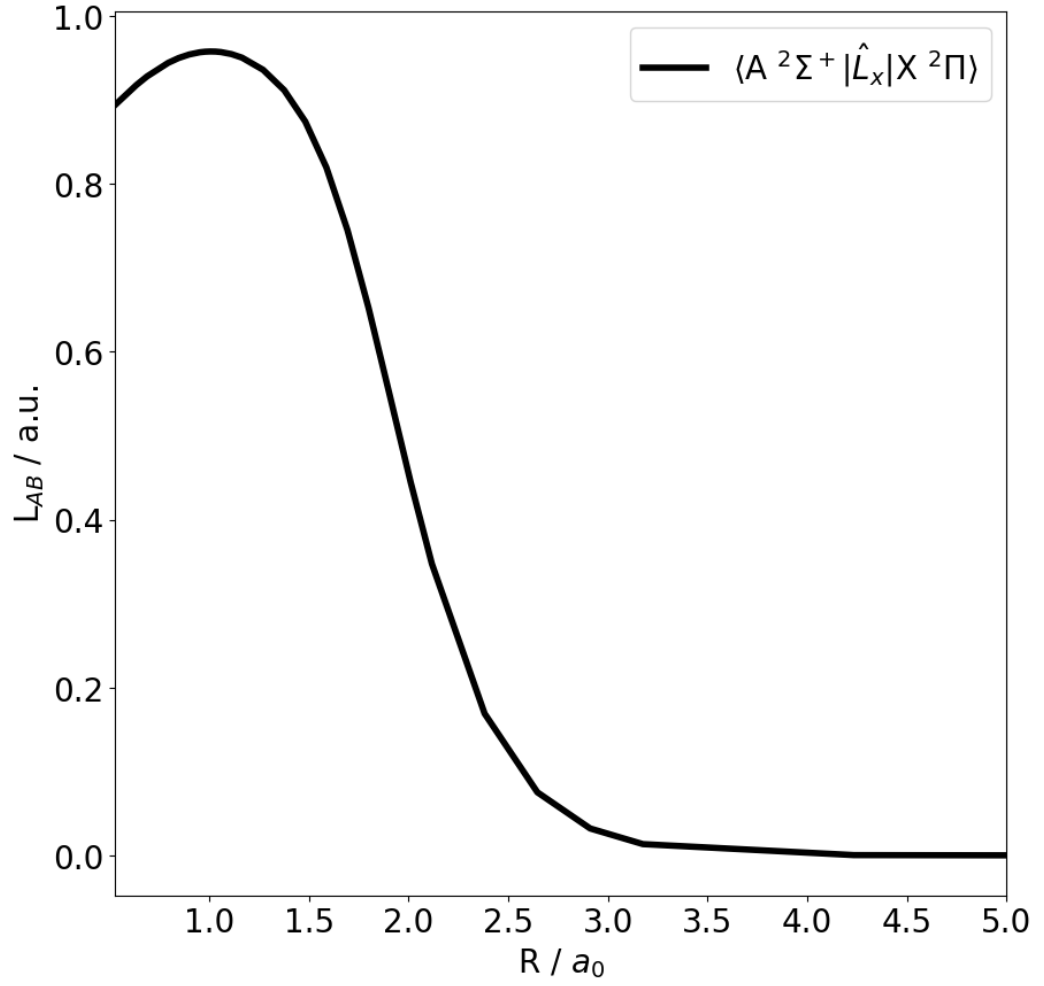


Figure 4.3: *Ab initio* L-uncoupling matrix elements for OH as computed in MOLPRO. In the Cartesian coordinate system, there is a factor of $\pm i$.

Table 4.5: Details of MOLPRO calculation for the $B^2\Sigma^+$, $C^2\Sigma^+$, and $1^2\Delta$ electronic states of OH.

Curve	SA-CASSCF	Space	Basis set
PECs			
$B^2\Sigma^+, C^2\Sigma^+, 1^2\Delta$	$A^2\Sigma^+, B^2\Sigma^+, C^2\Sigma^+, 1^2\Delta, +4A_1$	$6\sigma 2\pi$	aug-cc-pV6Z
(Transition) Dipole Moments			
$\langle X^2\Pi \hat{\mu}_x B^2\Sigma^+ \rangle$	$A^2\Sigma^+, B^2\Sigma^+, C^2\Sigma^+, 1^2\Delta, +4A_1$	$6\sigma 2\pi$	aug-cc-pV5Z
$\langle X^2\Pi \hat{\mu}_x C^2\Sigma^+ \rangle$	$A^2\Sigma^+, B^2\Sigma^+, C^2\Sigma^+, 1^2\Delta, +4A_1$	$6\sigma 2\pi$	aug-cc-pV5Z
$\langle X^2\Pi \hat{\mu}_x 1^2\Delta \rangle$	$A^2\Sigma^+, B^2\Sigma^+, C^2\Sigma^+, 1^2\Delta, +4A_1$	$6\sigma 2\pi$	aug-cc-pV5Z

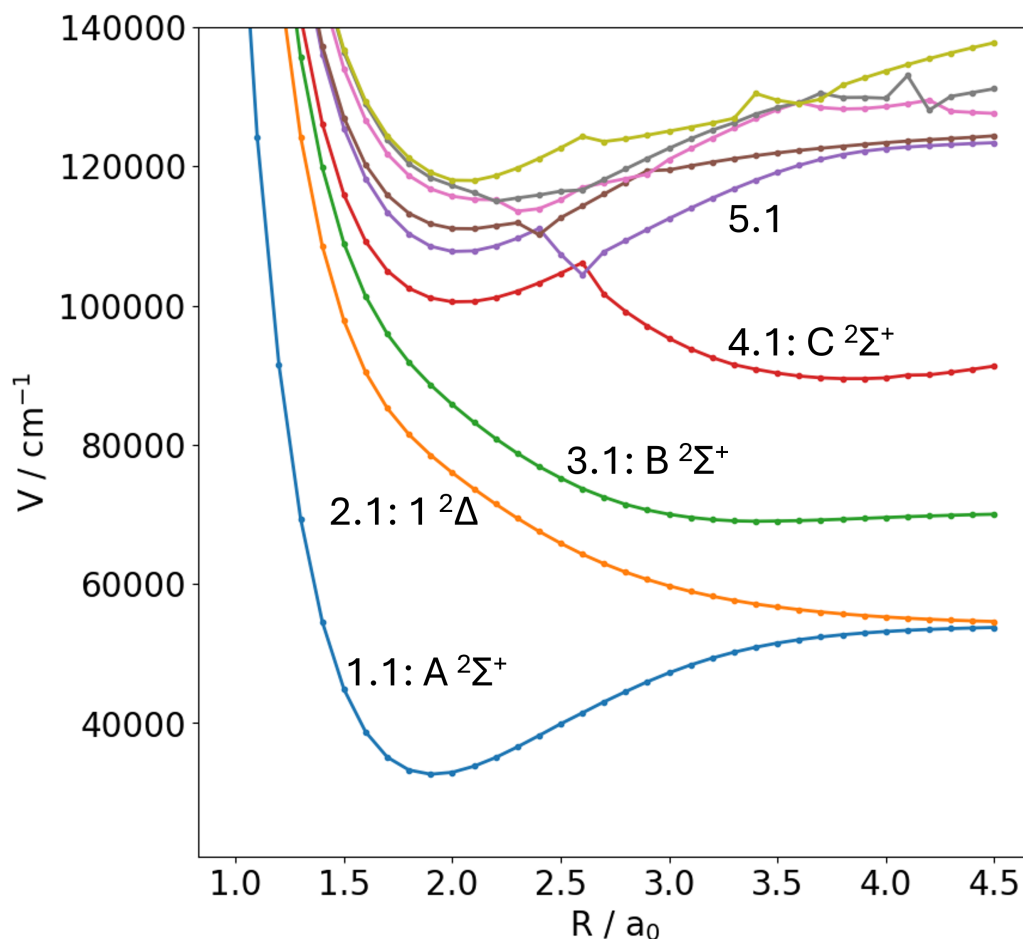


Figure 4.4: First 8 A_1 symmetry potential energy curves of OH as calculated in MOLPRO using the aug-cc-pV5Z basis set and $6\sigma 2\pi$ active space. The labelling here is [Energy Order].[Symmetry].

4.3 Spectroscopic Model

4.3.1 Global parameters

The curves produced above provide input to the nuclear motion code DUO (Yurchenko et al., 2016a), an open-source Fortran 2009 program which provides variational solutions to the coupled rovibronic Schrödinger equations for a general open-shell diatomic molecule. Rovibronic energy levels and transitions are evaluated for the mutually perturbed $X\ ^2\Pi$ and $A\ ^2\Sigma^+$ states. However, the *ab initio* curves are insufficient for accurate reproduction and extrapolation of energy levels of this system despite the high level of *ab initio* theory employed.

A number of global parameters need to be established before running a DUO calculation, they are as follows: The size of vibrational basis sets ($v_{\max}$) for each electronic state, the start ($R_{\min}$) and end (R_c) of the calculation box, the number of grid points, and the maximum value for J . These considerations are made to ensure converged solutions for the energy levels. The start and end of the box was set to 0.53 Å and 8 Å respectively with a grid size of 801 points.

When fitting the model, one may reduce the computational cost of solving the nuclear mo-

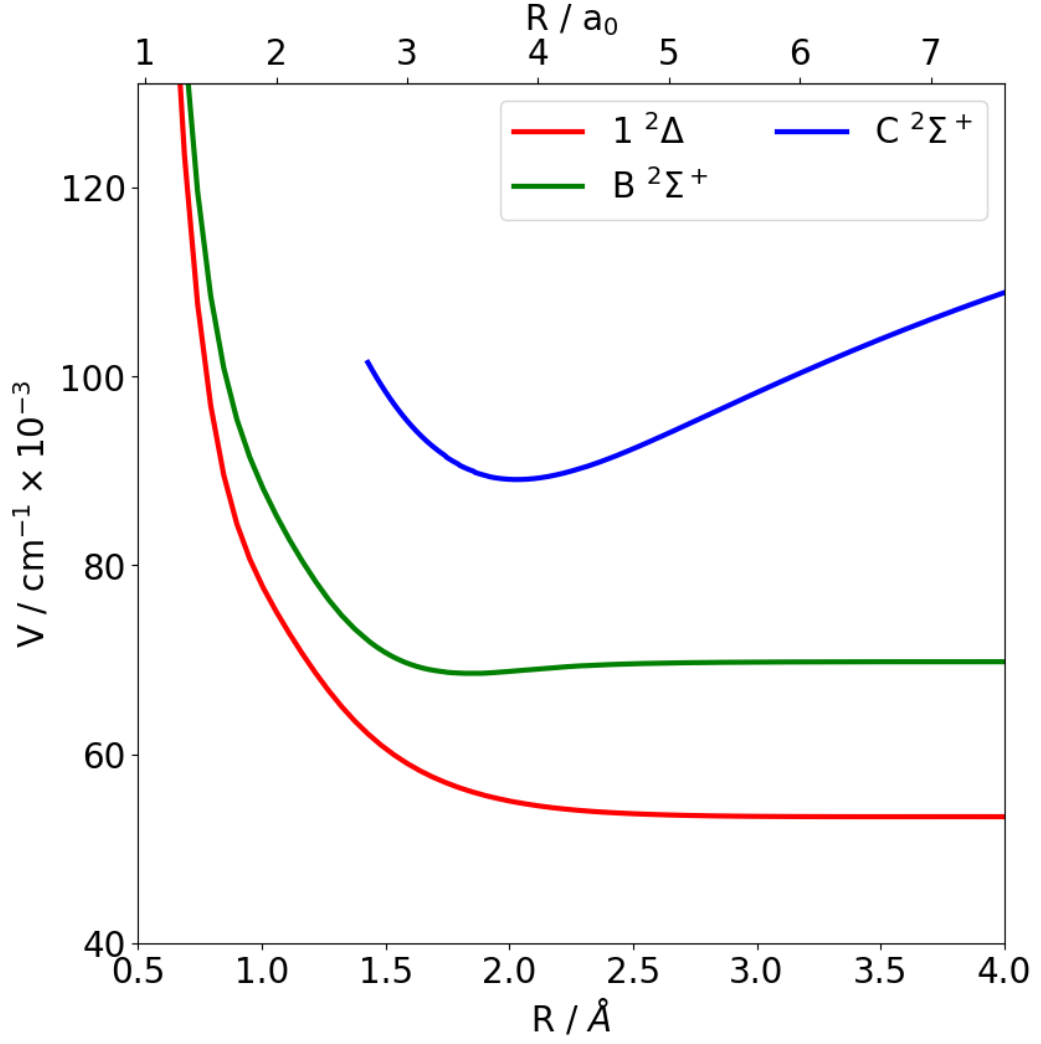


Figure 4.5: *Ab initio* potential energy curves for the $1\ ^2\Delta$, $B\ ^2\Sigma^+$, and $C\ ^2\Sigma^+$ states of OH.

tion problem by reducing the vibrational basis to cover only states present in the reference data, with the intent to increase the basis upon extrapolation to higher energies.

A consequence of this is that the model is built on solutions which are not fully converged. States with $v = v_{\max}$ are asymmetrically perturbed by local rovibronic states. Upon the increase of $v_{\max}$ to a higher value, $\tilde{v}_{\max}$, for use in prediction of higher energy states, new states are introduced above the states with $v = v_{\max}$. These come with additional perturbative effects on the lower states. This has a significant effect on the term values of the previously well-fitting rovibronic levels, and requires that the model be refit to accommodate this.

On the other end of this, one may start with a very large vibrational basis which ensures this problem does not materialise but this means that calculations are unnecessarily expensive. Instead it is beneficial to establish the minimal $v_{\max}$ whereby upon a further increase, the target energy levels are not affected, and so are converged.

$v_{\max}$ was selected for each electronic state iteratively. By extracting energy eigenvalues within the relevant fitting region (defined by the quantum number coverage of 4.2) for increasing $v_{\max}$, we can set $v_{\max}$ such that the energy levels are converged. This was found to occur when $v_{\max}^X \geq 110$ and $v_{\max}^A \geq 90$. The size of the vibrational basis sets were

hence set to 110 and 90 for the $X^2\Pi$ and $A^2\Sigma^+$ states respectively. This procedure was repeated for the $B^2\Sigma^+$ and $C^2\Sigma^+$ states and it was found that $\nu_{\max}^{B,C} \geq 10$ was sufficient. The maximum value for J , $J_{\max}$, was set to 50.5.

4.3.2 Fitting - $X^2\Pi$ and $A^2\Sigma^+$

The PECs and coupling curves were refined by making constrained adjustments to parameters which describe them with respect to a set of observed data, which can be of empirical energy levels or transitions. These data are supplied by the recent MARVEL data set's energy levels [Furtenbacher et al. \(2022\)](#). Curve refinement is performed in DUO by least squares fitting to this data set. DUO provides three types of fitting one can use; variation of parameters that describe a curve (Section 4.3.2.1), variation of parameters that describe a morphing function (*morphing*, see Section 4.3.2.2), and direct variation of individual grid points. In each case the optimization is based on a non-linear conjugate gradient method ([Yurchenko et al., 2016a](#)) with respect to an empirical data set.

4.3.2.1 Parameter variation fitting – pre-fitting

During parameter variation fitting, the curves must have some parametric form, and some initial set of parameters must be determined. For PECs, the form used in this study is the Extended Morse Oscillator (EMO) ([Le Roy, 2017a](#); [Yurchenko et al., 2016a](#); [Lee et al., 1999](#); [Le Roy et al., 2006](#)), given by

$$V_{EMO}(R) = T_e + (A_e - T_e) \left(1 - e^{-\beta(R)(R-R_e)}\right)^2, \quad (4.11)$$

where T_e is the potential minimum, $D_e = A_e - T_e$ is the dissociation energy relative to T_e , A_e is the dissociation asymptote, and R_e is the equilibrium bond length. $\beta(R)$ is a distance-dependent exponent coefficient defined by the expansion term with coefficients β_i with respect to the reduced coordinate ξ_p , first introduced by [Šurkus et al. \(1984\)](#) and are given by

$$\beta(R) = \sum_{i=0}^N \beta_i \xi_p(R)^i; \quad N = \begin{cases} N_R & \text{for } R > R_e \\ N_L & \text{for } R \leq R_e, \end{cases} \quad (4.12)$$

$$\xi_p(R) = \frac{R^p - R_e^p}{R^p + R_e^p}; \quad p = \begin{cases} p_R & \text{for } R > R_e \\ p_L & \text{for } R \leq R_e, \end{cases} \quad (4.13)$$

This parametric form was selected because it is very flexible. One can specify the behaviour around the equilibrium internuclear distance piece-wise using the parameters N_L , N_R , p_L , and p_R , where $N_L \leq N_R$. The value of N_R hence defines the order of the expansion. This means one can establish a family of potential energy curves where the fundamental shape is determined by the set of parameters, S , where

$$S = \{p_L, p_R, N_L, N_R\}; \quad \{p_L, p_R, N_L, N_R\} \in \mathbb{Z}, \quad N_R \geq N_L. \quad (4.14)$$

Table 4.6: Parameters, σ_i which best describe *ab initio* PECs of OH as calculated in Section 4.2.

Parameter	Units	X $^2\Pi$	A $^2\Sigma^+$
T_e	cm^{-1}	0	32612.251248000
R_e	$\text{\AA}$	0.970655035	1.013454000
A_e	cm^{-1}	37269.126195730	53204.256220000
p_L		4	3
p_R		3	3
N_L		6	4
N_R		8	8
β_0	$\text{\AA}^{-1}$	2.292052187	2.620396000
β_1	$\text{\AA}^{-1}$	-0.019995181	0.169768000
β_2	$\text{\AA}^{-1}$	0.198099686	0.465289000
β_3	$\text{\AA}^{-1}$	0.231459916	0.552208000
β_4	$\text{\AA}^{-1}$	-0.136025012	0.413921000
β_5	$\text{\AA}^{-1}$	-0.639517770	-5.174652000
β_6	$\text{\AA}^{-1}$	-0.277770706	9.999998000
β_7	$\text{\AA}^{-1}$	6.274892232	3.333865000
β_8	$\text{\AA}^{-1}$	-4.898195146	-9.999764000

For a given S , one can then find P which refines the shape to return appropriate energy levels, such that:

$$P = \{\beta_i, r_e, T_e, D_e\}; \quad i \leq N_R. \quad (4.15)$$

When fitting a PEC in DUO, S is fixed, and hence should be carefully chosen before optimizing P . Initial parameter selection was performed by extending the methods given in Chapter 3. Given that the elements of S are integers, one cannot use a standard optimization algorithm to optimize the values, and instead one must solve the problem iteratively. The optimization of S is therefore initiated by establishing the set,

$$\sigma_S = \{S_0, \dots, S_n\} \quad (4.16)$$

$$\equiv \{\{p_{L_0}, p_{R_0}, N_{L_0}, N_{R_0}\}, \dots, \{p_{L_n}, p_{R_n}, N_{L_n}, N_{R_n}\}\}, \quad (4.17)$$

which contains n elements of the set, S , as in Equation (4.14) such that,

$$S_i \neq S_j \quad \forall i, j; \quad i \neq j. \quad (4.18)$$

This is the set of values of p_L , p_R , N_L , and N_R over which we would like to test. The test consists of, for each S_i , finding the conjugate P_i by least-squares fitting against the *ab initio* grid points in PYTHON. In each case we find the reduced χ^2 test statistic, χ_v^2 and search for the (S, P) values which return the lowest value. These parameters are then used as a starting point for fitting the PECs against experimental data in DUO. See Table 4.6 for the σ_i parameters for the X $^2\Pi$ and A $^2\Sigma^+$ states in this study.

4.3.2.2 Morphing

As discussed above, morphing is another available technique for model refinement. In this case, one does not vary the curve in question directly, but instead varies a morphing

function, $f_m(R)$, which in turn, scales the *ab initio* curve, $f_{ai}(R)$ (Meuwly & Hutson, 1999; Skokov et al., 1999):

$$f_{\text{morphed}}(R) = f_{ai}(R)f_m(R). \quad (4.19)$$

As was done for NaO (see Chapter 3) a *Polynomial decay* morphing function of the following form was used:

$$f_m(R) = \sum_{k=0}^N B_k z^k (1 - \xi_p) + \xi_p B_\infty, \quad (4.20)$$

where

$$z(r) = (R - R_{\text{ref}}) e^{-\beta(R - R_{\text{ref}})^2 - \gamma(R - R_{\text{ref}})^4}.$$

ξ_p is as in Equation (4.13), B_k are variable expansion coefficients, β and γ are static coefficients typically set to 0.8 and 0.02 respectively, B_∞ is typically set to unity to preserve the asymptotic behaviour of f_{ai} , N is the order of expansion, and R_{ref} is the expansion center. R_{ref} is set to the equilibrium bond length of the lower energy electronic state. When fitting Equation 4.20, only the B_k parameters are floated.

4.3.2.3 Constraining Curves

The asymptotic energy limit for all the curves in Figure 4.1 was constrained by setting the value of D_e^X to the experimental value of D_0 from Joens (2001) with the added offset from the zero-point energy of the X $^2\Pi$ state, E_0^X calculated in DUO, hence

$$D_e^X = D_0 + E_0^X. \quad (4.21)$$

The remaining curves' D_e were constrained with respect to D_e^X such that their respective atomic limit spacings match those of Kramida et al. (2021).

4.3.3 Fitting - B $^2\Sigma^+$ and C $^2\Sigma^+$

These PECs were fit independently of the ground and first excited state as they are well separated from those states and their energy levels are not mutually perturbed by off-diagonal couplings of any kind. Initially there was a concern that since the A, B, and C states are all of the $^2\Sigma^+$ symmetry, they may influence each others' energy levels. It was found, however, that this was not the case. DUO calculations with the full vibrational basis in the A $^2\Sigma^+$ state from Section 4.3.1 were performed and compared with similar runs where the A $^2\Sigma^+$ state vibrational basis was set to have a max of $v = 1$. Comparing the energy levels of the B $^2\Sigma^+$ and C $^2\Sigma^+$ states in both cases returned the same results. The same procedure was performed to see if there is any interplay between the B $^2\Sigma^+$ and C $^2\Sigma^+$ states, and again it was confirmed that they are independent of each other, allowing for a very clean environment for fitting, where only one state needed to be considered at a time.

The need for off-diagonal couplings between the high lying excited states and the ground state was found empirically. A zeroth order polynomial off-diagonal spin-orbit coupling between these states and the ground state was initialised and floated. Upon running the fitting algorithm, this value diverged, however, the energies were unchanged, indicating that spin-orbit effects here are negligible.

These PECs of these states are different than those of the first two states. As is visible in

Figure 4.5, B $^2\Sigma^+$ is very shallow relative to the other states with $D_e(B) \approx 1400 \text{ cm}^{-1}$. Since the MARVEL levels available for the B $^2\Sigma^+$ state are very complete, going up to dissociation, and since the state is very shallow, the long-range shape of this potential is important. The extended Morse oscillator potential has seen criticism due to its inability to effectively model the long-range (Le Roy et al., 2006) and as such the Morse-Long range potential (MLR) (Le Roy & Henderson, 2007; Le Roy et al., 2009; Robert J. Le Roy & Li, 2011) is used here instead.

$$V(R) = T_e + (A_e - T_e) \left(1 - \frac{U(R)}{U(R_e)} e^{-\beta(R)\xi_p(R)} \right)^2, \quad (4.22)$$

$$U(R) = \sum_n \frac{C_n}{R^n}, \quad (4.23)$$

$$\beta(R) = \xi_p(R)\beta_\infty + (1 - \xi_p(R)) \sum_{i=0}^{\beta_{\max}} \beta_i \xi_q(R)^i. \quad (4.24)$$

Here, the Morse-like parameter β is similar to that of the EMO, where it is not a constant but is implemented as a function of R , where ξ_p is the reduced coordinate from Equation 4.13. The difference here is that the order, p , is not dependent on whether the potential is calculated to the left or right of the equilibrium bond length. There is also the added parameter q allowing for the use of two separate instances of this reduced coordinate. In this study, however, $q = p$ for simplicity. β_∞ here is constrained to have the following value:

$$\beta_\infty = \ln \left(\frac{2D_e}{U(R_e)} \right). \quad (4.25)$$

The result of this is constraint is:

$$V(R \rightarrow \infty) = U(R) = \sum_n \frac{C_n}{R^n}, \quad (4.26)$$

which is the important feature of this potential. The shape set of this potential hence becomes:

$$S = \{p, \beta_{\max}, \{C_i\}\}; \{p, \beta_{\max}, \{i\}\} \in \mathbb{Z}. \quad (4.27)$$

To model the long-range of B $^2\Sigma^+$, we consider its asymptotic behaviour, where it tends to $O(^1S) + H(^2S)$. In this limit, the primary forces between two neutral S states is Van der Waals, which have a potential form,

Table 4.7: Shape set for the B $^2\Sigma^+$ state for use in the Morse-Long range potential energy form.

Parameter	Value
$\beta_{\max}$	3
p	2
C_n	$n = 6$

$$V_{\text{vdW}} \propto \frac{1}{R^6}. \quad (4.28)$$

Hence in the limit that $R \rightarrow \infty$:

$$U(R) = \sum_n \frac{C_n}{R^n} = \begin{cases} \frac{C_6}{R^6} & \text{for } n = 6 \\ 0 & \text{otherwise.} \end{cases} \quad (4.29)$$

The C_6 coefficients of different species are themselves a topic of study. One of the first attempts to derive a general formalism for the C_6 coefficient was given by [Slater & Kirkwood \(1931\)](#). [Tang \(1969\)](#) later built upon this work to derive the C_6 coefficient of a heteronuclear molecule, $C_{6,AB}$ based on the C_6 coefficients of the individual atom pairs $C_{6,AA}$ and $C_{6,BB}$,

$$C_{6,AB} = \frac{2C_{6,AA}C_{6,BB}}{\frac{\alpha_A}{\alpha_B}C_{6,BB} + \frac{\alpha_B}{\alpha_A}C_{6,AA}}, \quad (4.30)$$

where $\alpha_{A,B}$ are the polarizabilities of the individual atoms. [Tkatchenko & Scheffler \(2009\)](#) and [Gould & Bučko \(2016\)](#) used this relationship in their own studies and the latter work found this to give good results. [Chu & Dalgarno \(2004\)](#); [Gould & Bučko \(2016\)](#) produced databases of theoretical C_6 coefficients for a variety of atom pairs, the latter of which have been used to calculate the C_6 coefficient of OH, and hence, B $^2\Sigma^+$. It is unclear whether these individual C_6 coefficients are for the ground state configurations of the atoms, but this is assumed to be the case. Given this, it should be noted that this would be an approximation of the true C_6 coefficient of B $^2\Sigma^+$ especially given that [Gould & Bučko \(2016\)](#) found that the formalism in Equation 4.30 was good in 80% of cases, where they had less than a 5% error compared to other calculations. The $C_{6,B \ ^2\Sigma^+}$ coefficient was found using this approximation to be $C_{6,B \ ^2\Sigma^+} \approx 47686.64 \text{ cm}^{-1} \text{ \AA}^6$:

Literature values for C_6 coefficients of excited atomic configurations do not appear to be available. From personal communication with S. N. Yurchenko, it was discovered that they are sometimes fit similarly to other floating parameters. This was attempted, however with little success as the coefficient simply diverged upon running the gradient descent algorithm. As the computation of C_6 coefficients is a not straightforward and is beyond the remit of this thesis, this approximation was made pragmatically.

With this value in mind, the pre-fitting procedure (Section 4.3.2.1) was performed and the following shape set (Equation 4.27) was determined for B $^2\Sigma^+$.

The vibrational structure (β_i) of $B^2\Sigma^+$ was fit to the *ab initio* curves from Section 4.2 and was left fixed. While fitting β_i to the MARVEL energies did somewhat improve the residuals to the MARVEL energies, this resulted in an unphysical curve which would overlap with the $C^2\Sigma^+$ state. $B^2\Sigma^+$ appears to be extremely sensitive to fitting the vibrational structure. This is likely due to most levels being close to dissociation, hence long-range effects playing a large role in the evaluation of the energy level positions. This is probably a consequence of the somewhat crude approximation made in determining $U(R)$. Instead a best attempt was made to fit this state by floating only T_e and R_e with the added spin-rotation constant γ , which has been used in effective Hamiltonian models for this state.

$C^2\Sigma^+$ also required the use of the MLR potential. While the long-range in $B^2\Sigma^+$ was dominated by Van der Waals effects, the long-range in $C^2\Sigma^+$ is dominated by ionic interactions (Langhoff et al., 1982) as can be seen from the *ab initio* $C \rightarrow C$ permanent dipole, which is approximately linear in R . The $C^2\Sigma^+$ state hence tends to $O^- + H^+$ and hence in the limit that $R \rightarrow \infty$:

$$U(R) = \sum_n \frac{C_n}{R^n} = \begin{cases} \frac{C_1}{R} & \text{for } n = 1 \\ 0 & \text{otherwise.} \end{cases} \quad (4.31)$$

But, since this is a Coulomb interaction, C_1 must be such that it is equal to unity in atomic units: $[E_H a_0]$, where E_H is the Hartree energy and a_0 is the Bohr radius. So all that is required to determine C_1 is a unit conversion to $\text{cm}^{-1} \text{\AA}$ resulting in $C_{1,C^2\Sigma^+} \approx 116140.93 \text{ cm}^{-1} \text{\AA}$:

The dissociation energy is determined by considering the energy difference:



$$(4.33)$$

Hence $D_e(C)$ is:

$$D_e(C) = D_e(X) + E_I(H) - E_{EA}(O) - T_e(C), \quad (4.34)$$

where E_I is the ionization energy of hydrogen and has been taken from Scheidegger & Merkt (2024) and E_{EA} is the electron affinity of oxygen and has been taken from Kristiansson et al. (2022). $D_e(C)$ and C_1 have been left fixed during the fitting procedure and the pre-fitting procedure was forsaken here in favour of doing this empirically. This was done due to the *ab initio* curves being incomplete at short range. As stated earlier, however, the *ab initio* calculation provided a starting value for T_e . The PEC parameters left floating here are β_0 , T_e , and R_e , with $p = 2$. As with $B^2\Sigma^+$, a spin-rotation constant was added as this had been used in the available effective Hamiltonian treatments (Coxon et al., 1991). Summarizing, the shape set is given in Table 4.8.

4.3.4 Summary of Shape sets and Initial Parameter sets

The shape sets discussed in the previous sections are summarized in Table 4.9.

Table 4.8: Shape set for the C $^2\Sigma^+$ state for use in the Morse-Long range potential energy form.

Parameter	Value
$\beta_{\max}$	0
p	2
C_n	$n = 1$

Table 4.9: Summary of the initial shape sets (see Section 4.3.2.1) for the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH.

Parameter - EMO	X2Pi	A2Sigma+	Parameter - MLR	B2Sigma+	C2Sigma+
p_L	4	3	p	2	2
p_R	3	3	$\beta_{\max}$	3	0
N_L	6	4	C_n	6	1
N_R	8	8			

These were initially paired with the following parameter sets:

4.4 Bound and unbound rovibronic states

Rovibronic states calculated with DUO are constrained by the boundary condition that the wavefunction, ψ is zero at the boundary where the potential $V = \infty$, or the critical internuclear distance, R_c . In this regime, all states are effectively treated as bound states, with a node at R_c . To treat unbound states rigorously using DUO, one must have R_c at ∞ which is not possible. In this section, the categorization of bound vs. unbound states in DUO is discussed. The details of how unbound states are treated in the context of spectral simulation of continuum absorption is discussed in Chapter 6, and the treatment of quasi-bound states is covered in Chapter 5 (see Section 4.5 for brief summaries of these methods).

An important clarification at this stage is that the rovibronic levels and their corresponding wavefunctions which are considered in this section are calculated from a spectroscopic model containing only X $^2\Pi$ and (A, B, C) $^2\Sigma^+$. In this treatment, the quasi-bound character induced by spin-orbit predissociation effects in A $^2\Sigma^+$ do not manifest as the relevant continuum states and couplings are not included in this model. Continuum states continue to be present, however.

The assumptions here are that: **1.** in the full treatment (predissociation included), if a quasi-bound state in A $^2\Sigma^+$ with a complete set of assigned quantum numbers $\mathbf{Q}$ exists, then the corresponding state in this four-state model with the same $\mathbf{Q}$ is bound and **2.** all states in the four-state model with $\mathbf{Q}$ which are unbound remain unbound in the full treatment. In reality, only levels in X $^2\Pi$ and A $^2\Sigma^+$ which are energetically lower than the dissociation limit of X $^2\Pi$ are truly bound due to predissociation effects. All other, higher energy, states are either continuum states or quasi-bound states. The aim of this section is to find states which should be included in the line list, which has the criterion that continuum states **are not** included, but quasi-bound states **are** included. With this assumption in place, states referred to as bound hereafter are necessarily bound only in this four-state treatment, but may be quasi-bound in the full treatment.

The purpose of doing this analysis is twofold. Firstly, it constrains the levels which are included in the final line list. Secondly it constrains the range of states in A $^2\Sigma^+$ which

Table 4.10: Summary of the initial parameter sets (see Section 4.3.2.1) for the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH.

		EMO	
Parameter	Units	X $^2\Pi$	A $^2\Sigma^+$
T_e	cm^{-1}	0.000000000000000	32612.251248
R_e	$\text{\AA}$	0.97065503463788	1.0134540000
A_e	cm^{-1}	37269.1261957300	53204.256220
p_L		4	3
p_L		3	3
N_L		6	4
N_R		8	8
β_0	$\text{\AA}^{-1}$	2.29205218744086	2.6203960
β_1	$\text{\AA}^{-1}$	-0.01999518061805	0.1697680
β_2	$\text{\AA}^{-1}$	0.19809968550173	0.4652890
β_3	$\text{\AA}^{-1}$	0.23145991619633	0.5522080
β_4	$\text{\AA}^{-1}$	-0.13602501203037	0.4139210
β_5	$\text{\AA}^{-1}$	-0.63951777041011	-5.174652
β_6	$\text{\AA}^{-1}$	-0.27777070558567	9.9999980
β_7	$\text{\AA}^{-1}$	6.27489223243852	3.3338650
β_8	$\text{\AA}^{-1}$	-4.89819514590987	-9.999764
		MLR	
Parameter	Units	B $^2\Sigma^+$	C $^2\Sigma^+$
T_e	cm^{-1}	70048.640000	^a 89072.338876
R_e	$\text{\AA}$	1.8627030000	^a 2.03204
A_e	cm^{-1}	71294.380000	135395.8469789
p		2	2
β_0	$\text{\AA}^{-1}$	-0.6569361	1
β_1	$\text{\AA}^{-1}$	6.320934	0
β_2	$\text{\AA}^{-1}$	10	0
β_3	$\text{\AA}^{-1}$	6.522668	0
C_0	$\text{cm}^{-1}\text{\AA}^0$	0	0
C_1	$\text{cm}^{-1}\text{\AA}^1$	0	^b 116140.9262795
C_2	$\text{cm}^{-1}\text{\AA}^2$	0	0
C_3	$\text{cm}^{-1}\text{\AA}^3$	0	0
C_4	$\text{cm}^{-1}\text{\AA}^4$	0	0
C_5	$\text{cm}^{-1}\text{\AA}^5$	0	0
C_6	$\text{cm}^{-1}\text{\AA}^6$	^b 47686.64	0

^aNot pre-fitted values, but simply taken from *ab initio*.^bCalculated see Section 4.3.3

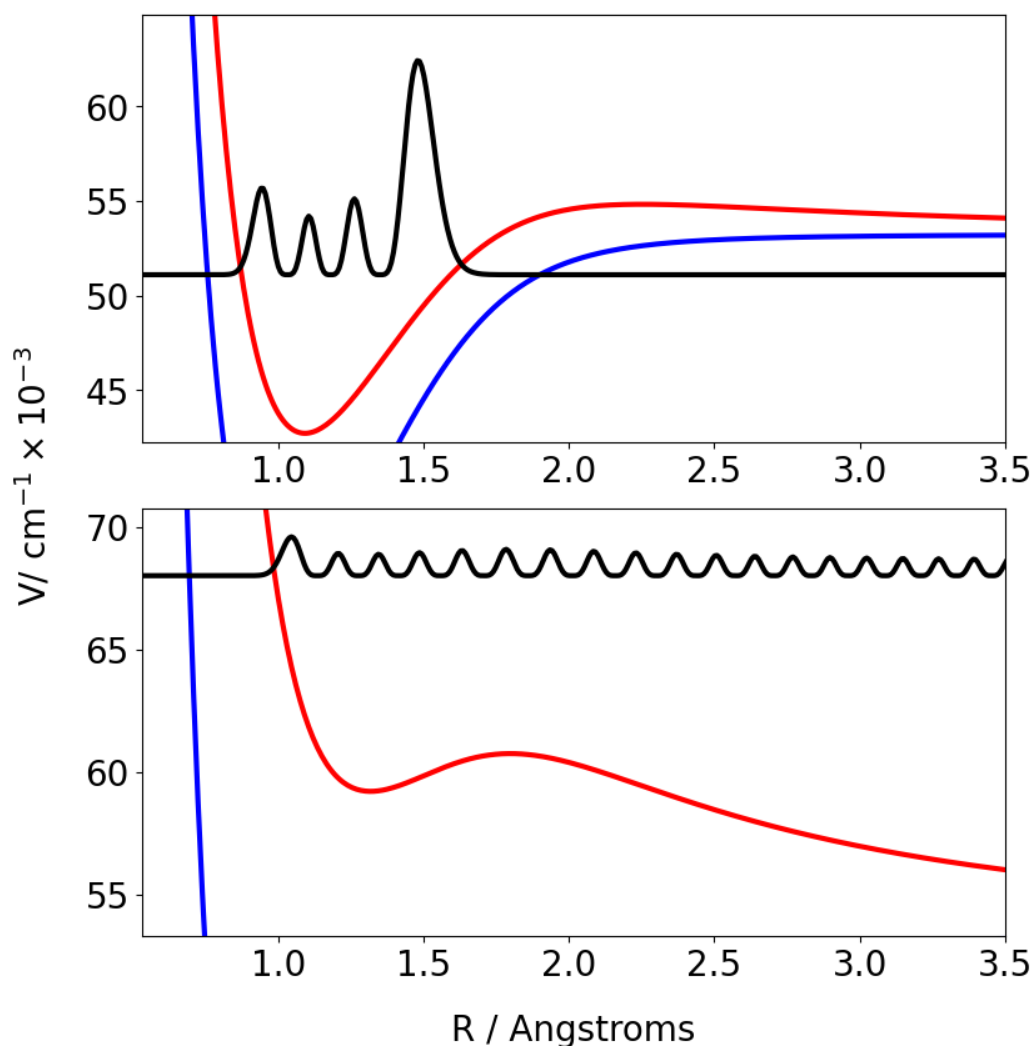


Figure 4.6: Example of bound state (upper) and unbound state (lower) wavefunction densities for the A $^2\Sigma^+$ state of OH. The red line is the effective potential $V_{\text{eff}}(R)$ (see Equation 4.38), and the blue line is the unperturbed potential $V(R)$. Baseline of the wavefunction has been placed to sit at level's energy, and the amplitude has been scaled for clarity only.

require predissociation lifetime calculation by requiring that such states are bound in this four-state model and also have energy greater than the dissociation limit of X $^2\Pi$.

4.4.1 Differentiating between bound and unbound states

As stated above, the boundary conditions on ψ and $\partial_R \psi$ results in all states effectively being treated as bound states. There is, however, a unique character to the wavefunction of bound states and unbound states even in the strictly bound regime in which DUO calculations are performed. Due to the presence of an effective infinite potential at the boundary, R_c , bound state wavefunction solutions tunnel through the right hand side of the potential well to reach zero and exhibit an exponential decay form in this region. On the other hand, for unbound states, as there is no potential barrier through which to tunnel, they exhibit a sinusoidal wave form. This difference is showcased in Figure 4.6.

As the characteristic of a bound state is a decaying wavefunction with close to zero ampli-

tude at R_c , in the region between $R_c - \varepsilon$ and R_c , where ε is some small length, the integral, $\int_{R_c-\varepsilon}^{R_c} |\psi^2(R)| dR$ is also close to zero. For unbound states this integral is not close to zero.

In the rigorous case, where $R_c \rightarrow \infty$:

$$\int_{R_c-\varepsilon}^{R_c} |\psi(R)|^2 dR = \begin{cases} 0 & \text{for bound states} \\ > 0 & \text{for unbound states.} \end{cases} \quad (4.35)$$

Numerically, this problem is not so clear cut and one must establish a threshold value above which states are labelled as unbound. The value of the integral is also dependent on ε and as such the threshold is dependent on the value of ε taken. Loosely, one can think of δ_I as a function of ε where the function returns a “useful” value for the threshold. Hence we have the threshold, $\delta_I(\varepsilon)$ and equation 4.35 becomes:

$$\int_{R_c-\varepsilon}^{R_c} |\psi(R)|^2 dR = \begin{cases} \leq \delta_I(\varepsilon) & \text{for bound states} \\ > \delta_I(\varepsilon) & \text{for unbound states.} \end{cases} \quad (4.36)$$

In studying the wavefunctions of OH, a value of ε is taken at 0.5 Å which is default in DUO. One may use other values. As default, the value of δ_I in DUO is set to $\sim 10^{-8}$. Note, that this value is somewhat arbitrary and there does not appear to be an intuitive value one can take for δ_I . Also, the wavefunction densities $|\psi|^2(R)$ are not currently normalised automatically in DUO. It was found, numerically, that,

$$\int_{R_{\min}}^{R_c} |\psi(R)|^2 dR = \frac{1}{\rho_{\text{grid}}}, \quad (4.37)$$

where $\rho_{\text{grid}} = \frac{N_p}{R_c - R_{\min}}$, for a total number of grid points N_p . Even if the densities were normalised, however, the lack of physical intuition for δ_I remains. The question now is how can a reasonable value of δ_I be determined?

Before continuing further, it is important at this stage to suggest another method to categorize bound vs. unbound states. The potential energy curve, $V(R)$ becomes distorted at high rotational quanta, as the molecule becomes stretched. Hence, the effective equilibrium bond length for a given J increases. To account for this, one can use the effective potential form (Kozin et al., 1999),

$$V_{\text{eff}}(R) = V(R) + B(R)J(J+1), \quad (4.38)$$

where $B = \frac{h}{8\pi^2 c \mu R^2}$ in cm^{-1} , c is the speed of light, μ is the reduced mass of the molecule, and h is Planck’s constant. This rotational term increases the effective dissociation energy (here defined as the potential maximum to the right side of R_e), of the molecule, $\tilde{D}_e(J)$ ($\tilde{D}_e(0) = D_e$), and in cases where the reduced mass is low, such as in OH, this effect can be significant. In Figure 4.7, we see how as J increases, so does $\tilde{D}_e(J)$. Indeed, $T_e(J)$ is

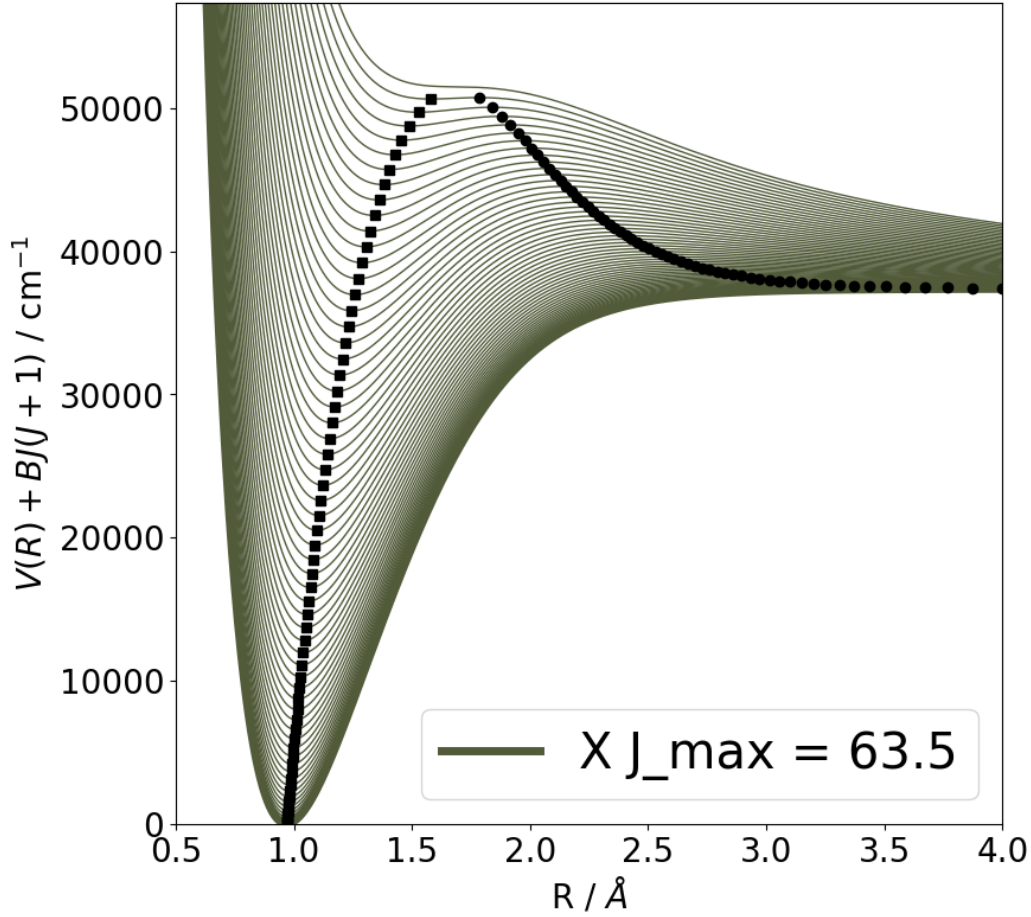


Figure 4.7: Effective potential energy curves of OH X $^2\Pi$ state for every J up to 63.5. Black dots indicate $\tilde{D}_e(J)$ at $\tilde{R}(J)$ and black squares indicate $T_e(J)$ at $R_e(J)$.

also increasing and the resulting effective potential energy curve becomes shallower. The position of the minimum, R_e is also shifted by the rotational perturbation and becomes a function of J . For higher J at long range, $\tilde{D}_e(J)$ is no longer asymptotic and instead occurs at a turning point at some $R = \tilde{R}(J)$, causing a barrier through which the wavefunction can tunnel. This tunnelling broadens the energy level, causing rotational predissociation which is discussed in more detail Chapter 5.

To this end, one can approximately assume that a state is bound for a given J if its energy falls between $T_e(J)$ and $\tilde{D}_e(J)$. While this makes some intuitive sense, this is a more crude approximation than the rigorous analysis of the wavefunctions. It is however, useful to compare this crude model to the results from the wavefunction in terms of efficacy in categorizing different state types.

We arrive at an appropriate value of δ_I , in part, by comparing these two models. We define two categories here, Type C, and Type W bound/unbound, corresponding to the effective, *centrifugal* potential approximation and *wavefunction* treatment respectively.

An energy level is Type C bound if its term value lies between $T_e(J)$ and $\tilde{D}_e(J)$ and is Type W bound if $\int_{R_c-\epsilon}^{R_c} |\psi^2(R)| dR < \delta_I$.

We also define three types of potential energy: *Unperturbed* ($V(R)$), *perturbed* ($V_{\text{eff}}(R;J)$, with a finite $\tilde{D}_e(J)$), and *repulsive* (No minima/maxima); in Figure 4.7, one can see that

the repulsive potential forms at $J \geq 63.5$.

The remaining criterion for the value of δ_I is that all states which are known to be bound experimentally, must be bound in the wavefunction treatment. In this case, this is found by calculating $\int_{R_c-\epsilon}^{R_c} |\psi^2(R)| dR$ for all states using the spectroscopic model from Section 4.3 and isolating the states which appear in the MARVEL dataset. This dataset is quite complete and goes up in energy up to D_e for the X $^2\Pi$, A $^2\Sigma^+$, and B $^2\Sigma^+$ states. Hence this is a good measurement for reasonable bound integral values.

Figure 4.8 shows that the majority of states with MARVEL energies stay below 10^{-8} . This supports the original value of the threshold integral. All the MARVEL levels presented in this figure have term values below the electronic state dissociation energy, D_e . The threshold value of 10^{-8} does not extend well for classifying bound states when levels with energy above D_e but below $\tilde{D}_e(J)$ (which are quasi-bound due to shape resonances) are considered.

Extending the plot to higher energies we notice that at some J there is a discontinuity in the integral where it suddenly rises, indicating that the region is transitioning from bound to unbound. We find evidence that this is the case when considering the $v = 0$ case of the A $^2\Sigma^+$ state. This vibrational level contains the most MARVEL levels and goes up to $J = 36.5$. At this J , the integral is of the order of 10^{-13} . When considering all levels that are calculable, at $J = 37.5$ the integral increases suddenly to 10^{-3} . A similar discontinuity occurs at $v = 1$.

We examine the full picture and look for discontinuities. Figure 4.9 shows that the majority of states pre-discontinuity appear below around 10^{-6} . This threshold allows for the inclusion of many borderline states, but does not include states which lie at $v = 10+$ for the A $^2\Sigma^+$ state, which have not been detected experimentally. The X $^2\Pi$ state is clearer in that the integral quite consistently increases from 10^{-20} to 10^{-3} .

It is clear that this method for determining a δ_I is very approximate. When producing a linelist, the aim is to have only bound states present in the .STATES and .TRANS file. When considering the A $^2\Sigma^+$ state, where the line between bound and unbound in the wavefunction treatment is not well defined, this is difficult to do. The decision was made that it is better to include too many states in the line list rather than too few, especially since states which are unbound are expected to have very low intensities so should not affect the spectrum simulation significantly. Such states are not excluded, however, and are instead treated as continuum transitions (see Section 4.5 for a brief summary and Chapter 6 for further details).

Energy levels are assigned tags to indicate whether they are bound or unbound. In the wavefunction treatment, states are assigned Type W bound or Type W unbound tags depending if their $\int_{R_c-\epsilon}^{R_c} |\psi^2(R)| dR$ is less than or greater than $\delta_I = 10^{-6}$ respectively. In the effective potential treatment, states are assigned Type C bound or Type C unbound tags if the term values are or are not between $[T_e(J), \tilde{D}_e(J)]$ respectively. Comparing the Type W and Type C tags shows that many states in the effective potential approximation which would be assigned as bound have been assigned as Type W unbound, see Table 4.11.

We see that approximately two thirds of A $^2\Sigma^+$ Type C bound states have been assigned Type W unbound status and similarly this happens to half of the X $^2\Pi$ state. Figure 4.10 shows an example of one such state in A $^2\Sigma^+$. It is clear that this is repulsive state as

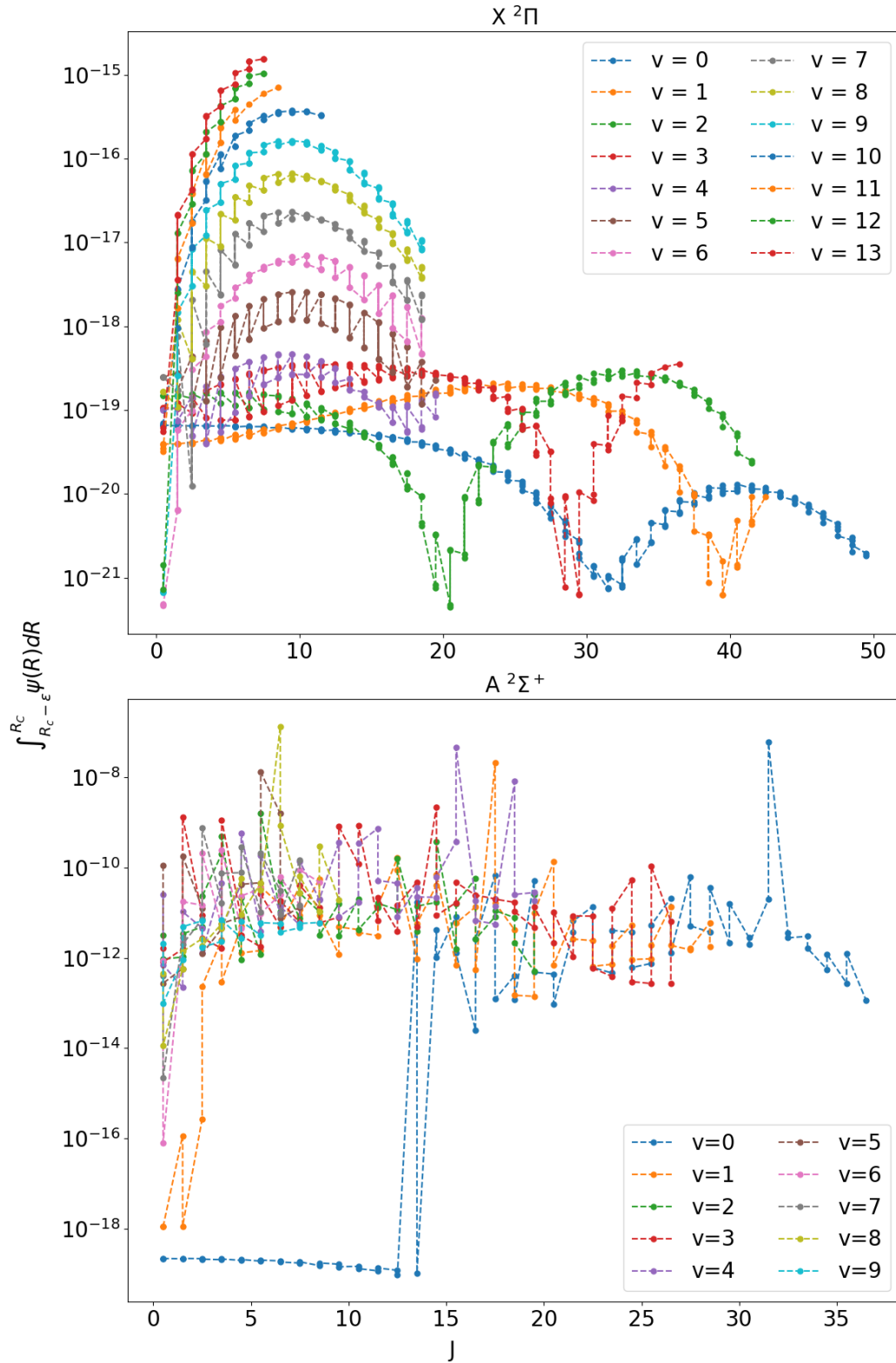


Figure 4.8: $\int_{R_c-\epsilon}^{R_c} \psi^2(R) dR$ for each MARVEL level of the $X^2\Pi$ and $A^2\Sigma^+$ states of OH.

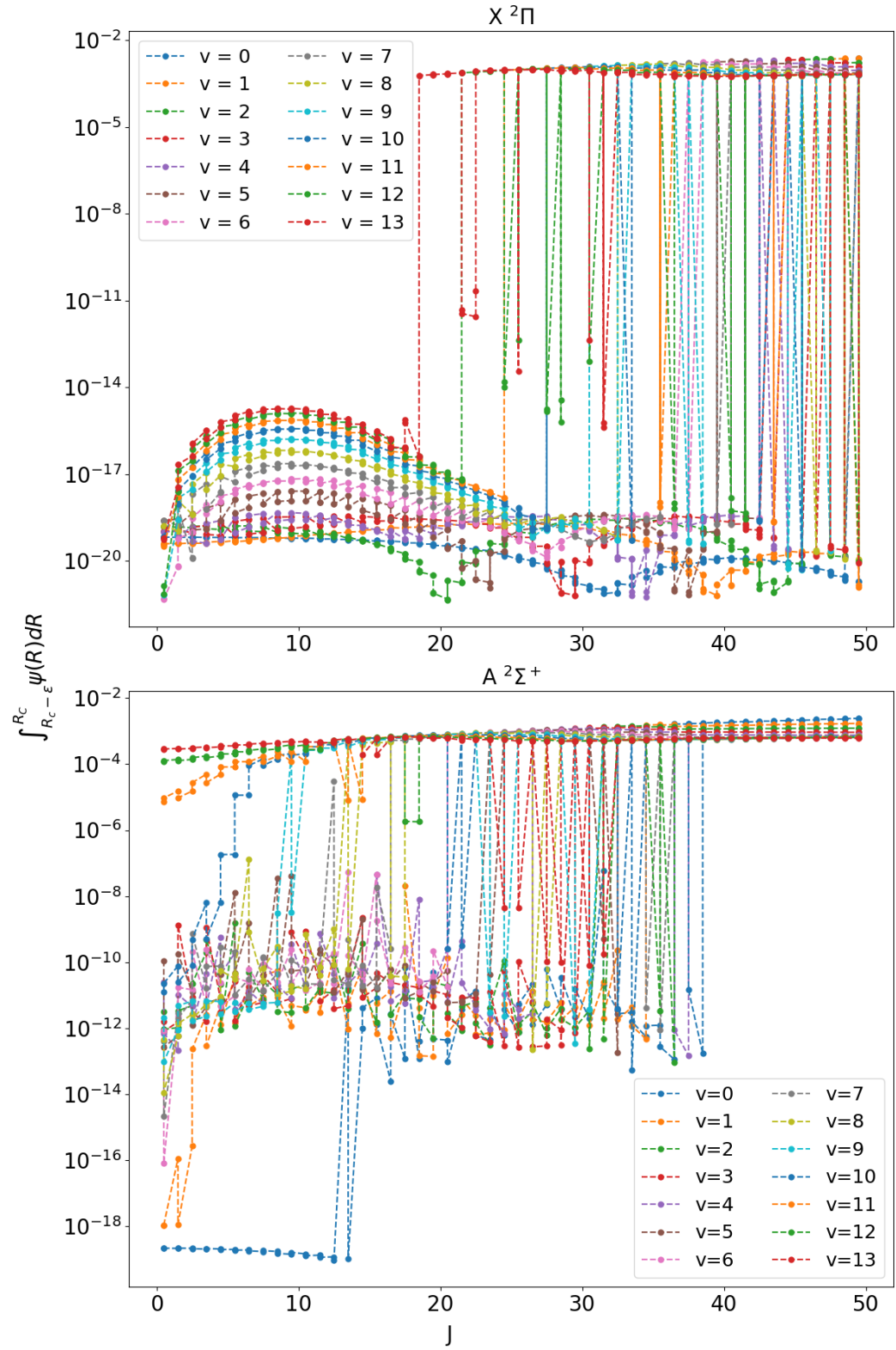


Figure 4.9: $\int_{R_c-\varepsilon}^{R_c} |\psi^2(R)| dR$ for each v, J of the $X\ ^2\Pi$ and $A\ ^2\Sigma^+$ states of OH.

Table 4.11: Tabulated comparison between Type C and Type W categorizations of bound vs. unbound states. Type C unbound states are states for which $T_e(J), \tilde{D}_e(J)$ are finite but $E > \tilde{D}_e(J)$, this is distinct from Repulsive, where in the effective potential approximation, all states are unbound as $T_e(J), \tilde{D}_e(J)$ are undefined. Dark states are states where $E < T_e(J)$ and are present likely due to misassignments in the manifold. Calculated with $\varepsilon = 0.5 \text{ \AA}$ and $\delta_I = 10^{-6}$.

Manifold	Type C	Count(Type W Unbound)	Count(Type W Bound)
X $^2\Pi$	Bound	2300	2250
	Unbound	17195	0
A $^2\Sigma^+$	Bound	968	547
	Dark	559	0
	Unbound	13268	0
	Repulsive	300	0
B $^2\Sigma^+$	Bound	156	59
	Dark	121	0
	Unbound	6383	3
	Repulsive	6443	0

Table 4.12: Tabulated comparison between Type C and Type W categorizations of bound vs. unbound states. Calculated with $\varepsilon = 0.5 \text{ \AA}$ and $\delta_I = 6.7 \times 10^{-4}$.

Manifold	Type C	Count(Type W Unbound)	Count(Type W Bound)
X $^2\Pi$	Bound	718	3832
	Unbound	222	16973
A $^2\Sigma^+$	Bound	229	1286
	Dark	116	443
	Unbound	93	13175
	Repulsive	16	284
B $^2\Sigma^+$	Bound	28	187
	Dark	62	59
	Unbound	103	6283
	Repulsive	307	6136

the amplitude of the wavefunction density is entirely to the right of the rotational barrier. This shows a limitation in considering only the energy in the categorization of bound and unbound rovibronic levels, as this level's energy is between $T_e(J)$ and $\tilde{D}_e(J)$.

Focusing specifically on the X $^2\Pi$ and A $^2\Sigma^+$ states for simplicity, the average integral for these states is $\sim 6.7 \times 10^{-4}$ and is distributed as in Figure 4.11.

Increasing the threshold to this average value is unfavourable as this allows for the majority of Type C unbound states to be categorized as Type W bound as can be seen in Table 4.12.

This also further highlights the inefficacy of the effective potential approximation as it has been applied here. Considering only the energy value of a given level ignores the details of what is now, effectively, a scattering problem.

At this point it is important to note that all but 12 of the 3154 energies with this opposite categorization are for cases where the energy of the level is greater than the unperturbed

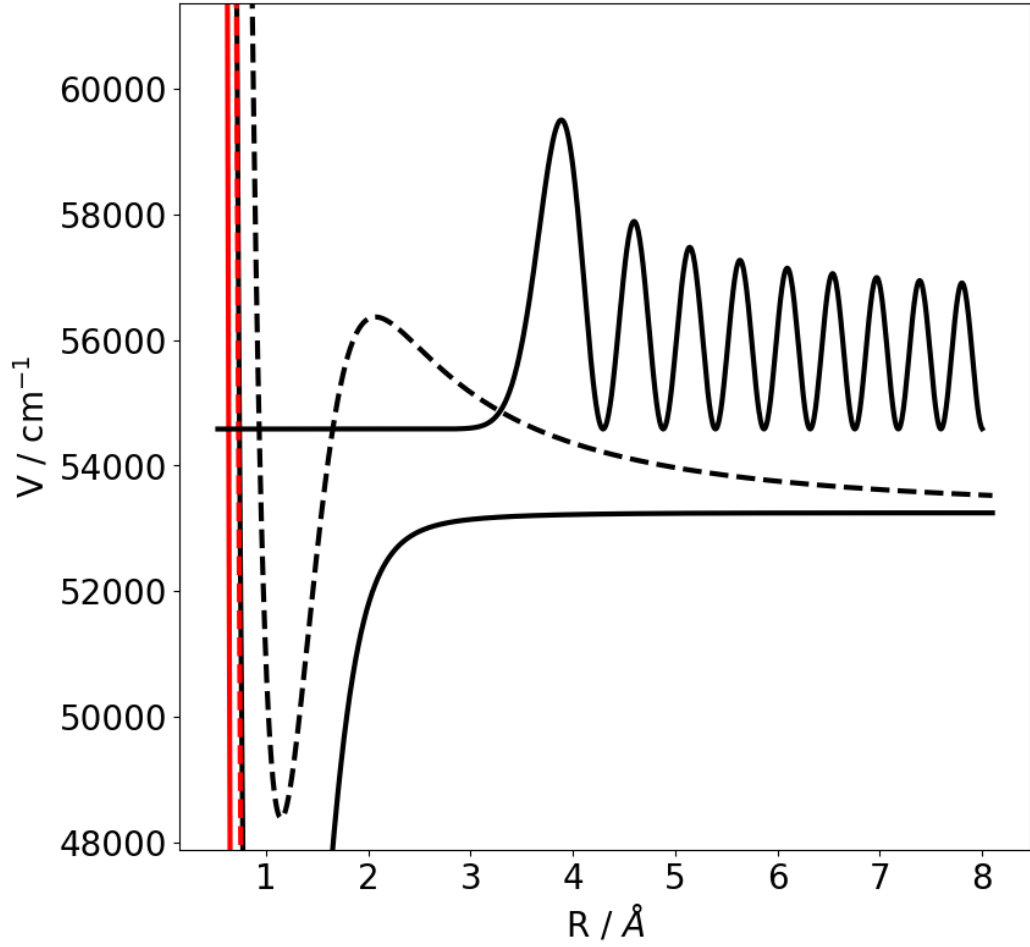


Figure 4.10: Example of a wavefunction where Type C is bound but Type W is unbound. The black lines are the effective and unperturbed PECs for the A $^2\Sigma^+$ state, and the red lines for the X $^2\Pi$ state. The wavefunction has been scaled for visibility and shifted to lie at the correct energy.

dissociation energy of the relevant PEC and none of these states have been observed experimentally as is corroborated in the discussion of Figure 4.8 earlier.

To conclude the analysis of this problem, it is necessary to consider the impact of the exclusion of these energy levels on the line list and integrated intensities of these lines. Intensity calculations are performed for $T = [300, 2000, 5000]$ K for all transitions where the final state types are:

- Subset 1 - $^1\sigma$: Type C bound + Type W unbound
- Subset 2 - $^2\sigma$: Type C bound + Type W bound

Intensities are calculated through the formalism from Yurchenko et al. (2018c):

$$I(f \leftarrow i) = \frac{g_f^{\text{tot}} A_{fi}}{8\pi c \nu_{fi}^2} \frac{e^{-c_2 E_i/T} (1 - e^{-c_2 \nu_{fi}/T})}{Q(T)}, \quad (4.39)$$

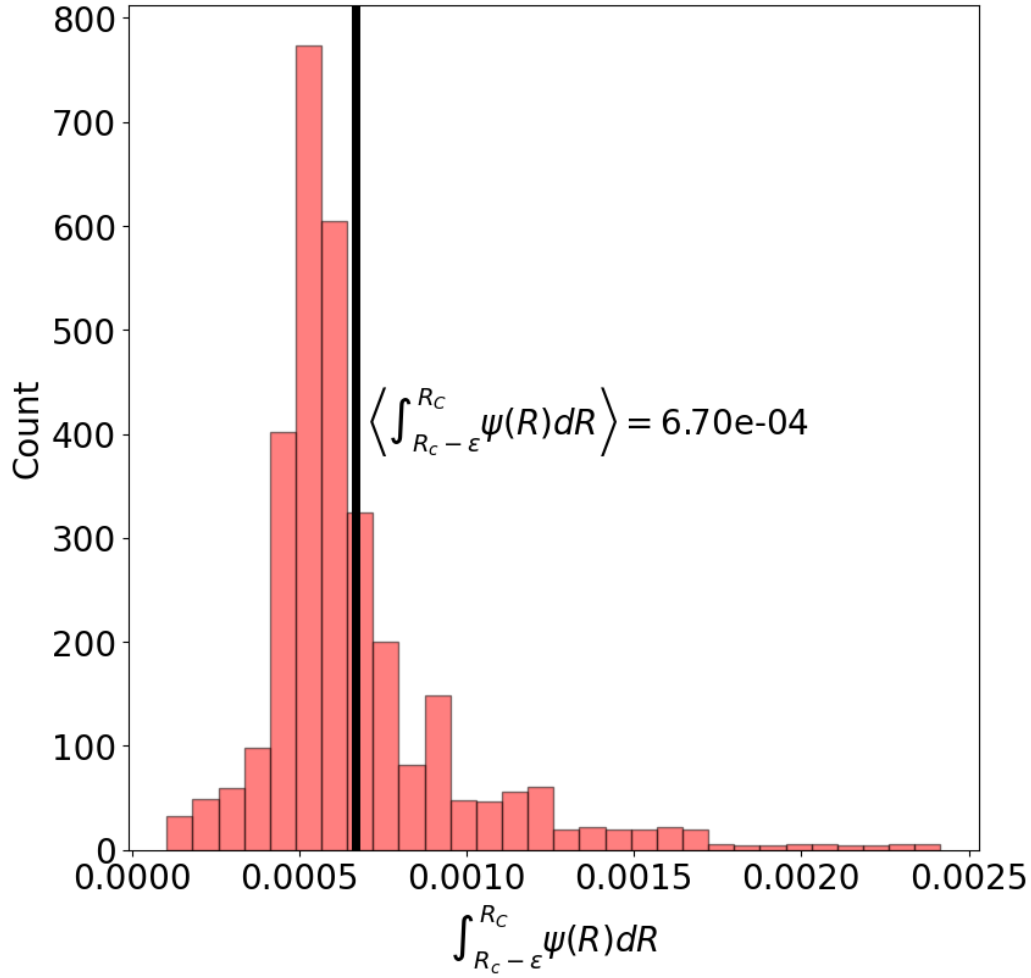


Figure 4.11: Distribution of $\int_{R_c-\epsilon}^{R_c} |\psi^2(R)| dR$ values for X $^2\Pi$ and A $^2\Sigma^+$ rovibronic levels where the Type C categorization is bound and Type W categorization is unbound.

where the partition function $Q(T)$ is defined as:

$$Q(T) = \sum_n g_n^{\text{tot}} e^{-c_2 E_n / T}, \quad (4.40)$$

where the total degeneracy, $g_n^{\text{tot}} = g_n^{ns} (2J_n + 1)$ for the nuclear-spin statistic g_n^{ns} . $c_2 = 1/k_b$ is the second radiation constant in cm K and T is the temperature in K.

The intensities for these two subsets are then summed and compared in Figure 4.12. It is visible that the intensity reduction by excluding these states from the line list, especially at lower temperatures is not significant, even considering that the majority of states are excluded. At 5000 K, less than 1 % of the integrated intensity is from these excluded states. It is unlikely that this is of importance. In light of this analysis, the threshold value has been chosen such that $\delta_I = 10^{-6}$ as this has been found to exclude all high energy unbound states while preserving intensity to the highest reasonable amount. Reiterating, these lines are not excluded in the simulation of the absorption cross-section, and are instead shifted to be part of the continuum analysis, meaning that none of this intensity, however small, will be neglected.

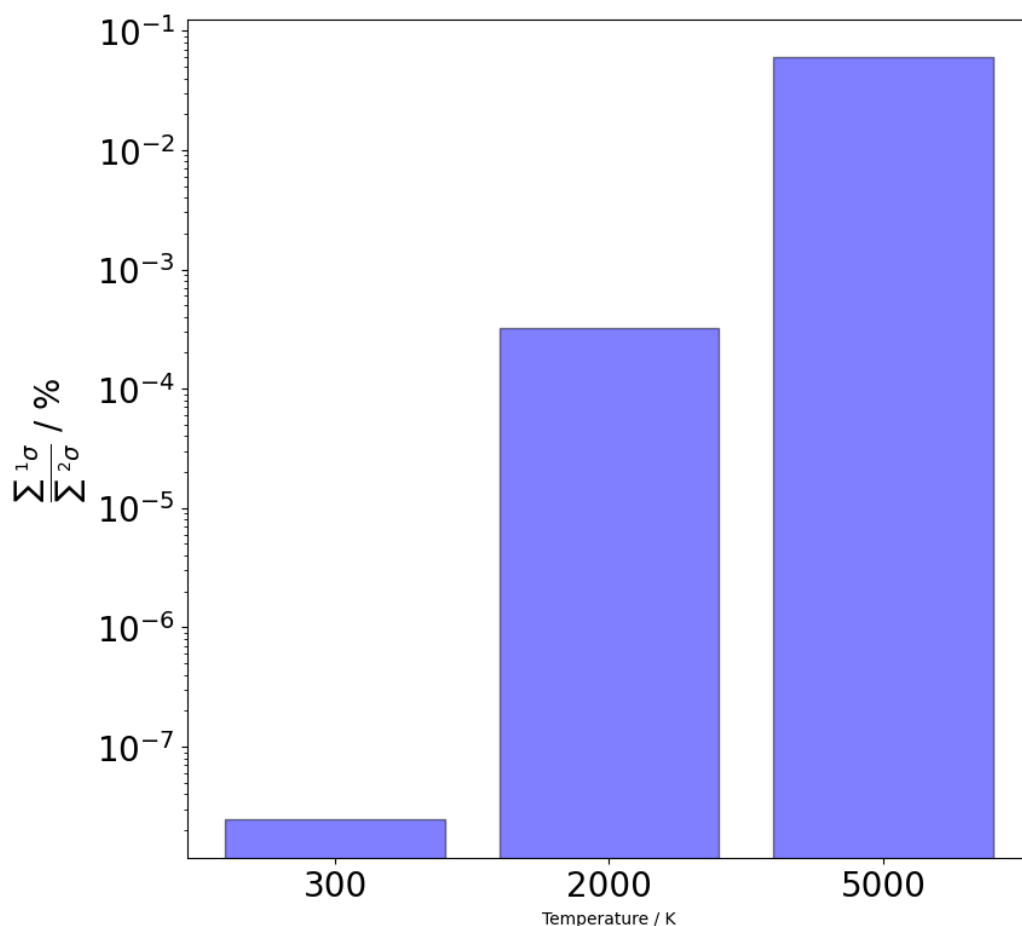


Figure 4.12: Ratio of summed intensities between subsets 1 and 2: $\frac{\sum 1\sigma}{\sum 2\sigma}$ calculated for $T = [300, 2000, 5000]K$.

Figure 4.13, separates the potential energy curve into three distinct regions. Region I covers the potential well, Region II covers the space between the right side of the well and R_c , and Region III covers the space above $\tilde{D}_e(J)$. As was stated above, the effective potential categorization is not a sufficient metric for determining if a state is bound or unbound, due to the presence of states in Region II. This introduces another element of uncertainty when considering the quantum number labelling. As discussed in Section 2.1.3, J and τ are the only rigorous labels applied. The rest are best estimates based on energy ordering and basis set contributions. The scheme in which the calculations for OH are performed is such that the vibrational quanta are counted in order of energy within the J, τ symmetry block. This is already not a perfect solution as discussed, but becomes even more problematic when considering these types of states. Vibrational quanta are counted, assigned to an electronic state, and then normalised to start at 0 for a given state. One can visualise the PEC in Region II, effectively as a repulsive PEC, $A^* {}^2\Sigma^+$. During the calculation, it is not easily differentiable whether a state belongs to $A {}^2\Sigma^+$ or $A^* {}^2\Sigma^+$. These repulsive states then have a meaningful effect on the vibrational labelling of the bound states, which results in bound states with abnormally high vibrational quanta labelled as bound. This is not a problem when simulating the spectrum, as these quantum numbers are not considered, only the rigorous quantum numbers from before along with their enumerator, n (see Section 2.1.3). This does mean, however, that when producing the line list, that the quantum labels must be considered unreliable for all levels with energy above D_e for a given electronic state.

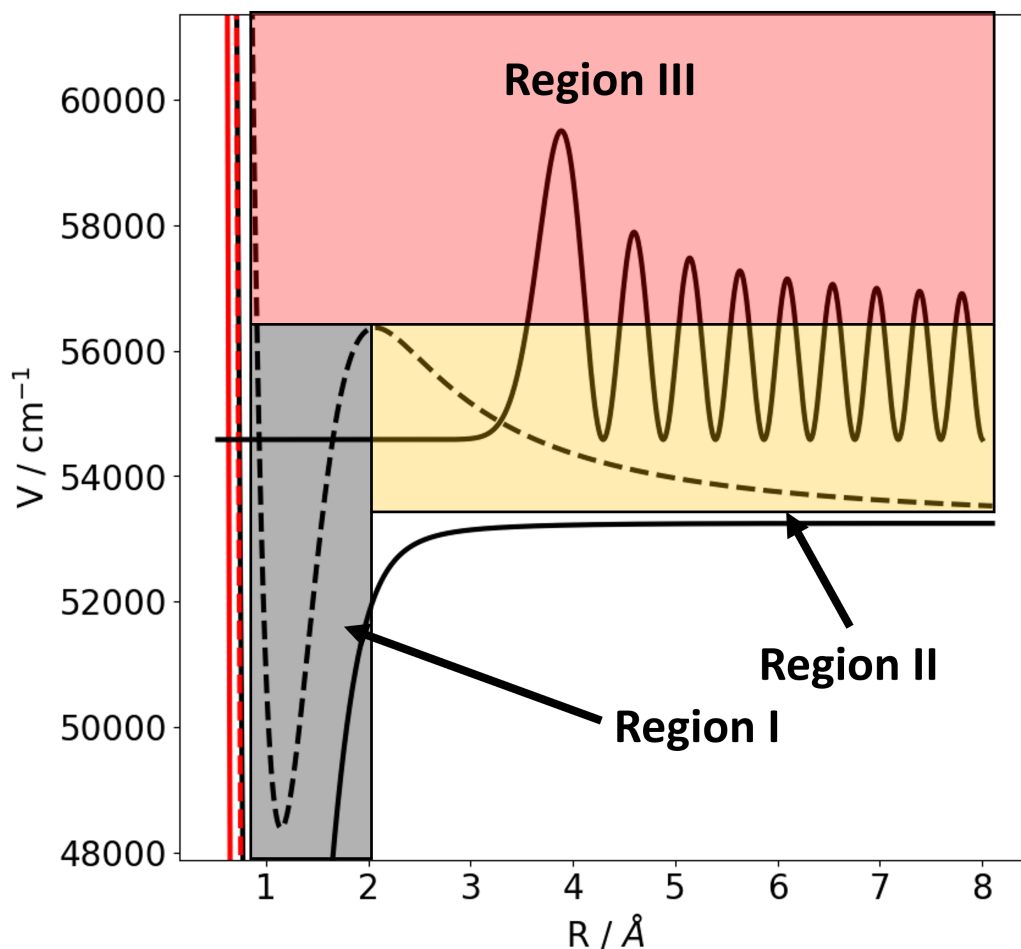


Figure 4.13: Example of a wavefunction where Type C is bound but Type W is unbound.

4.5 Simulation of Absorption Spectra

The simulation of the absorption spectrum has been done slightly differently for OH compared to NaO. While NaO's absorption spectra are computed with EXOCROSS, the spectra for OH use the new PYEXOCROSS program (Zhang et al., 2024b). Also, in OH, there is the added complexity of lifetime line broadening, and the inclusion of continuum absorption cross-sections in the photoabsorption spectrum. In order to be described fully, these cases need to be treated separately and with some care. With NaO, the model did not allow for the treatment of such effects, and so it was straightforward to produce cross-sections with a predetermined line profile. Furthermore, the NaO line list covers much lower frequencies, so such a treatment is likely unnecessary. This section will briefly cover the different treatments for predissociative states and continuum states but will not go deeply into the details of the physics, nor the methods of their computation, however a brief summary is provided here to introduce the topics.

As per Section 2.1.3, the boundary conditions impose discretized continuum spectra. Upon increase of R_c (end of the calculation box), one finds that continuum states with the same quantum numbers have lower energy. Bound electronic states with spin-orbit coupling to continuum states will hence also see their energy levels shift upon an increase of R_c due to a mutual perturbation between their bound rovibronic (which are in this regime quasi-bound) and the continuum rovibronic levels. These shifts in energy amount to resonances

between quasi-bound levels and continuum levels and the strength of the resonance can be quantified to produce resonance widths. From these we can arrive at the **predissociation lifetimes** (see Chapter 5 for more details). The resonance widths are used to inform the line broadening parameters for Bound-Quasibound transitions as is described in the following Section (specifically 4.5.1.2).

While this discretized continuum spectrum is useful in producing predissociation lifetimes, it is problematic when producing continuum absorption cross-sections. Such cross-sections are expected to be smooth and continuous due to the expected infinite density of states for repulsive electronic states. Chapter 6 post-processes these discretized spectra by applying a Gaussian smoothing procedure to redistribute intensity as to produce smooth **continuum absorption** spectra. This has the effect of redistributing intensity while maintaining the total integrated intensity as the leveraged Gaussian distribution is normalised. This allows for the calculation of accurate photodissociation rates while also giving physical cross-sections. These cross-sections are included in the full photoabsorption cross-section as per Section 4.5.3,

4.5.1 Line broadening

In this project, two types of broadening (Hartmann et al., 2008) have been treated explicitly, Doppler broadening and lifetime broadening, of which there are two sub-types, radiative, and predissociative. Pressure broadening effects also included automatically by PYEX-OCCROSS (see Zhang et al. (2024b) for details) and is defined modelled using a Lorentzian or Voigt line profile depending on whether the pressure is high or moderate (Yurchenko et al., 2018c). Doppler broadening is caused by the Brownian motion of particles in the gas phase. This is modelled using the Gaussian line profile.

The lifetime broadenings, both radiative (natural), and predissociative, arise from a shortening of the lifetime of the upper state due to, in essence, the Heisenberg uncertainty principle. In the case of radiative lifetime broadening, this is in relation to the radiative lifetime of the upper state; for predissociative line broadening, it is in relation to the predissociation lifetimes.

4.5.1.1 Doppler Broadening

Doppler broadening is a temperature-dependent effect which broadens absorption lines with a Gaussian line profile.

$$G(\nu; \sigma_D) = \frac{1}{\sigma_D \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{\nu - \nu_{fi}}{\sigma_D} \right)^2}, \quad (4.41)$$

where σ_D is the Doppler profile's standard deviation defined as,

$$\sigma_D = \frac{\Gamma_D}{2\sqrt{2\ln 2}}, \quad (4.42)$$

where Γ_D is the full-width at half-maximum (FWHM) calculated by,

$$\Gamma_D = \sqrt{\frac{8N_A k_B T \ln 2}{M}} \frac{v_{fi}}{c}. \quad (4.43)$$

Here, N_A is Avogadro's constant [mol^{-1}], k_B is the Boltzmann constant [erg K], T is the temperature [K], c is the speed of light [cm s^{-1}], M is the molar mass of the molecule [g mol^{-1}], and v_{fi} is the line position [cm^{-1}]. This broadening parameter is calculated for each line and each line is appropriately broadened using PYEXOCROSS (Zhang et al., 2024b).

4.5.1.2 Lifetime broadening

There are two lifetimes to consider in the case of OH; the radiative lifetime (natural lifetime), τ_{rad} and the predissociation lifetime, τ_{prediss} , (see Chapter 5). In each case the lifetime broadening is modeled using the Lorentzian (Cauchy-Lorentz) line profile,

$$L(\nu; \Gamma) = \frac{\frac{1}{\pi} \left(\frac{1}{2}\Gamma\right)}{(\nu - \nu_{fi})^2 + \left(\frac{1}{2}\Gamma\right)^2}, \quad (4.44)$$

where, Γ , is again, the FWHM which is calculated as,

$$\Gamma(f) = \frac{1}{2\pi c \tau(f)}, \quad (4.45)$$

where the f denotes that this is the lifetime of the upper state in the transition, τ is the lifetime in s, and c is the speed of light in cm s^{-1} . To account for the two sources of lifetime broadening, one sums their individual broadening parameters,

$$\Gamma_{\text{tot}} = \Gamma_{\text{rad}} + \Gamma_{\text{prediss}}. \quad (4.46)$$

Hence, as per Equation 4.45 we arrive at the total lifetime,

$$\tau_{\text{tot}} = \frac{\tau_{\text{rad}} + \tau_{\text{prediss}}}{\tau_{\text{rad}} \tau_{\text{prediss}}} \quad (4.47)$$

This value is stored in the .STATES file for OH and is then used in conjunction with Equation 4.45 in the PYEXOCROSS calculation for broadening. Chapter 5 details the calculation of the predissociation lifetime components in Equation 4.47. The radiative lifetime of an electronic state is related to the reduced sum of Einstein-A coefficients that pertain to that state:

$$\tau_{\text{rad}}(f) = \sum_i \frac{1}{A_{fi}}, \quad (4.48)$$

where τ_{rad} is the radiative lifetime of the upper/final state f and A_{fi} are its Einstein-A coefficients.

4.5.2 Voigt line profile

The full treatment to include broadening induced by Doppler, lifetime, and pressure effects necessitates the description of both the Gaussian and Lorentzian distributions. Doing this simultaneously requires the convolution of the two distributions, resulting in the Voigt line profile $V(x; \sigma_D, \Gamma_\tau)$.

$$V(x; \sigma_D, \Gamma_\tau) = \int_{-\infty}^{\infty} G(x'; \sigma_D) L(x - x'; \Gamma_\tau), \quad (4.49)$$

$$\lim_{\sigma_D \rightarrow 0} V(x; \sigma_D, \Gamma_\tau) = L(x - x'; \Gamma_\tau), \quad (4.50)$$

$$\lim_{\Gamma_\tau \rightarrow 0} V(x; \sigma_D, \Gamma_\tau) = G(x'; \sigma_D). \quad (4.51)$$

Indeed, in the limit where there is a clear dominance by one type of broadening, we can approximate the line to high fidelity using only the dominant distribution as shown in Eqs. 4.50 and 4.51. This line profile has no closed form solution and instead is related to the real part of the Faddeeva function, $w(z)$ as,

$$V(x; \sigma, \Gamma) = \frac{\Re(w(z))}{\sigma\sqrt{2\pi}}, \quad (4.52)$$

$$z = \frac{x + i\Gamma}{\sigma\sqrt{2}}. \quad (4.53)$$

One convolutes the intensity for a given line from Equation 4.39 by ensuring that the integral of the line profile P is equal to the intensity but since this distribution is normalised one can just multiply the line profile by the intensity to get the radiative cross-section of that line, σ .

$$\sigma = I(f, i) \times P. \quad (4.54)$$

4.5.3 Continuum absorption and Photoabsorption Spectra

Continuum absorption cross-sections are computed in this section as part of the temperature-dependent photoabsorption spectrum which is given in nm as opposed to cm^{-1} . This was first done in the AlHambra linelist for AlH Yurchenko et al. (2018b) and is replicated here. Direct continuum transitions going from $X \rightarrow R$ where $R \in$

$[1^2\Sigma^-, 1^2\Delta, A^2\Sigma^+, B^2\Sigma^+]$ is a repulsive electronic state. Note that for $R = A^2\Sigma^+, B^2\Sigma^+$, only the states which are Type W unbound (see Section 4.4) are considered in this calculation.

The photoabsorption cross-sections consist of appropriately broadened Bound-Bound / Bound-Quasibound (B2B) transitions and appropriately smoothed Bound-Repulsive (B2R) transitions (see Chapter 6).

Photoabsorption cross-sections are calculated for temperatures, T , in the range of 100 to $T_{\max}$ where $T_{\max}$ is defined as the highest temperature for which the partition function $Q(T)$ (Equation 4.40) is converged (see Section 4.6.2) in steps of 100 K.

The B2B and B2R cross-sections are computed and treated separately and then added to produce the final photoabsorption spectra.

4.6 Results

4.6.1 Spectroscopic model of OH

Fitting the hydroxyl radical turned out not to be straightforward. The $X^2\Pi$ and $A^2\Sigma^+$ electronic states are strongly coupled and mutually perturb each other. This makes fitting the states independently infeasible, and greatly increases the complexity in modelling. Furthermore, the $A^2\Sigma^+$ state is strongly perturbed by the local repulsive states $1^2\Sigma^-, 4^2\Sigma^-, 4^2\Pi$. The effects of these states are present in the experimental energy levels implicitly. Attempts were made to fit these perturbations using diagonal (in electronic state) constants like spin-rotation and the Born-Oppenheimer-Breaking radial property function (Le Roy & Huang, 2002; Yurchenko et al., 2016a), which allows for further refinement of rotational structure. However, this was not sufficient without the aforementioned coupling to the $X^2\Pi$ state while retaining sensible numbers for the magnitudes of the constants, and even with unphysical values in these constants, the energies were less accurate. Hence, the attempt to decouple the states somewhat was abandoned and it was determined that it does not warrant further study. As a result, it is suspected that the $\langle X|\hat{\xi}|A\rangle$ coupling term is somewhat overcompensating for the effects of the missing coupling to the continuum. A treatment of the continuum in a way which makes it possible to fit cases like the $A^2\Sigma^+$ state of OH is discussed in Section 5.3.7.

The $B^2\Sigma^+$ state presented different challenges, as it was found that this state could be treated independently from the lower lying electronic states. Despite this, compared to other line lists, the $B^2\Sigma^+$ state model has a lower level of accuracy. This is likely due to the energy levels having an apparent high level of sensitivity to the shape of the potential due to its shallow and narrow shape. Furthermore, modelling of the long-range proved to be difficult due to a limited understanding of the C_6 coefficients. At this stage multiple techniques were attempted to fit the model. Some time was spent developing a PYTHON wrapper for DUO, PYFIT, to leverage the advanced fitting algorithms readily available¹. Several attempts were made to use these algorithms to fit the whole model, including an 80,000 iteration run using the Dual-Annealing optimization algorithm built into the SCIPY² package (Xiang et al., 1997), however, this was not successful. The study of C_6 coefficients is outside of the remit of this thesis, and the importance of the $B^2\Sigma^+$ state is likely to be

¹PYFIT is available for download at github.com/GBMitev/pyfit

²SCIPY documentation is available at docs.scipy.org/doc/scipy/

Table 4.13: Root-mean square errors for each v , State in the MYTHOS model energies as compared to empirical energy levels from MARVEL dataset by [Furtenbacher et al. \(2022\)](#). Total RMS = 2.67370 cm^{-1} .

v	RMS(v)			
	X $^2\Pi$	A $^2\Sigma^+$	B $^2\Sigma^+$	C $^2\Sigma^+$
0	0.25837	0.13691	19.47553	0.42361
1	0.15237	0.16864	12.13049	0.52267
2	0.21468	1.06652		
3	0.12111	0.83290		
4	0.10389	0.65688		
5	0.07103	1.86516		
6	0.09688	2.87405		
7	0.14397	4.36275		
8	0.15329	1.99729		
9	0.28788	4.33298		
10	0.30826			
11	0.52650			
12	0.93193			
13	0.83994			
Total	0.27462	1.68878	16.59641	0.47572

very small due to the Franck-Condon region overlapping with the $v \geq 7$ vibrational state of X $^2\Pi$. Transitions to the B $^2\Sigma^+$ state are hence feasible only in extremely hot environments where populations in higher vibrational states are greater. Lastly, B $^2\Sigma^+$ exhibits a strong continuum absorption cross-section, and the relevant broadening here overshadows the bound-to-bound transitions, especially in hot environments.

The C $^2\Sigma^+$ state was, in comparison, straightforward to fit for two main reasons. The number of available data points is limited, so achieving a “good fit” is easier as complicated vibrational and rotational structures do not have a sufficient energy range to reveal themselves. Moreover, the available data points had a high level of uncertainty, so fitting was halted at a higher RMS that would otherwise be the case. The principle here is that if the fitting residuals are significantly smaller than the average uncertainty of the data points then the model is in all likelihood over-fitted and would have very poor extrapolation.

A visualisation of the fitting residuals is provided in Figure 4.14 and root-mean-square errors aggregated by vibrational quantum numbers are given in Table 4.13.

4.6.1.1 Constrained Parameters

In order to achieve physical results with a capacity for reliable extrapolation, certain quantities are fixed. The fixed parameters which have been described throughout the previous sections are tabulated in Table 4.14.

4.6.1.2 Potential energy and coupling curves

Refinement of the curves representing the coupled model of the four states, X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ in DUO was performed by floating the parameters, $R_e(X,A,B,C)$, $T_e(X,A,B,C)$, $\beta_i(X,A,B,C)$ (PECs) and B_k (spin-orbit and L-uncoupling curves)

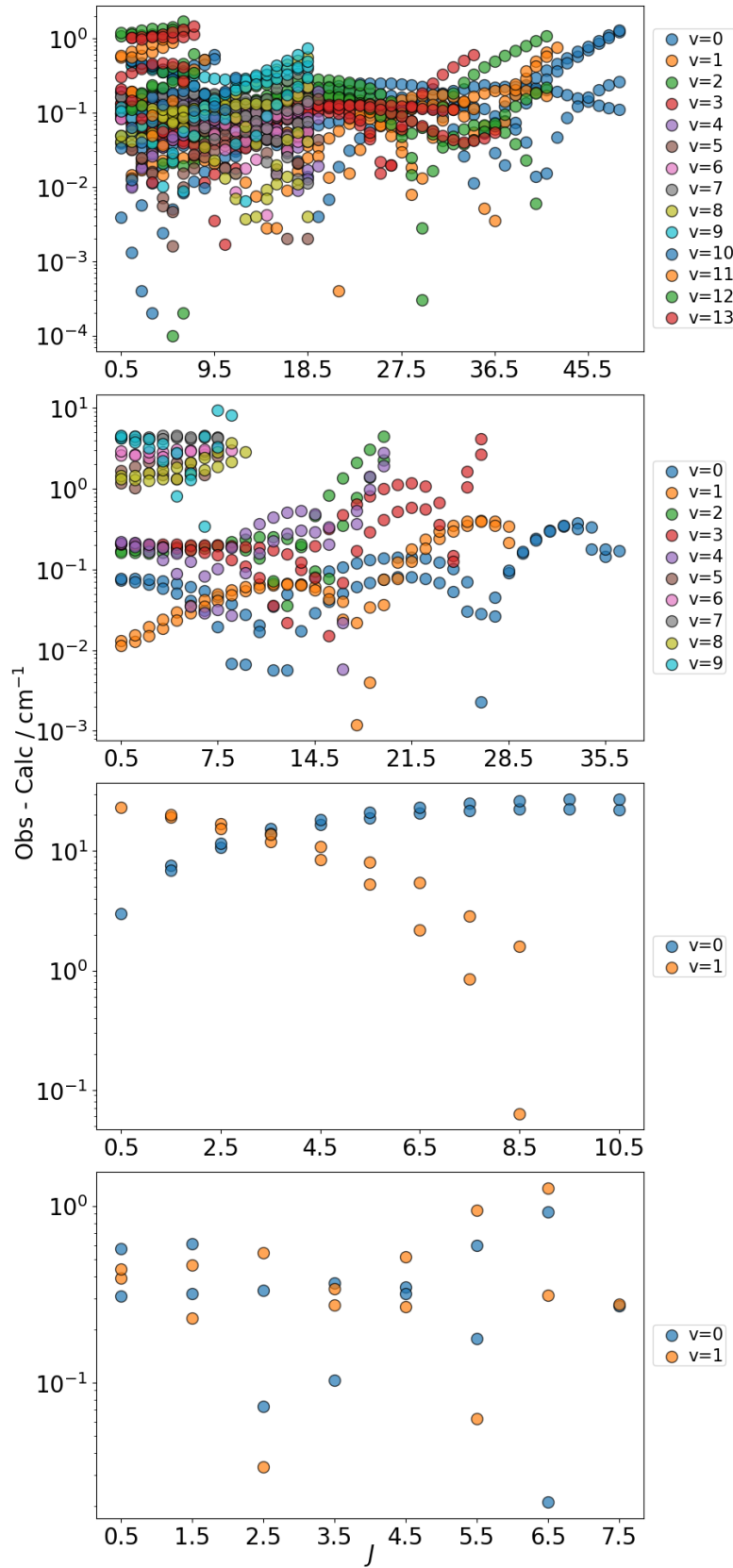


Figure 4.14: Fitting residual values for the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$ and C $^2\Sigma^+$ states of OH when compared against MARVEL energy levels from [Furtenbacher et al. \(2022\)](#).

Table 4.14: Fixed parameters for spectroscopic model of OH. Units: $[A_e] = \text{cm}^{-1}$, $[C_n] = \text{cm}^{-1} \text{\AA}^{-n}$.

State	Parameter	Value	Type
X $^2\Pi$	A_e	37377.215614	Semi-Empirical
A $^2\Sigma^+$	A_e	53245.077614	Semi-Empirical
B $^2\Sigma^+$	A_e	71169.803014	Semi-Empirical
	C_6	47686.640000	Theoretical ^a
C $^2\Sigma^+$	A_e	135271.377666	Empirical ^a
	C_1	116140.926280	Empirical ^a

^aSee section 4.3.3 for derivations.

Couplings to other electronic states have not been considered here for sake of simplicity in the model. Furthermore, couplings to the repulsive electronic states, 1 ($^2\Sigma^-$, $^2\Delta$, $^4\Sigma^-$, $^4\Pi$), have not been considered either, which are known to play a crucial role in the fine structure splitting of the ground state (Kozlov et al., 2024). The impact that coupling to the continuum has on the energy levels of the A $^2\Sigma^+$ state is explored in Section 5.5.3 where it is found that inclusion of these spin-orbit couplings can shift the energy levels by up to $\sim 10 \text{ cm}^{-1}$.

Along with the adjusted PECs and the *morphed* coupling curves, two more empirical, diagonal constants have been introduced to account for the aforementioned missing considerations (Tennyson et al., 2016a). These are the spin-rotation, $\gamma(X, A, B, C)$, and the Λ -doubling, $\alpha_{p2q}(X)$ and $q(X)$ (Brown et al., 1987). The inclusion of such factors was necessary to refine the energy level reproduction without the introduction of further electronic states or off-diagonal couplings. These factors have been seen in effective Hamiltonian treatments of these states (Coxon et al., 1991).

A polynomial function $C(R)$ has been used as the parametric representation for these empirical factors,

$$C(R) = \sum_{i=0} A_i (R - R_e)^i, \quad (4.55)$$

where A_i is the polynomial expansion coefficient. For all factors, $A_i = 0$ for $i \geq 1$, except for $\gamma(B)$, where A_1 has also been fitted due to the complex rotational structure.

In DUO, one can fit the spectroscopic model both against data sets of energy levels and of transitions. The process taken in this work was to fit against the experimentally derived MARVEL energy levels by Furtenbacher et al. (2022).

A summary of fitted parameters is available in Tables 4.15 and 4.16 and visualisations of the final PECs and morphed coupling curves are made available in Figures 4.15, 4.16, and 4.17.

4.6.1.3 Transition and permanent dipole moment curves

The *ab initio* permanent and transition dipole moments for the OH molecule are presented in Figures 4.18 and 4.19. The transition dipole moments are in good agreement with the available literature values from van der Loo & Groenenboom (2005); Yousefi et al. (2018); Langhoff et al. (1982); van Dishoeck et al. (1983); Brooke et al. (2016); Yarkony (1992)

Table 4.15: Summary of the PEC parameters obtained from least squares fitting the X $^2\Pi$, A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ states of OH to MARVEL energy levels from [Furtenbacher et al. \(2022\)](#) in Duo ([Yurchenko et al., 2016a](#)). All the figures are kept for the sake of preserving accuracy and reproducibility.

		EMO	
Parameter	Units	X $^2\Pi$	A $^2\Sigma^+$
T_e	cm^{-1}	0	32664.0787475633
R_e	$\text{\AA}$	0.96980955252619	1.01227279150395
A_e	cm^{-1}	37377.2156140000	53245.0776140000
PL		4	3
PR		3	3
N_L		6	4
N_R		9	8
β_0	$\text{\AA}^{-1}$	2.29114763515499	2.63267869514865
β_1	$\text{\AA}^{-1}$	-0.00752718263809	0.14810142856264
β_2	$\text{\AA}^{-1}$	0.14648108707352	0.30397704416271
β_3	$\text{\AA}^{-1}$	-0.03978705095141	0.76035976404173
β_4	$\text{\AA}^{-1}$	0.20728393915919	1.42883481603977
β_5	$\text{\AA}^{-1}$	1.63907964222671	-5.63390009269025
β_6	$\text{\AA}^{-1}$	1.89971668669960	-1.11159937530779
β_7	$\text{\AA}^{-1}$	-17.69236906412280	25.39105709283100
β_8	$\text{\AA}^{-1}$	28.03677681912920	-22.13134352625050
β_9	$\text{\AA}^{-1}$	-13.33391470046090	
		MLR	
Parameter		B $^2\Sigma^+$	C $^2\Sigma^+$
T_e	cm^{-1}	69794.8138036000	89441.3285886000
R_e	$\text{\AA}$	1.86270304000000	2.03580048967547
A_e	cm^{-1}	71169.8030140000	135271.3776661260
p		2	2
β_0	$\text{\AA}^{-1}$	-0.65693572301821	0.39005685999852
β_1	$\text{\AA}^{-1}$	6.32093459267704	
β_2	$\text{\AA}^{-1}$	9.99999999998589	
β_3	$\text{\AA}^{-1}$	6.52266741818112	
C_0	cm^{-1}		
C_1	$\text{cm}^{-1}\text{\AA}$		116140.9262795
C_2	$\text{cm}^{-1}\text{\AA}^2$		
C_3	$\text{cm}^{-1}\text{\AA}^3$		
C_4	$\text{cm}^{-1}\text{\AA}^4$		
C_5	$\text{cm}^{-1}\text{\AA}^5$		
C_6	$\text{cm}^{-1}\text{\AA}^6$	47686.64	

Table 4.16: Summary of the *morphing* and empirical parameters obtained from least squares fitting the $X^2\Pi$, $A^2\Sigma^+$, $B^2\Sigma^+$, and $C^2\Sigma^+$ states of OH to MARVEL energy levels and transitions from [Furtenbacher et al. \(2022\)](#) in Duo [Yurchenko et al. \(2016a\)](#).

Parameter ^a	Curve		
	$\langle X^2\Pi \hat{H}_{SO} X^2\Pi \rangle$	$\langle X^2\Pi \hat{H}_{SO} A^2\Sigma^+ \rangle$	$\langle X^2\Pi \hat{L}_x A^2\Sigma^+ \rangle$
R_e	0.97065503463788	0.97065503463788	0.97044438749810
β	0.8	0.8	0.8
γ	0.02	0.02	0.02
p	6	6	2
B_0	1.00712138450024	0.96550172058320	0.98872259326879
B_1	0	0.17125561235784	-0.06366509311814
B_2	0.20646896201794		
B_∞	1	1	1
Parameter ^b			
Curve	A_0	A_1	R_e
$\gamma(X)$	0.00001761088251		
$\gamma(A)$	0.00857815595162		
$\alpha_{p2q}(X)$	-0.01231377184945		
$q(X)$	0.00012124819881		
$\gamma(B)$	10.74842994562280	-6.27942731658091	1.82291255925743
$\gamma(C)$	1.01998967064829		

^aParameters here are in relation to the those which describe the morphing function from Equation 4.20.

^bParameters here are in relation to those which describe the polynomial function from Equation 4.55

and a comparison is available in Figure 4.20. Earlier in the text, it was stated that $C^2\Sigma^+$ is ionic at long range. This is confirmed by its permanent dipole moment from Figure 4.18 which, at long range, scales linearly with R .

The dipoles presented in these figures are *ab initio* and are used as such in the DUO input file for the calculation of Einstein-A coefficients. In the nuclear motion calculation, the ground state permanent dipole was originally represented in the form of 28 grid points between ~ 0.53 and ~ 5.3 Å. The DUO defined grid is significantly more dense, with 1001 points between 0.53 and 8 Å. Values between the input grid points are found by interpolation using cubic splines in DUO.

X-X transition intensities are expected to be negatively correlated with vibrational excitations and there is some proportionality such that,

$$\log_{10} I(\Delta_v) = -K_v \Delta_v, \quad (4.56)$$

where $\Delta_v = v_f - v_i$, I is the intensity, and K is some constant of proportionality. It was found by [Medvedev et al. \(2016\)](#) that at high Δ_v , this relationship can be broken resulting in an unphysical flattening, and even an increase of the intensity. They identify that the primary culprit in this situation is the numerical noise added by the aforementioned interpolation. Hence, the representation of the dipole is an important aspect in physical modelling. The method suggested in this work is to represent the dipole not as grid points, and instead to

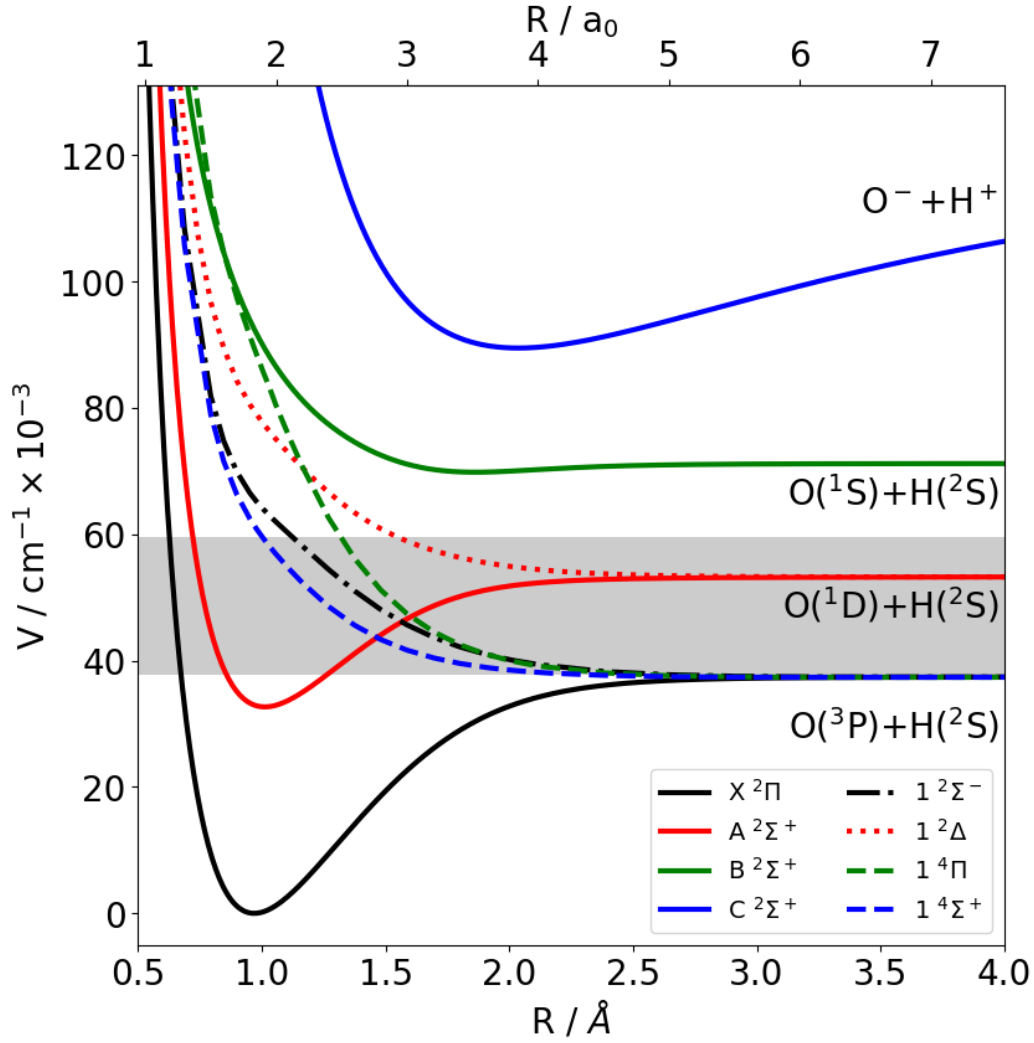


Figure 4.15: PECs used in spectroscopic model of OH. Solid lines: B2B linelist, Dashed lines: Predissociative broadening only, Dotted lines: Continuum absorption only, Dotted+Dashed: Continuum absorption + Predissociative broadening. The area in grey contains all $A\ ^2\Sigma^+$ rovibronic levels with predissociative broadening.

find an analytic representation. [Medvedev & Ushakov \(2022\)](#) suggested the *irregular DMC* form as in Equation 4.57 which is fitted to the *ab initio* grid points to produce an analytical representation of the *ab initio* dipole moment.

$$D(R) = \chi(R; c_2, \dots, c_6) \sum_{i=0}^6 b_i T_i(z(R)), \quad (4.57)$$

$$\chi(R; c_2, \dots, c_6) = \frac{(1 - e^{-c_2 R})^3}{\sqrt{(R^2 - c_3^2)^2 + c_4^2} \sqrt{(R^2 - c_5^2)^2 + c_6^2}}, \quad (4.58)$$

$$z(R) = 1 - 2e^{-c_1 R}, \quad (4.59)$$

where T_i are the Chebyshev polynomials of the first kind, and b_i and c_i are variable param-

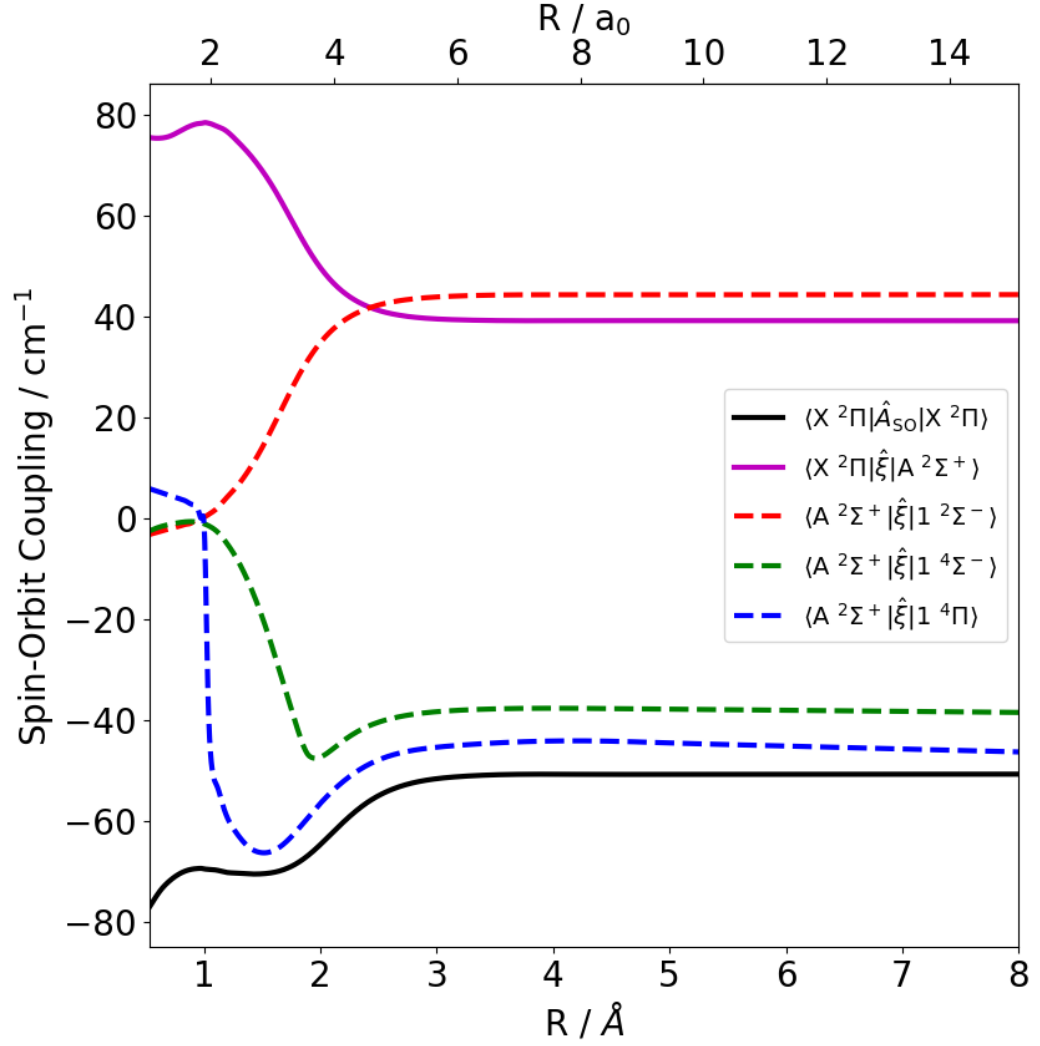


Figure 4.16: Spin-orbit couplings used in spectroscopic model of OH. Solid lines: B2B linelist, Dashed lines: Predissociative broadening only.

eters. This form was successfully used by [Brady et al. \(2023\)](#) to produce such a representation for the ground state permanent dipole of SO. [Medvedev et al. \(2024\)](#) found that the intensities past $\Delta_v \geq 6$ from [Brooke et al. \(2016\)](#) are unreliable due to the aforementioned intensity flattening. To test this, intensities are calculated using the original grid point representation from this work, the grid point representation from [Brooke et al. \(2016\)](#), and analytic representations of both curves, which are then examined. Figure 4.21 presents the grid point and analytic representations of these dipoles and their fit residuals.

Intensities are then computed and plotted in chunks covering a single Δ_v , the maximum of each subset is then found and Equation 4.56 is fit to these points. The resulting R^2 value (Equation) is measured by fitting between $v = 0$ and $v = 12$:

$$R^2 = 1 - \frac{\sum_i \left(\hat{\mu}_i^{\text{grid}} - \hat{\mu}_i^{\text{fitted}} \right)^2}{\sum_i \left(\hat{\mu}_i^{\text{grid}} - \langle \hat{\mu}_i^{\text{grid}} \rangle \right)^2}. \quad (4.60)$$

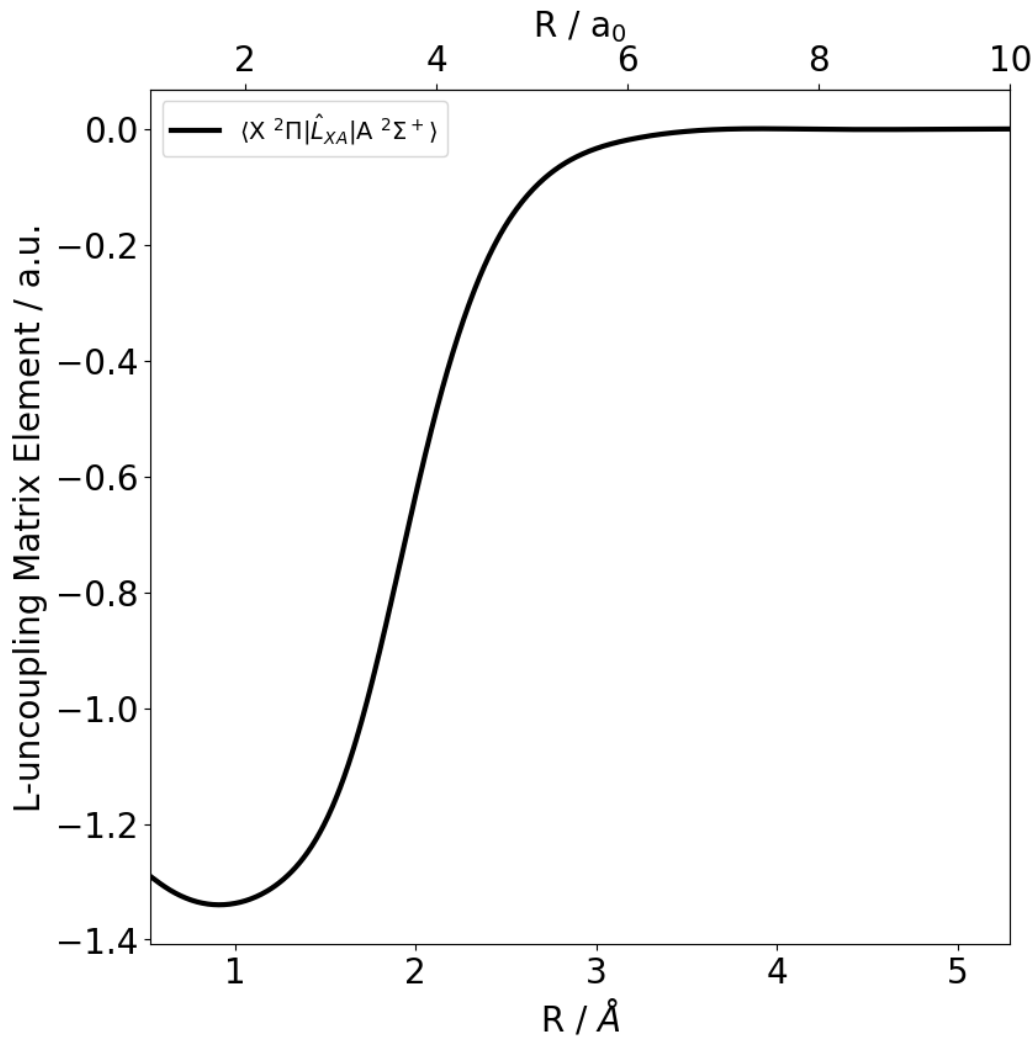


Figure 4.17: L-uncoupling curve used in spectroscopic model of OH.

From Figure 4.22, it appears that the dipole from Brooke et al. (2016) is not appropriate for modelling transitions with $\Delta_v > 7 \rightarrow 9$, returning a similar conclusion to that of Medvedev et al. (2024). The grid point representation returns unphysical intensities at $\Delta_v = 9$. Fitting the dipole returns an unphysical intensity at $\Delta_v = 7$, however, which is unexpected. Fitting an analytic representation of the dipole is challenging, and the best fit for this dipole returned an RMS of order 10^{-4} . This is likely an insufficient accuracy for modelling these intensities. The *ab initio* dipole from this work returned better results, with intensities obeying Equation 4.56 up to $\Delta_v = 11$ for the grid point representation and $\Delta_v = 12$ for the analytic representation, with a fit RMS of order 10^{-5} . In this work, the fitted *ab initio* dipole was hence chosen to model the intensities.

Recently, Chang et al. (2023) measured experimental line intensities for the P-branch rovibrational transitions in $X^2\Pi$ for the $v'' \rightarrow v' = 0 \rightarrow 1$ vibrational band, reporting that the intensities of the HITRAN line list are ~ 1.4 times stronger than their measured intensities. These transition intensities were compared with the corresponding calculated intensities and it was found that agreement with HITRAN is conserved within uncertainty. The HITRAN intensity uncertainties for OH are all $\geq 10\%$, and an average of $\sim 5\%$ difference is found between the MYTHOS and HITRAN intensities is found, with all lines agreeing

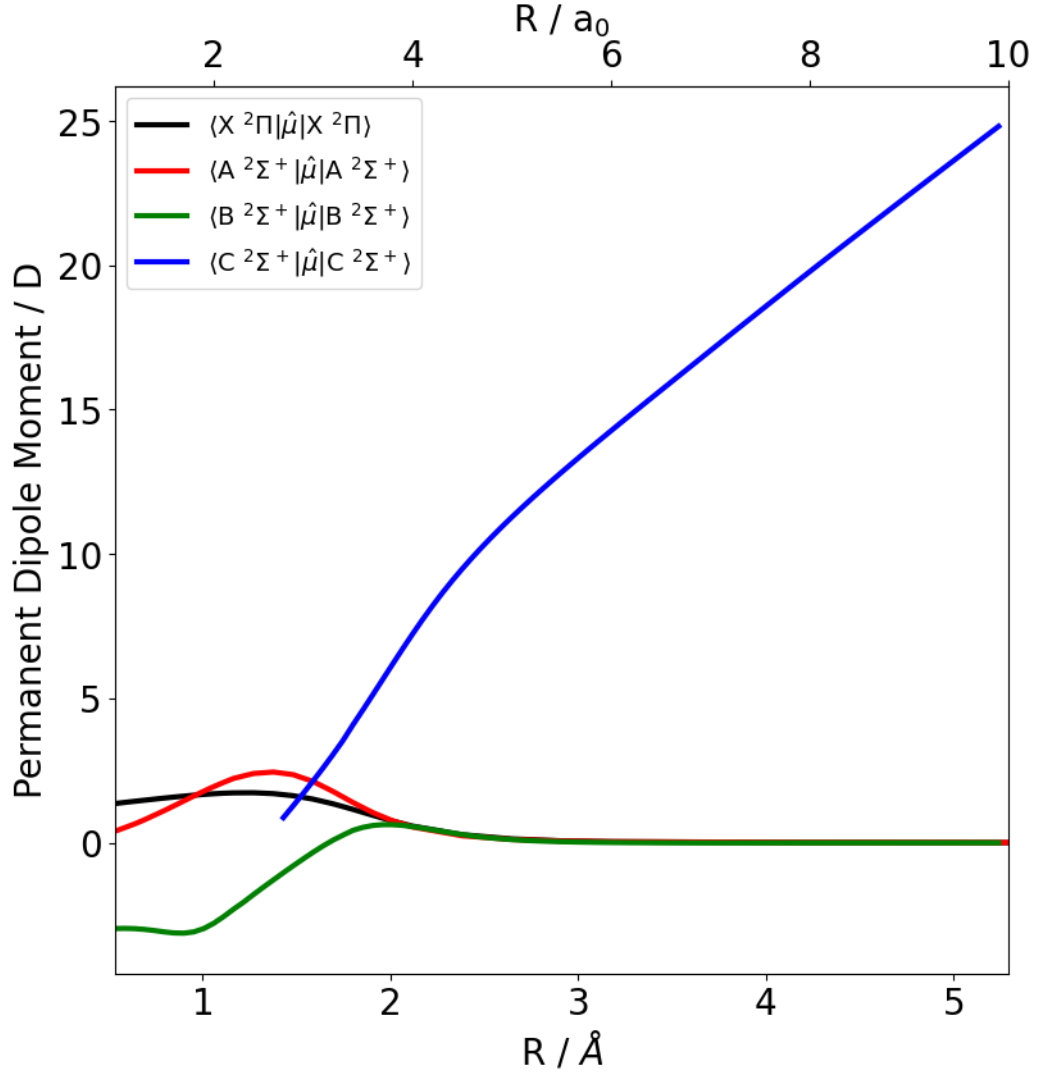


Figure 4.18: Permanent dipole moment curves used in spectroscopic model of OH. These are *ab initio*, and are taken directly from MOLPRO.

within uncertainty. Disagreement is found between MYTHOS and the measured lines, with our intensities being around 40% higher.

Table 4.17 summarises these findings and presents percentage differences between the MYTHOS intensities and those of HITRAN and the experiment. While these results are troubling, this does not provide sufficient evidence to scale the current dipoles in the model as the measured values only cover a narrow slice in J and v . Furthermore, they only consider one branch of transitions. It is not known if such a trend should continue upon the inclusion of further rovibrational transitions, and so, for the time being, the model is left as is.

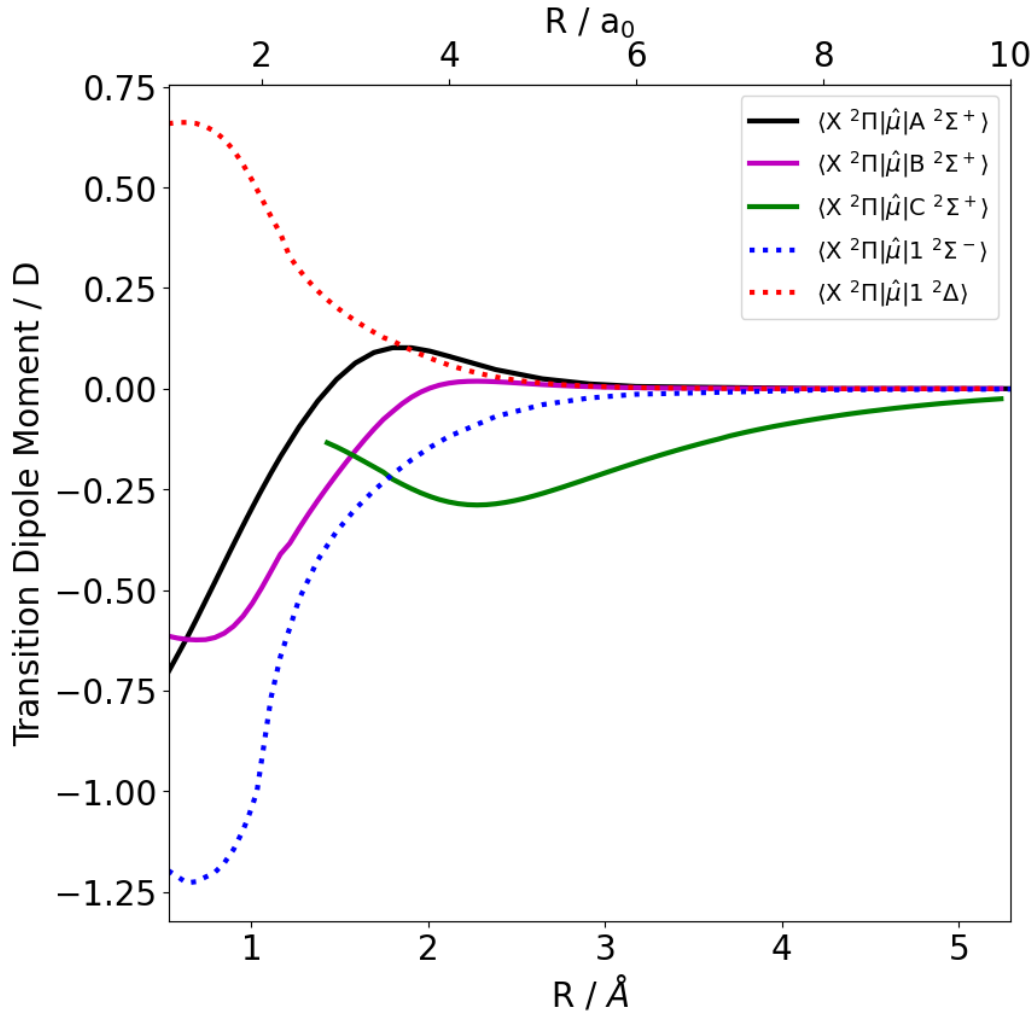


Figure 4.19: Transition dipole moment curves used in spectroscopic model of OH. These are *ab initio*, and are taken directly from MOLPRO, x-component only. Solid lines: B2B linelist, Dotted lines: Continuum absorption Only

4.6.2 Partition function

The temperature-dependent partition function for OH was calculated as the sum from Equation 4.40. For convenience the equation is rewritten below,

$$Q(T) = \sum_n g_n^{\text{tot}} e^{-c_2 E_n / T}.$$

As $Q(T)$ sums over J , the value of $Q(T)$ at some T depends on the value of J_{max} . To ensure completeness of the line list, it is a requirement that, up to a given temperature (in the case of this line list, 8000 K) the value of $Q(T = 8000)$ converges with J_{max} .

In order to test this convergence against J_{max} one can study how the value J_{max} impacts the value of $Q(T)$. Defining $Q(T; J_{\text{max}})$,

$$Q(T; J_{\text{max}}) = \sum_n g_n^{\text{ns}} (2J_n + 1) e^{-c_2 E_n / T} \text{ for } J_n \leq J_{\text{max}}, \quad (4.61)$$

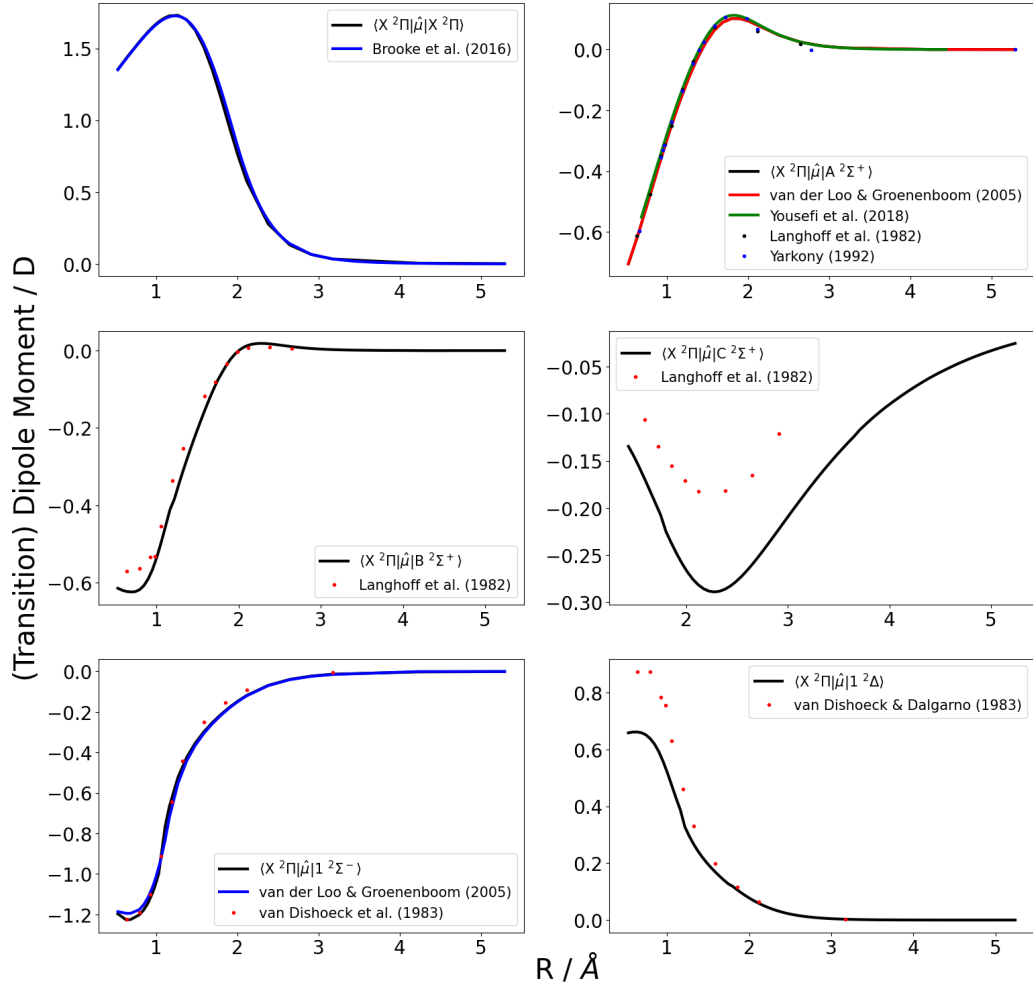


Figure 4.20: Comparison of *ab initio* (T)DMCs from this work (black) and those from (Brooke et al., 2016; van der Loo & Groenenboom, 2005; Yousefi et al., 2018; Langhoff et al., 1982; van Dishoeck et al., 1983; van Dishoeck & Dalgarno, 1983).

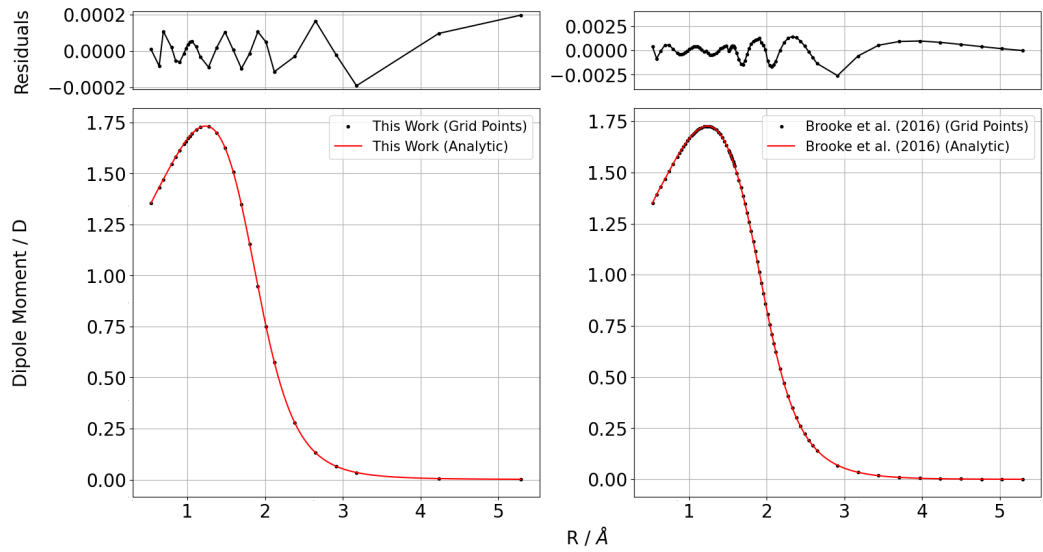


Figure 4.21: Grid point and analytic representations of the X-X permanent dipole moment of OH. Left: This work, Right: Brooke et al. (2016).

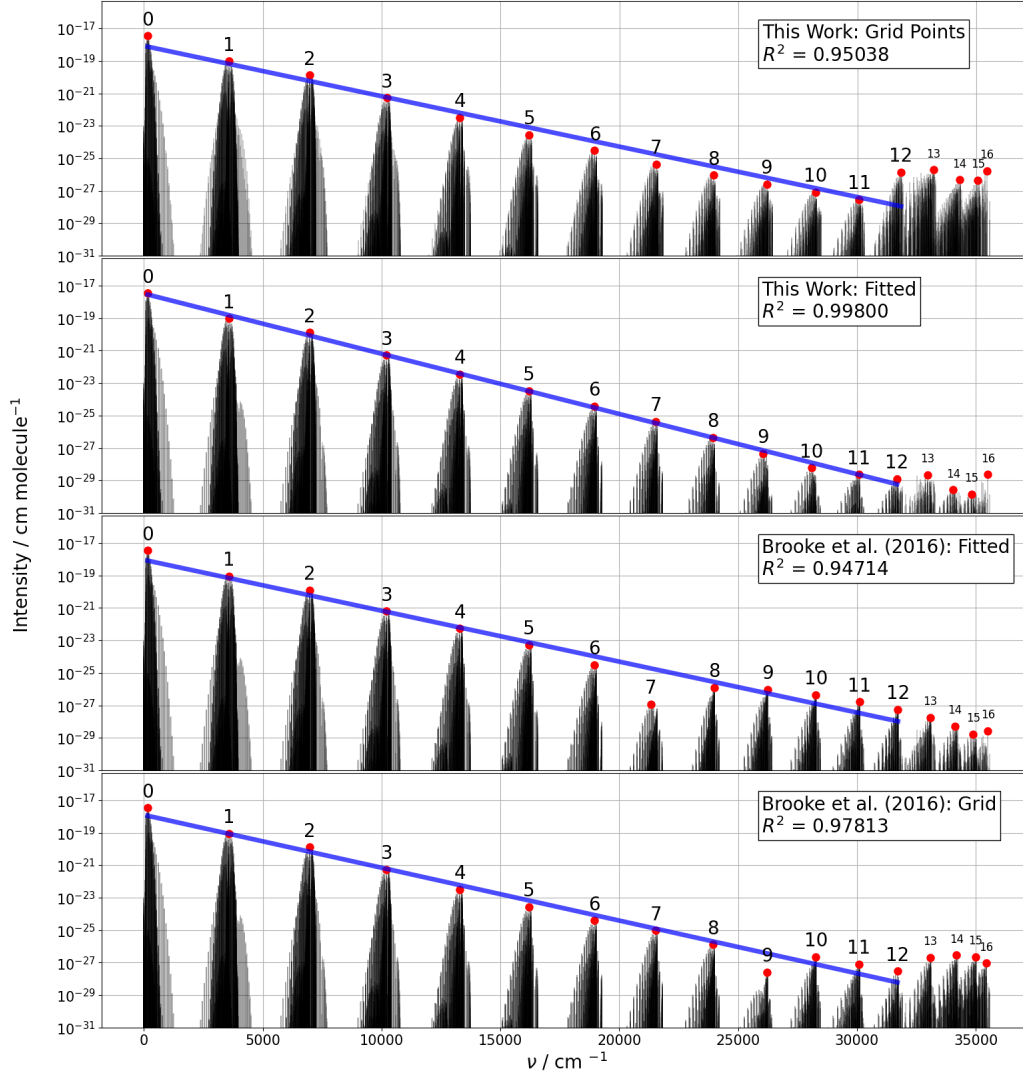


Figure 4.22: Hydroxyl ground-to-ground transitions with different representation of the ground state permanent dipole. Dipoles from sec: 4.2 and Brooke et al. (2016). Numbers represent Δ_v . Red dots are maxima for given Δ_v . Blue line is a fitted through points with $\Delta_v \leq 12$.

so that the difference,

$$D_Q(T, J_{\max}) = Q(T; J_{\max}) - Q(T; J_{\max} - 1). \quad (4.62)$$

In this study, the rotational basis is set to a maximum $J_{\max} = 49.5$. An estimate for the convergence, Δ_Q is hence given by,

$$\Delta_Q(T) = 1 - \frac{D_Q(T, J_{\max})}{Q(T; J_{\max} - 1)}. \quad (4.63)$$

A visualisation of this is presented in Figure 4.23, where it is clear that up to 10,000 K,

Table 4.17: Comparison between calculated (MYTHOS) line intensities in the X $^2\Pi$ state $v'' \rightarrow v'' = 0 \rightarrow 1$ vibrational band and their HITRAN (Gordon et al., 2022) and measured (Chang et al., 2023) counterparts. Percentage differences are calculated as $\Delta = (I_{\text{MYTHOS}} - I_{\text{Reference}}) / (I_{\text{Reference}}) \times 100$. $\langle \Delta \rangle$ is the average percentage difference.

Quantum Numbers			Line Intensities / cm molecule $^{-1} \times 10^{-20}$			$\Delta / \%$	
Branch	J''	e/f''	MYTHOS	HITRAN	Measured	HITRAN	Measured
P	2.5	e	5.93	5.60	4.15	5.85%	42.84%
P	2.5	e	3.29	3.14	2.41	4.86%	36.62%
P	2.5	f	5.86	5.59	4.15	4.78%	41.13%
P	2.5	f	3.30	3.14	2.41	5.11%	36.94%
P	3.5	f	2.69	2.54	1.91	5.94%	40.89%
P	3.5	e	2.66	2.55	1.91	4.38%	39.36%
P	4.5	e	4.89	4.56	3.38	7.14%	44.55%
P	4.5	e	1.60	1.54	1.09	4.09%	47.07%
P	4.5	f	4.74	4.54	3.38	4.37%	40.19%
P	4.5	f	1.63	1.54	1.09	6.16%	49.98%
$\langle \Delta \rangle$						5.27%	41.96%

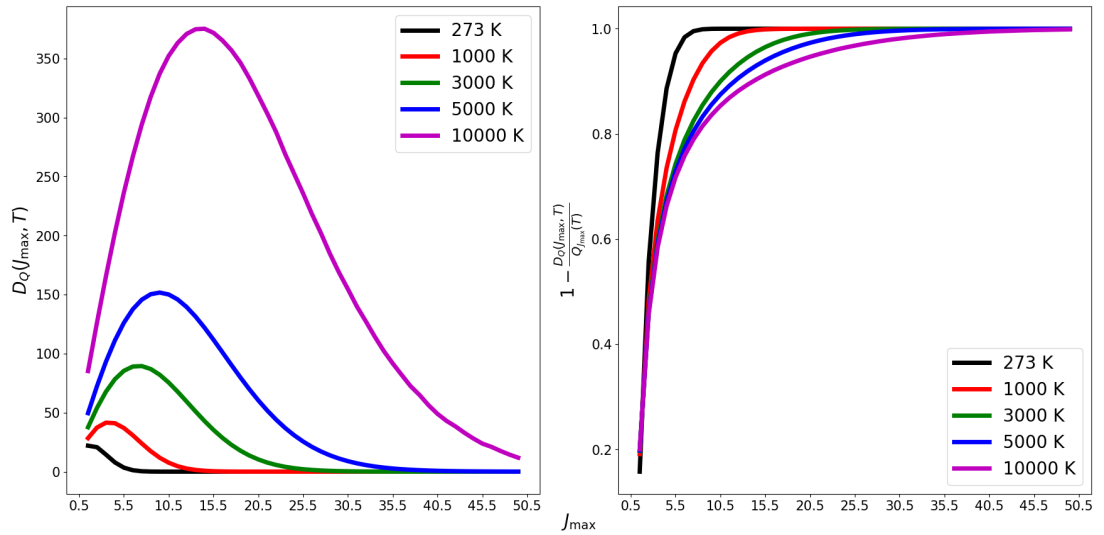


Figure 4.23: Convergence of the partition function of OH as a function of J_{max} .

there is a good level of convergence and $\Delta_Q(T = 10,000) = 99.87\%$.

4.6.2.1 Comparison with literature values

The JPL database (Pickett et al., 1998) provides partition function values up to $T = 300$ K. Barklem & Collet (2016) provide numerical values for the partition functions of OH up to 10,000 K which have been multiplied by two to account for different treatments of the nuclear spin degeneracy, which for OH has a value of $g_{\text{ns}} = 2$. Sauval & Tatum (1984) provide a polynomial expansion form of the partition function of OH which they claim is good between 1,000 K and 9,000 K. The polynomial takes the form:

$$\log_{10} Q(T) = \sum_0^{n_{\max}} a_n \log_{10}(5040/T)^n. \quad (4.64)$$

Sauval & Tatum (1984) give a_n up to $n = 3$. Again, the results of this polynomial have been multiplied by two to account for the nuclear spin degeneracy. Figure 4.24 presents a comparison between this work and the sources listed above. For lower temperatures, there is poor agreement with Barklem & Collet (2016) and Sauval & Tatum (1984) and good agreement is returned at higher temperatures. The values from these sources are based on calculated, rather than experimental molecular constants from Huber & Herzberg (1979), however, and we believe that our partition function in this region is correct as the energy levels from this work’s model have been supplemented with the MARVEL energy levels from Furtenbacher et al. (2022) as per the procedures by Bowesman et al. (2021, 2024b) and McKemmish et al. (2024). Furthermore, there is good agreement with Pickett et al. (1998) at all temperatures. However, our results slightly higher, as we have a larger vibrational basis and more electronic states. We return good agreement with HITRAN (Gamache et al., 2017).

4.6.3 Line list and bound to bound transitions

DUO was used to produce an OH line list which is called MYTHOS and is part of the ExoMol 2024 data release. This linelist is given in the ExoMol format (Tennyson et al., 2014, 2020) according to the latest standards (Tennyson et al., 2023). In this standard we include the predissociation lifetimes convoluted with the radiative lifetime as per equation 4.47. Furthermore, this dataset is hybridized (McKemmish et al., 2024) by substituting, wherever possible, the MARVEL energy levels from Furtenbacher et al. (2022) in place of calculated levels. Where not possible, energy levels are calculated using the spectroscopic model or interpolated using the predicted shifts algorithm (Bowesman et al., 2021, 2024b). This algorithm also estimates uncertainties of such interpolated levels and calculated levels. Energies substituted with MARVEL energy levels maintain the empirical MARVEL uncertainty. The predicted shifts calculations have been performed by Charles A. Bowesman.

Hence this linelist is accurate and suitable for high resolution studies up to 8,000 K and up to $\sim 132,000 \text{ cm}^{-1}$ ($> 76 \text{ nm}$). The linelist contains 10,606 rovibronic states and 1,685,102 dipole allowed X-X, A-A, B-B, C-C, and X-ABC bound-bound and bound-quasibound transitions. Before the procedure in Section 4.4, 58,289 states and 47,419,460 transitions were calculated, excess states and transitions were used in the photoabsorption spectrum as continuum absorption cross-sections alongside the transitions from $X \ ^2\Pi$ to $1 \ ^2\Sigma^-$ and $1 \ ^2\Delta$.

In line with current standards, two additional columns are added. “Type” indicates whether a state has MARVEL energy (Ma), calculated from the spectroscopic model (Ca), or been produced from the predicted shifts algorithm (PS). E_{Calc} gives the calculated energy, which, in cases that the Type is Ca, would be equal to the energy column, E . A sample from the .STATES file is given in Table 4.18. Similarly, an extract of the .TRANS file is given in Table 4.19.

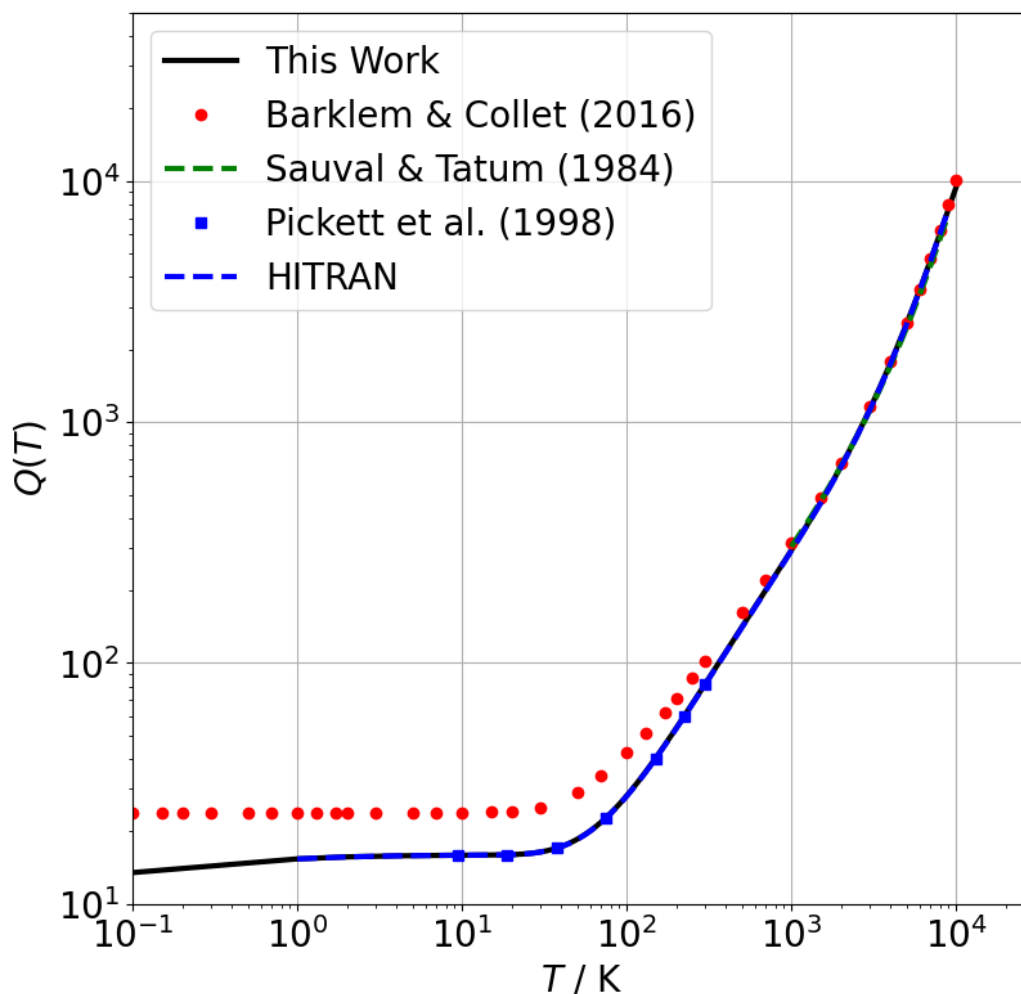


Figure 4.24: Comparison of partition function between this work and [Barklem & Collet \(2016\)](#); [Sauval & Tatum \(1984\)](#), JPL ([Pickett et al., 1998](#)), and HITRAN ([Gamache et al., 2017](#))

4.6.4 Simulation of absorption spectrum

The absorption spectrum of OH is simulated in two parts, bound-bound/quasibound transitions which are broadened appropriately using Voigt profiles as per Section 4.5.1, and the bound-unbound continuum absorption transitions which are discussed in Chapter 6. The cross-sections are computed using PYEXOCROSS ([Zhang et al., 2024b](#)) and for the two cases the calculations are done independently and then added together afterwards.

A comparison between the transition stick spectra of this work and the available spectra from HITRAN is made available in Figure 4.25. This reference line list from HITRAN ([Gordon et al., 2022](#)) is based on the available MoLLIST data ([Yousefi et al., 2018](#))

The MYTHOS line list extends the X-A transitions and provides previously unavailable transitions to the B and C states. Where quantum numbers coincide, there is good agreement on position and intensity.

The full photoabsorption cross-section was simulated by applying a Voigt profile (Equation 4.49) to all bound-bound transitions to include their lifetime, Doppler, and pressure

Table 4.18: Sample of the .STATES file produced by DUO for OH. Uncertainties using predicted shifts procedure from [Bowesman et al. \(2021, 2024b\)](#); [McKemmish et al. \(2024\)](#). The lifetimes are convolutions of predissociative (Chapter 5) and radiative lifetimes, and Lande-g factors, (g_L) are produced using DUO as per [Semenov et al. \(2017\)](#).

n	E	g^{tot}	J	Δ	τ	g_L	$+/-$	e/f	State	ν	Λ	Σ	Ω	Type	E_{Calc}
1	126.292196	4	0.5	0.001	28.563	-0.000755	+	e	X2Pi	0	1	-0.5	0.5	Ma	126.2526
2	3695.355577	4	0.5	0.001118	0.056453	-0.000755	+	e	X2Pi	1	1	-0.5	0.5	Ma	3695.477
3	7098.826455	4	0.5	0.001118	0.030017	-0.000755	+	e	X2Pi	2	1	-0.5	0.5	Ma	7098.923
4	10338.617460	4	0.5	0.001225	0.020636	-0.000754	+	e	X2Pi	3	1	-0.5	0.5	Ma	10338.75
5	13415.819989	4	0.5	0.001225	0.015441	-0.000754	+	e	X2Pi	4	1	-0.5	0.5	Ma	13416.01
6	16330.523242	4	0.5	0.001225	0.011937	-0.000754	+	e	X2Pi	5	1	-0.5	0.5	Ma	16330.62
7	19081.594976	4	0.5	0.001225	0.009373	-0.000754	+	e	X2Pi	6	1	-0.5	0.5	Ma	19081.51
8	21666.391134	4	0.5	0.001225	0.007465	-0.000753	+	e	X2Pi	7	1	-0.5	0.5	Ma	21666.22
9	24080.351827	4	0.5	0.001225	0.006074	-0.000753	+	e	X2Pi	8	1	-0.5	0.5	Ma	24080.3
10	26316.481722	4	0.5	0.001225	0.005107	-0.000753	+	e	X2Pi	9	1	-0.5	0.5	Ma	26316.59

n : State counting number,

E : State energy in cm^{-1} ,

g^{tot} : Total degeneracy of the state,

J : Angular momentum quantum number,

Δ : Energy level uncertainty in cm^{-1} ,

τ : Lifetime of the state in seconds,

g_L : Landé g factor ([Semenov et al., 2017](#)),

$+/-$: Parity,

e/f : Rotationless parity,

State: Electronic state, given as X2Pi, A2Sigma+, B2Sigma+, or C2Sigma+ for X $^2\Pi$,

A $^2\Sigma^+$, B $^2\Sigma^+$, and C $^2\Sigma^+$ respectively

ν : Vibrational quantum number,

Λ : Projection of electronic angular momentum,

Σ : Projection of electronic spin,

Ω : $\Lambda + \Sigma$ (Projection of total electron angular momentum),

Type: Ma - Marvelised, Ca - Calculated, PS - predicted shifts interpolation,

E_{Calc} : Calculated DUO energy directly from spectroscopic model

Table 4.19: Sample of the .TRANS file produced by DUO for OH.

n_f	n_i	A (s^{-1})	ν (cm^{-1})
1114	988	6.4725E-17	0.001643
636	510	1.1482E-16	0.002989
254	381	1.9358E-15	0.003251
1268	1394	5.8108E-17	0.004522
252	379	2.8534E-14	0.006179
1385	1259	1.4371E-15	0.006428
763	890	5.7538E-16	0.006531
1261	1387	1.8765E-15	0.007636
250	377	1.5369E-13	0.009289
1142	1016	1.2792E-15	0.010669

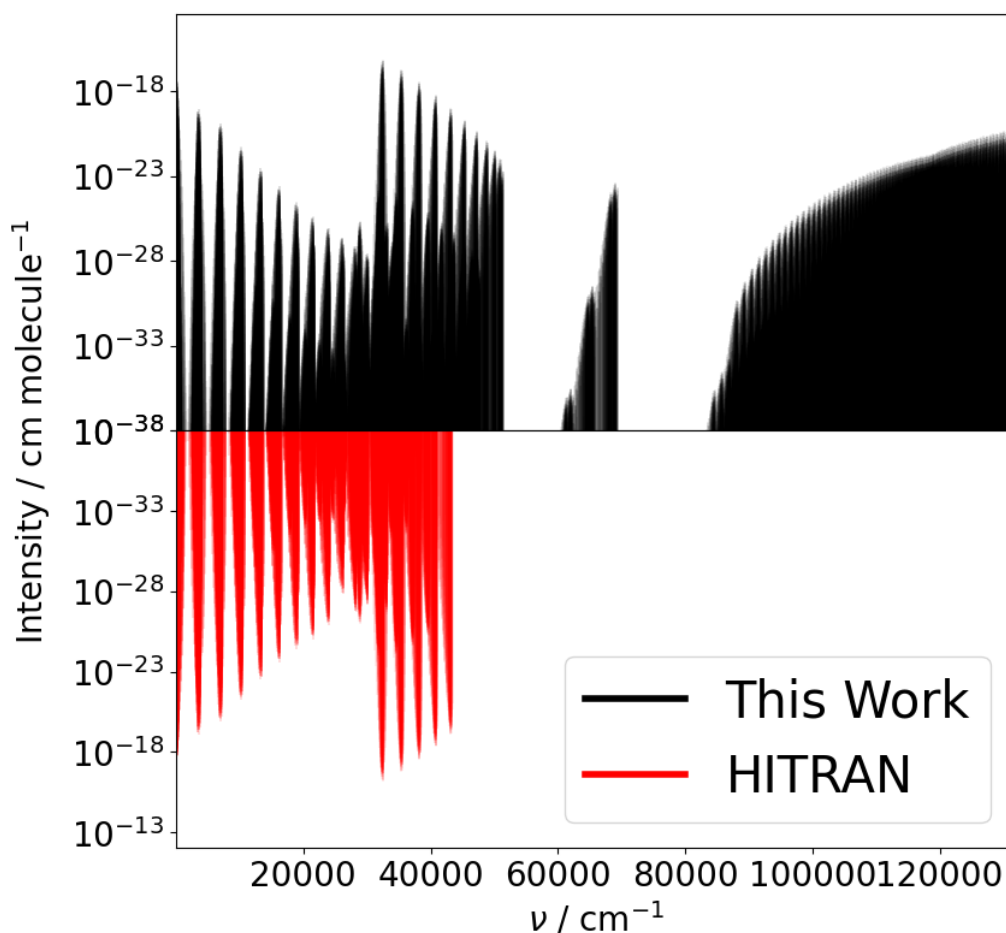


Figure 4.25: Comparison of stick spectra produced with $^{16}\text{O}^1\text{H}$ MYTHOS line list and the HITRAN line list (Gordon et al., 2022).

broadening effects. In addition, the continuum absorption cross-sections are included by computing discretised spectra for each direct dissociation channel and post-processing to produce continuous spectra as per Section 4.5. Further details on the methodology are given in Chapter 6.

These cross-sections are computed from $T = 100$ K to 8000 K in steps of 100 K and examples are given for $T \in [300, 1000, 2000, 5000]$ K in Figure 4.26.

The Leiden database (Hrodmarsson & van Dishoeck, 2023) provides photoabsorption cross-sections for OH. These cross-sections do not consider temperature and so are assumed to be at low T . A 1 K calculation is produced and Figure 4.27 presents a comparison between the cross-sections from this work and from Leiden. It appears that the reference material does not consider much of the lower energy regions covered by rovibrational transitions in $X^2\Pi$ and misses much of the predissociation structure of the $A^2\Sigma^+$ state. Otherwise, there appears to be a good agreement in the continuum absorption region, except for the small “bump” around 55,000 cm^{-1} . It is not certain what this is caused by. Above 80,000 cm^{-1} agreement is poor, this is because the model in this work fails to include the effects caused by higher energy Rydberg states which had not been included in the MARVEL dataset (Furtenbacher et al., 2022) such as the $2^2\Pi$, $3^2\Pi$, and $D^2\Sigma^-$ states. Further discussion on this region is provided in Sections 6.1 and 6.4.

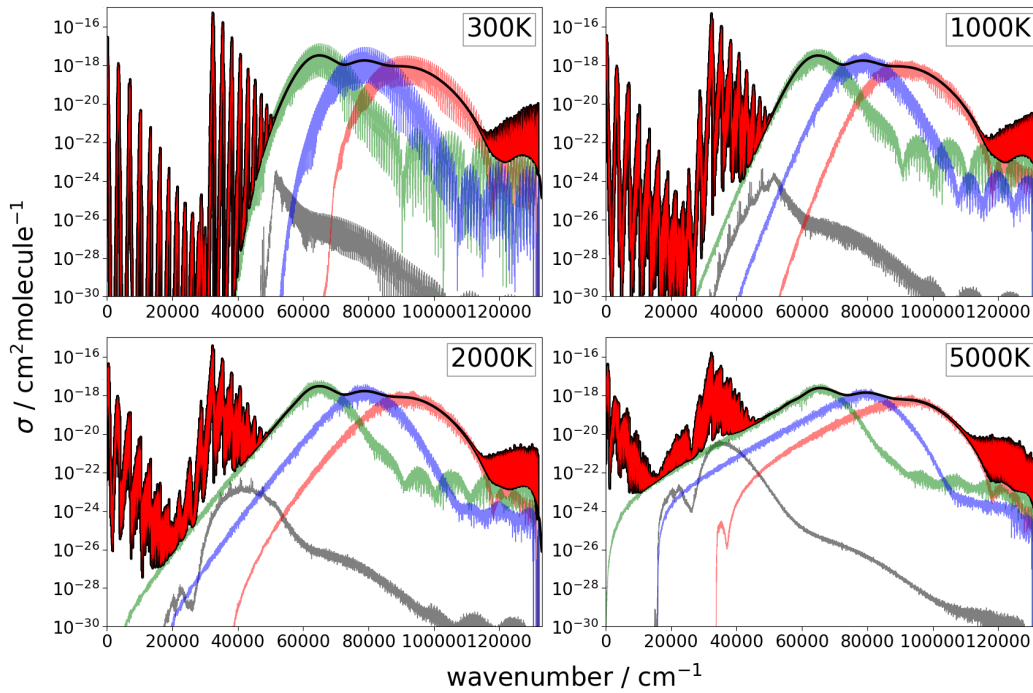


Figure 4.26: Computed temperature-dependent photoabsorption cross-sections of the transitions of OH for varying temperature.

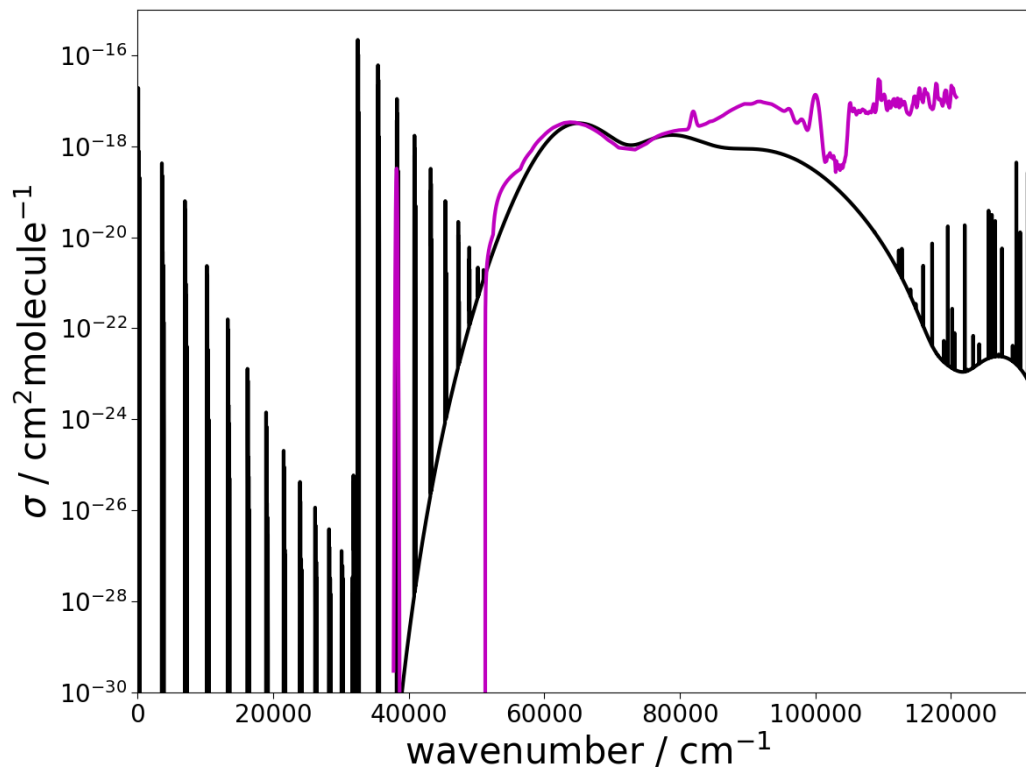


Figure 4.27: Comparison between the photoabsorption cross-section of OH computed in this work (black) at 1 K and cross-section given by Leiden database ([Hrodmarsson & van Dishoeck, 2023](#)) (magenta).

4.7 Conclusions and Future Work

An update to the OH MOLLIST line list called MYTHOS is presented covering regions up to $130,000\text{ cm}^{-1}$ in energy ($> 77\text{ nm}$ in wavelength). *Ab initio* electronic structure calculations of eight electronic states have been performed covering these states' PECs, corresponding diagonal/off-diagonal coupling curves, and (transition) dipole moment curves (Section 4.2). This *ab initio* study was heavily influenced by the works of [van der Loo & Groenenboom \(2005\)](#), who provided optimal CAS-SCF active spaces for use in MOLPRO.

The line list's constituent files contain all bound states and bound-bound transitions, ideally with little or no excess unbound lines. To achieve this, a framework for identifying bound and unbound states was explored, leveraging the close-to-boundary regions of the wavefunctions of individual states; this leads to bound-bound (B2B: line list) and bound-unbound (B2U) datasets.

Temperature-dependent photoabsorption spectra for $T \in [1, 300, 1000, 2000, 5000]\text{ K}$ are presented in Figures 4.26 and 4.27, with good agreement with the available Leiden dataset ([Hrodmarsson & van Dishoeck, 2023](#)) up to $80,000\text{ cm}^{-1}$ ($\sim 125\text{ nm}$) at 1 K. The photoabsorption cross-section presented here provides more information on the structure of transitions below $\sim 50,000\text{ cm}^{-1}$ ($\gtrsim 200\text{ nm}$), including rovibrational transitions in $X^2\Pi$ and a complete description of the predissociative transitions of $A^2\Sigma^+ \leftarrow X^2\Pi$ (see Chapter 5 for more details). Continuum absorption effects above $\sim 50,000\text{ cm}^{-1}$ ($\lesssim 200\text{ nm}$) stem from transitions from the $X^2\Pi$ state to the $1^2\Sigma^-$, $1^2\Delta$, and $B^2\Sigma^+$ states (see Chapter 6 for more details).

Above $80,000\text{ cm}^{-1}$, one must consider the effects of multiple other states to properly model the spectrum. These states include, but are not limited to, the $2^2\Pi$, $3^2\Pi$, and $D^2\Sigma^-$ states. These electronic states have been studied by [van Dishoeck et al. \(1984\)](#); [van Dishoeck & Dalgarno \(1984b\)](#) and are known to be important sources of dissociation for OH above $80,000\text{ cm}^{-1}$ through direct continuum absorption from $X^2\Pi \rightarrow 2^2\Pi$, predissociation to the $2^2\Pi$ state from $B^2\Sigma^+$, $3^2\Pi$, $C^2\Sigma^+$, and $D^2\Sigma^-$, and spontaneous radiative decay from $D^2\Sigma^-$ ([van Dishoeck & Dalgarno, 1984b](#); [van der Loo & Groenenboom, 2005](#); [Greenslade et al., 2005](#)). Performing further, high quality electronic structure calculations to cover some of these states, and modelling their spectra including their dissociative mechanisms has hence been left as future work. Furthermore, the rotational predissociative effects of the $A^2\Sigma^+$ state has not been studied in great detail here and is also left as future work.

For the time being, however, this model extends the current ExoMol and HITRAN OH line list higher in energy by $\sim 90,000\text{ cm}^{-1}$, and produces a photoabsorption spectrum covering an additional $\sim 36,000\text{ cm}^{-1}$ in energy with good agreement with the reference material.

4.7.1 Data Availability

The DUO model, including potential energy curves, spin-orbit coupling curves, electronic angular momentum coupling curves, and (transition) dipole moment curves; the MYTHOS line list .STATES and .TRANS files; temperature-dependent continuum absorption cross-sections for $T \in [100, 200, \dots, 8000]\text{ K}$; and the computed partition function are all available at www.exomol.com.

Chapter 5

Predissociation of Diatomic Molecules

5.1 Introduction

Predissociation is a dissociative process wherein a quasi-bound rovibronic level decays into the continuum through some mechanism. This is distinct from direct photodissociation, where a spin-allowed transition occurs from a lower, bound electronic state to an upper, unbound electronic state. Due to predissociative effects, we see that the lifetimes of rovibronic levels in bound electronic states are shortened significantly when compared to their radiative lifetimes. Spectroscopically, predissociation manifests itself in the broadening of lines where the upper state is predissociative through lifetime broadening as discussed in Section 4.5.1. Predissociation broadening distributes the intensity of a line over a wider area, thus reducing the peak intensity. One important consequence of this is that it can allow for abundance measurements of molecules in optically thick environments, where they would otherwise be undetectable due to a saturation of the absorption spectrum (Pavlenko et al., 2022).

Two mechanisms for predissociation are discussed here: Spin-orbit induced predissociation, and rotational predissociation. Spin-orbit predissociation is caused by the interaction of a rovibronic level of a bound electronic state, such as the $A^2\Sigma^+$ state of OH, with local repulsive electronic states through spin-orbit coupling. Through this interaction, the bound state can decay into a local repulsive state, and hence, dissociate into the continuum. Rotational predissociation occurs in rovibronic levels where the energy of the level is above the dissociation limit of the state. These states exist due to the rotational barrier of the potential energy resulting in the effective potential from Equation 4.38. Rovibronic states can tunnel through the induced potential barrier and come out on the dissociative portion of the effective potential, predissociating. Toy models of these two types of predissociation can be seen in Figure 5.1.

Rotational predissociation was first studied in ExoMol by Yurchenko et al. (2024), stimulated by the detection of AlH in the spectrum of Proxima Centauri (Pavlenko et al., 2022). Further details on rotational predissociation are provided in Section 5.4.

The contents of this chapter are mainly concerning the calculation of spin-orbit induced predissociation lifetimes and spin-orbit broadening parameters of the $A^2\Sigma^+$ state as coupled to the repulsive $1(^2\Sigma^-, ^4\Sigma^-, ^4\Pi)$ states. Sections 5.2 and 5.3 discuss the general procedure and numerical methods developed to perform calculations for the spin-orbit predissociation of the diatomic molecules OH, SH, and SD. A full description of the resulting lifetimes

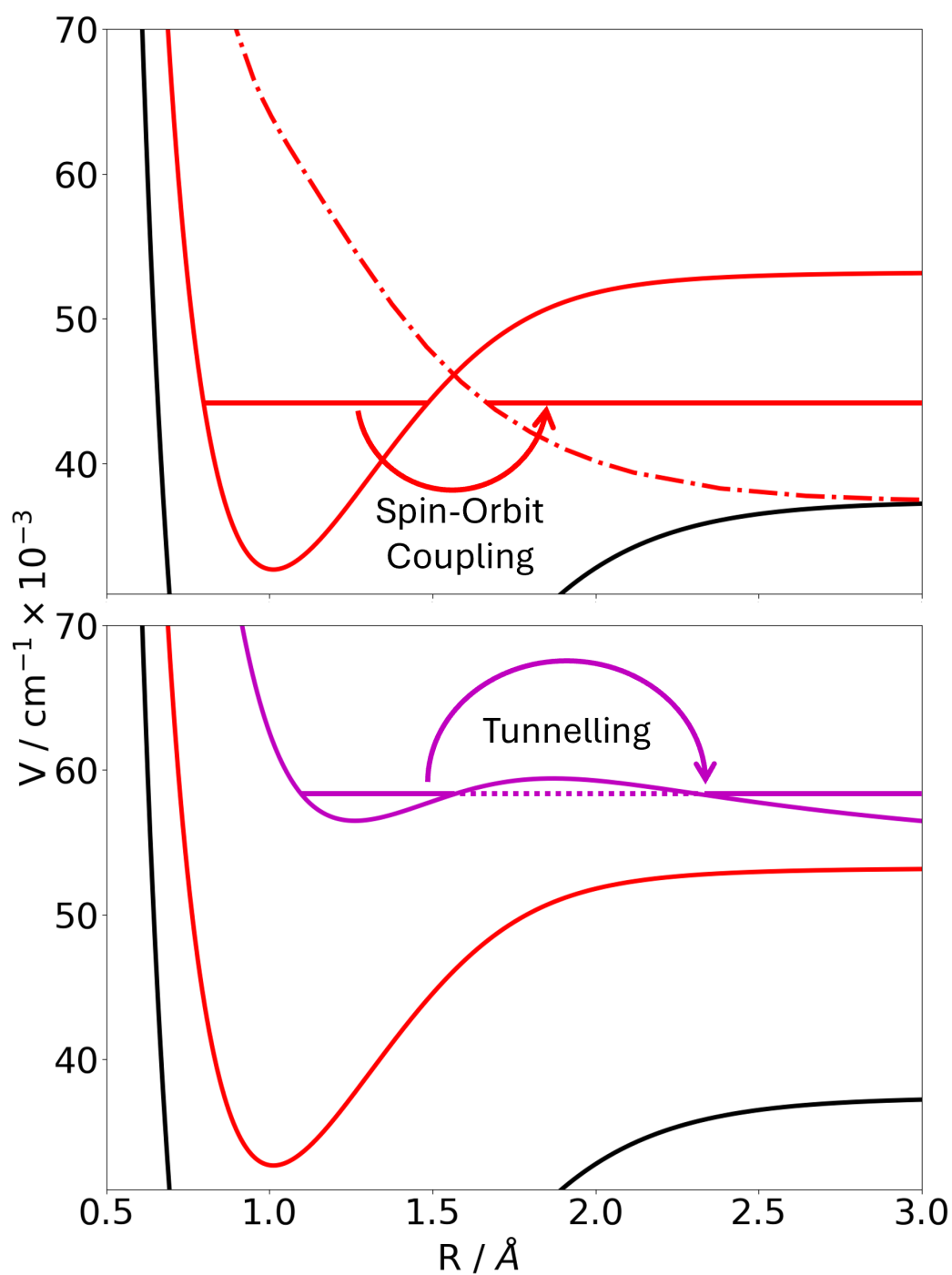


Figure 5.1: Toy models describing predissociative mechanisms. Left: Spin-orbit induced predissociation. Right: rotational predissociation.

and broadening parameters of OH is given in Section 5.5 and preliminary results for SH are given Section 5.6.

Many approaches can be taken to study predissociative states, broadly, one can put these methods into five categories: Scattering, perturbation, time-dependent, complex absorption, and stabilization methods. These methods have a spectrum of both how approximate, accurate, and expensive they are. Generally, cheaper methods are more approximate and less accurate.

Parlant & Yarkony (1999) used a full **scattering calculation** to compute predissociation lifetimes for rotationally resolved levels of OH using the time delay method (Smith, 1960), where one extracts the time-delay matrix from the S -matrix. This method has also been applied within the ExoMol group to compute resonances (Little et al., 2017; Little & Tenyson, 2014).

Perturbation theory methods rely on an assumption that resonant states are well separated and do not solve the fully coupled nuclear motion problem. Furthermore, they require that the basis functions be carefully considered when performing calculations, as results are not invariant to basis function transformation. Effectively, in these methods, the calculation of the predissociation lifetime is based on the Fermi Golden rule and the following relation can be found, (Sink et al., 1980; Sink & Bandrauk, 1979; Lefebvre-Brion & Field, 2004; Yarkony, 1992):

$$\tau_{\text{so}}(\text{A } ^2\Sigma^+, v, J, N, p)^{-1} = 2\pi \sum_{L, N'} |\langle \Psi(\text{A } ^2\Sigma^+, v, J, N, p) | \hat{H}_{\text{so}} | \Psi(L, E, J, N', p) \rangle |^2 \quad (5.1)$$

using Hund's case (b) basis functions as was done by Yarkony (1992), where L is a given continuum state. The solutions to the continuum wavefunctions, $\Psi(L, E, J, N', p)$, are done on a grid between $0.05 \leq R \leq 10 a_0$, discretizing the continuum. This method, while based on multi-channel scattering theory, is an approximation, and the results of the above matrix element calculations likely differ under variation of the grid boundaries.

Time dependent methods such as the Fourier Grid Hamiltonian (Pellegrini et al. (2002) and the references therein) or Filter Diagonalization Method (Dulieu et al. (1997) and the references therein) methods work on the principle of setting a predissociative state into some initial state at time, $t = 0$, and propagating the state until some time $t = T$. One can then calculate the correlation function,

$$C(T) = \langle \psi_0 | e^{-i\mathbf{H}T} | \psi_0 \rangle = \langle \psi_0 | \psi_T \rangle, \quad (5.2)$$

giving the part of the wave initial wavefunction which “survives” the delay. Hence the lifetime can be computed as (Kokoouline et al., 2000),

$$\tau = -\frac{\ln |C(T_1)| - \ln |C(T_2)|}{2(T_1 - T_2)} \quad (5.3)$$

Complex absorbing potentials modify the Hamiltonian such that (Silva et al., 2008; Gyamfi & Jagau, 2024; Osséni et al., 2009; Lefebvre-Brion & Field, 2004),

$$\hat{H}_{\text{CAP}} = \hat{H} - i\eta\hat{W}, \quad (5.4)$$

where η is a real scalar and $\hat{W}$ is a Hermitian operator. The associated Schrödinger equation,

$$\hat{H}_{\text{CAP}}|\Psi\rangle = (E_r - i\Gamma/2)|\Psi\rangle, \quad (5.5)$$

where E_r is the resonance energy, and Γ is the resonance width, from which one can extract the lifetime as $\tau \propto \Gamma^{-1}$.

Finally, one can build a methodology around the **stabilization method** (Hazi & Taylor, 1970; Bacic & Simons, 1982; Mandelshtam et al., 1993). Calculations based on this method leverage the instability of continuum state term values with respect to the extension of the right-side boundary, R_c . This method is discussed in detail and applied in the following sections.

5.2 Spin-Orbit Predissociation Lifetimes - General Procedure

5.2.1 Leveraging Duo Spectroscopic Models - Stabilization Method

A benefit of the methods presented in this chapter is that it does not require the implementation of any new physics into the DUO program. Unlike the complex potential methods, this allows for us to retain real eigenvalues. This section will cover the general procedure taken to calculate spin-orbit predissociation lifetimes and widths of diatomic molecules with examples from the calculations of OH lifetimes.

Instead, the spectroscopic model produced in Chapter 4 is leveraged and a variation of the stabilization method is applied. As discussed in Chapters. 2, 3, and 4, DUO sets boundary conditions such that there is a boundary at $R = R_c$ such that $|\psi(R_c)|^2 = 0$ should R_c be large enough.

In Figure 5.2, the two green horizontal lines illustrate unbound state energy levels retrieved from DUO calculations with different right-side box limits, R_c . Both sets of calculations are performed with the same left-side box limit R_{min} . By construction the nuclear motion wavefunctions are only finite between R_c and R_{min} .

The two green unbound state energy levels have the same quantum numbers $J, v, \tau, \Sigma, \Lambda, \Omega$, however, $E_{R_c=3\text{\AA}}$ returns a higher term value than $E_{R_c=4\text{\AA}}$. This is akin to the particle in a box, where increasing the size of the box compresses the distribution of energy levels closer to zero. Repeated calculations over varying R_c in DUO for iso-numeric continuum energy levels exhibits a relationship where the term values decrease with R_c , this is referred to as the *energy profile* of the continuum energy level.

It is worth noting at this stage, that v here is not a true vibrational quantum number. For continuum states, the concept of vibrational quanta is effectively meaningless, and in this context, acts simply as a counting number. While for the single continuum state case, this is a reasonable approximation, however, it becomes problematic in the multi-state case, where “accurately” assigning this quantum number becomes a bit more of a make-work activity. Seeing these states, however, as iso-numeric in a loose sense is beneficial to help visualise the effect R_c has on term value structure in this instantaneously bound treatment

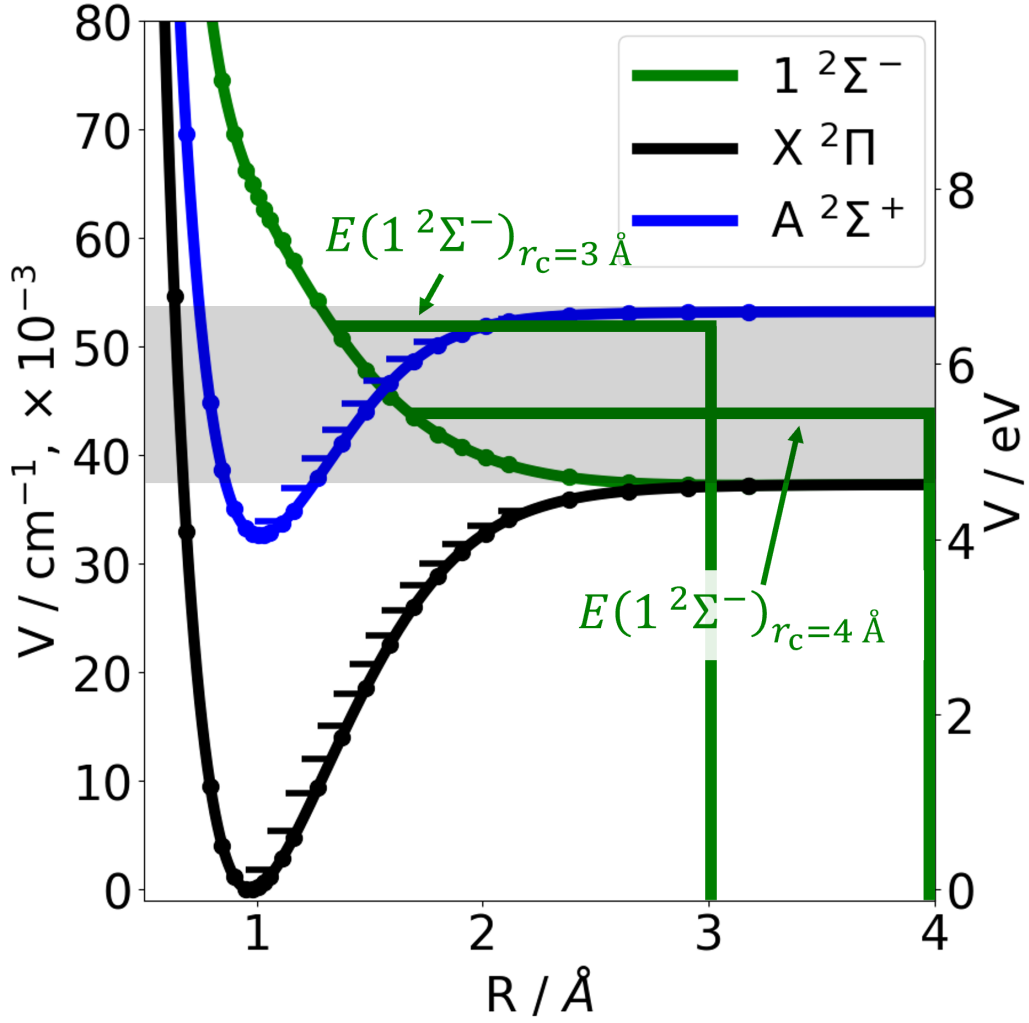


Figure 5.2: A toy model of OH consisting of the $X\ ^2\Pi$, $A\ ^2\Sigma^+$, and $1\ ^2\Sigma^-$ electronic states. The two green levels, $E(1\ ^2\Sigma^-)_{r_c=3,4\ \text{\AA}}$ are continuum levels in the $1\ ^2\Sigma^-$ electronic state with the same quantum numbers, however with different right-side box limits, R_c . This highlights the box size dependence of repulsive state energy levels. The shaded region covers energy levels between D_e^X and D_e^A .

of the continuum.

The spin-orbit interaction between the $1\ ^2\Sigma^-$ and $A\ ^2\Sigma^+$ states, $\langle^2\Sigma^-|\xi|^2\Sigma^+\rangle$, hence displaces the $A\ ^2\Sigma^+$ state levels, which would otherwise be stable under variation of R_c . This *induced energy profile*, allows us to study the predissociation characteristics of the quasi-bound $A\ ^2\Sigma^+$ state levels.

Since repulsive electronic states have an infinitely dense set of continuum states, the position of the predissociating state, $|A, J, v, p\rangle$, where J is the rotational quanta, v is the vibrational quanta, and p is the parity, has an uncertainty in the energy caused by resonances with those repulsive states. Note that for the $A\ ^2\Sigma^+$ state, $\{J, v, p\}$ is a complete set of quantum numbers as $|\Lambda| = 0$, hence $\Sigma = \Omega$. As a convention in DUO for $^2\Sigma^+$ states, the sign of Σ correlates with the parity as; $\Sigma = \frac{1}{2}$ for $p = +$; $-\frac{1}{2}$ for $p = -$. This infinite set of states cannot be recovered using bound state methods for solving the Schrödinger equation, such as used by DUO, although scattering methods can be employed while using DUO just

for the inner region (Rivlin et al., 2019).

Here the continuum is approximated through discretization (Pezzella et al., 2021) and adapting the stabilization method to characterise the quasi-bound states. In this method, effective infinite potential walls are assumed at the box limits $[R_{\min}, R_c]$. This leads to bound-like rovibronic solutions even for continuum or quasi-bound states. By changing the position of R_c , different continuum state term values are generated for iso-numeric continuum states. The continuum is hence probed discretely, and induced shifts in the quasi-bound states can be quantified as follows:

For a given box size, $R_c - R_{\min}$, one can compute the term values, $\tilde{E}(A, J, v, p)|_{R_c}$ of the given set of quasi-bound, meta-stable states $\{|A, J, v, p\rangle\}$. By varying R_c , one can then establish the parametric dependence $\tilde{E}(A, J, v, p; R_c)$.

In this study, R_c was varied in the range $R_c \in [8.000, 8.999]$ Å with a uniform spacing of 999 values - a grid spacing of $\delta_{R_c} = 0.001$ Å.

Figures 5.3 and 5.4 illustrate the box-size dependence of the two $A^2\Sigma^+$ quasi-bound states of OH, $|A^2\Sigma^+, J = 0.5, v = 4, e\rangle$ and $|A^2\Sigma^+, J = 0.5, v = 2, e\rangle$. The behaviour is seen to be periodic with discontinuities at visually regular intervals and a central energy region, or centroid in the middle. The typical resonance-like shapes are due to the interaction with continuum states. The discontinuities occur at the geometries where a crossing continuum state goes from pushing the quasi-bound level down to pushing it up and provide the energy level resonances from which we can calculate the predissociation lifetimes. The line broadening parameter Γ , and hence the spin-orbit predissociation lifetime of the state, $\tau_{\text{so}} \propto \Gamma^{-1}$, are associated with the widths of these resonances.

The interaction between $A^2\Sigma^+$ and the three continuum states, $1^2\Sigma^-, 4\Sigma^-, 4\Pi$ are through the corresponding spin-orbit couplings as shown in Figure 4.16. There are several structures visible in Figure 5.3, the asymptotes with the large wings and the asymptotes with the small wings. The substructures are caused by spin-orbit interactions with different continua. The individual contributions can be resolved by performing calculations with only one of the three repulsive states and associated spin-orbit couplings present at a time, as illustrated in Figure 5.4 for the $|A, J = 0.5, v = 2, e\rangle$ state. This state has been chosen for its simplicity. It shows that all three states contribute to the minor asymptotic wings, but only the $1^4\Sigma^-$ state contributes to the major wings. This makes the $1^4\Sigma^-$ state a bigger contributor to the predissociative decay for this particular state, as it has a greater effect on the broadening. This result is corroborated by Li & Zhang (2011) who show that the $1^4\Sigma^-$ state is the primary predissociation branch for this vibrational band.

For energy levels above D_e^X , $X^2\Pi$ state rovibronic levels become unbound and contribute to the perturbation of the $A^2\Sigma^+$ state level energies and hence provide an additional avenue for predissociation through the ground electronic state (see Figure 5.5). The effect of predissociation through the $X^2\Pi$ state is small, but has been reported previously by Parlant & Yarkony (1999).

5.2.2 Statistical Treatment

To calculate the predissociation lifetime from the above results one must quantify the variation around the centroid. To do this, we calculate the integral normalised histogram of the energy data points centered around the mean ($E(R_c) - \langle E(R_c) \rangle$). This energy distribution

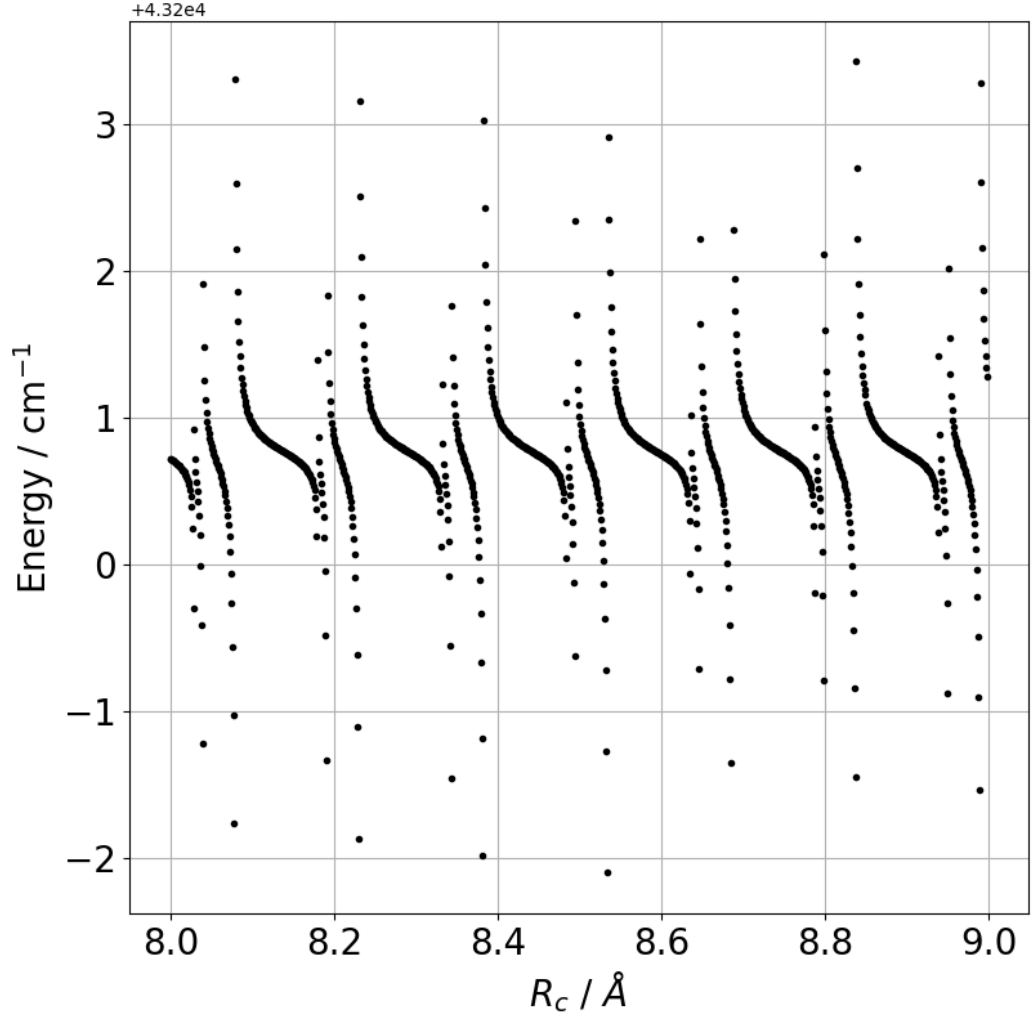


Figure 5.3: The term value of the $|A^2\Sigma^+, J = 0.5, v = 4, e\rangle$ state as a function of the box length of the calculation in DUO, the variation of the energy is induced by crossings with energy levels in the repulsive states $1^2\Sigma^-$, $1^4\Sigma^-$, and $1^4\Pi$.

is then modelled as a Lorentzian distribution,

$$L(\tilde{E}; \tilde{E}_0, \Gamma) = \frac{\frac{1}{\pi}(\frac{1}{2}\Gamma)}{(\tilde{E} - \tilde{E}_0)^2 + (\frac{1}{2}\Gamma)^2}, \quad (5.6)$$

where $\tilde{E}_0$ is the peak position of the Lorentzian in cm^{-1} and Γ is the full-width at half-maximum - the line broadening parameter, in cm^{-1} . The parameters, $P_L = \{\tilde{E}_0, \Gamma\}$, can be trained to best represent the histogram, and then the line broadening parameter is inverted via the relationship,

$$\tau_{\text{so}} = \frac{1}{2\pi c \Gamma}, \quad (5.7)$$

where c is the speed of light in cm s^{-1} .

The training of these parameters is not straightforward, despite the relative simplicity of a

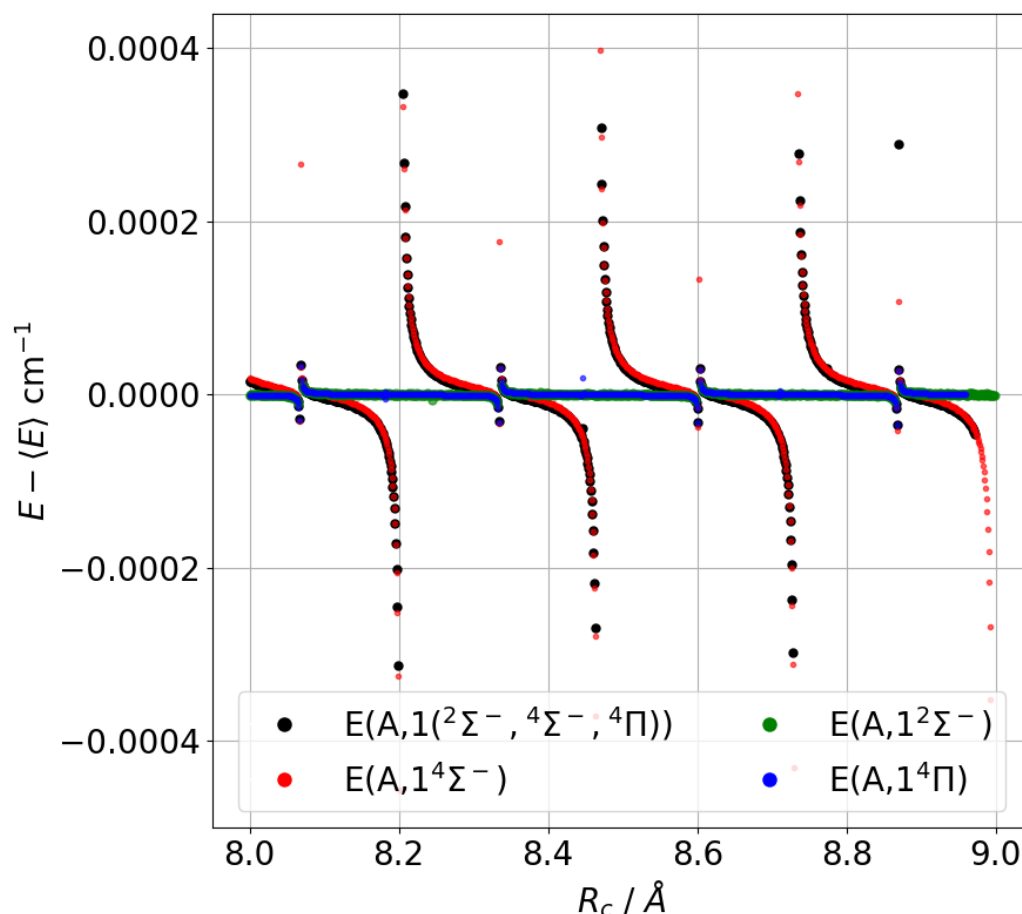


Figure 5.4: Term value of the $|A^2\Sigma^+, J = 0.5, v = 2, e\rangle$ state as a function of the box length of the calculation in DUO. The different colors correspond to different spin-orbit contributions.

2-parameter model, and this is discussed in Section 5.3. A visualisation of a fitted histogram is available in Figure 5.6.

5.3 Spin-Orbit Predissociation Lifetimes - Numerical Treatment

While a two parameter fitting problem is typically not difficult to solve, several considerations need to be made to ensure reliable and consistent results. This section describes the numerical considerations taken to wrangle, fit, and estimate uncertainties for predissociation lifetimes using the treatment in Section, 5.2.1. The procedures outlined in this section have been compiled into an installable PYTHON package called BINSLT, and this has been made available on the ExoMol github (github.com/exomol).

5.3.1 Centring energy profile

As explained Section 2.1.3, the quantum numbers, J and τ are rigorous and all other numbers are formally, well approximated labels. One method to assign the vibrational quantum label, v , is by counting the rovibronic states of a given electronic state in order of increasing energy within a J, τ symmetry block. This can lead to misassignments especially when one

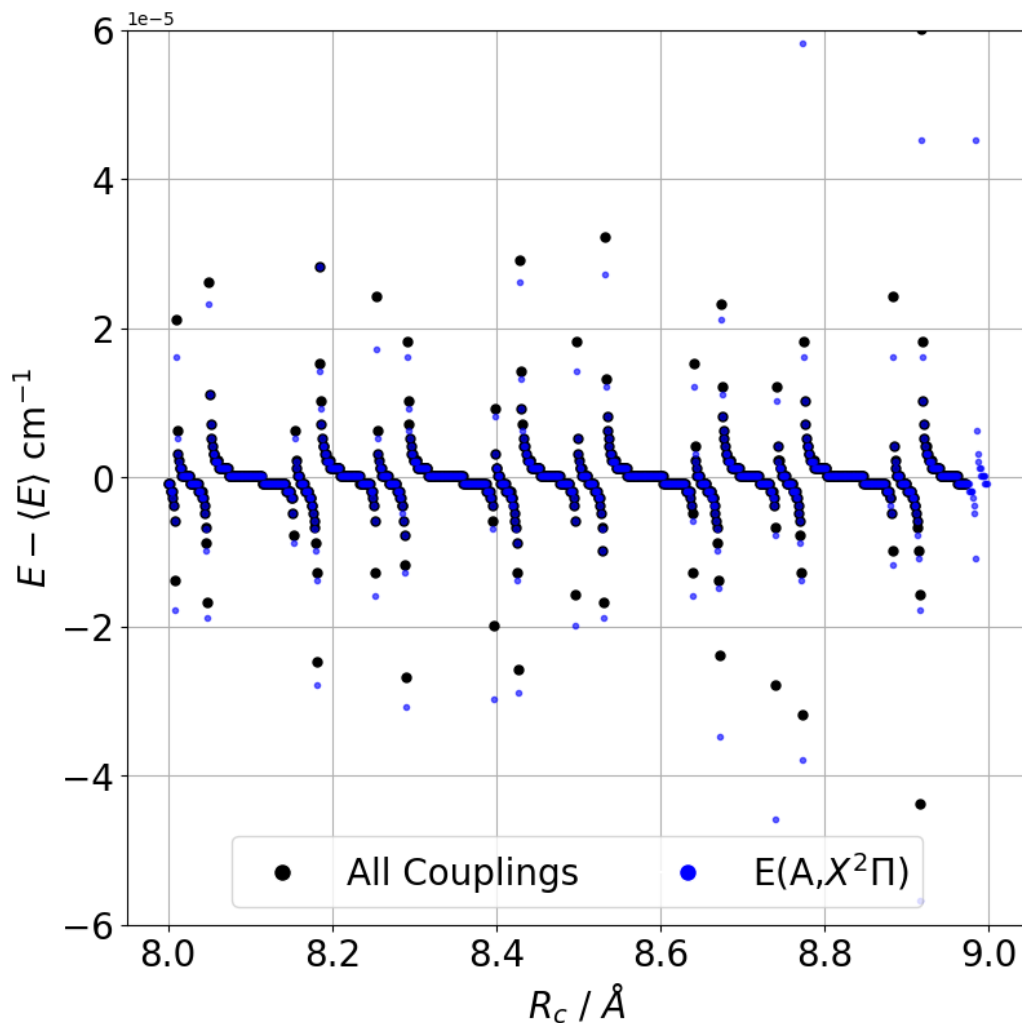


Figure 5.5: Term value of the $|A^2\Sigma^+, J = 13.5, v = 1, f\rangle$ state as a function of the box length for a DUO calculation including the $X^2\Pi$ and $A^2\Sigma^+$ states only. The blue markers represent a shift in energy induced by the spin-orbit coupling between the $X^2\Pi$ and $A^2\Sigma^+$ states on the $A^2\Sigma^+$ state level. Energy profile is down shifted by $\langle E \rangle$ (see Equation 5.8) so that it is centered on zero.

considers many energy levels in close proximity to one another and in cases where $E > D_e$ as discussed in Section 4.4. This manifests itself in energy profiles such as that in in Figure 5.7

In this figure there is a bimodal distribution of energy. This is likely not an effect of the spin-orbit interaction, but rather the lower energy data have been misassigned. Ignoring there data points and “zooming” into region (a) we can resolve the familiar energy profile. The ideal scenario when fitting a Lorentzian is to have excess data points removed such that there are more or less an equal number of data points either side of the centroid as fitting a symmetrical distribution to symmetrical data is easier than fitting to asymmetrical data.

The data is treated here by centring the data on the centroid. The position of the centroid is estimated to be equal to $\langle E \rangle$, where this is some measure of central tendency, for example, mean or median. Hence, we adjust the initial dataset E_i to get the centered dataset, E_c ,

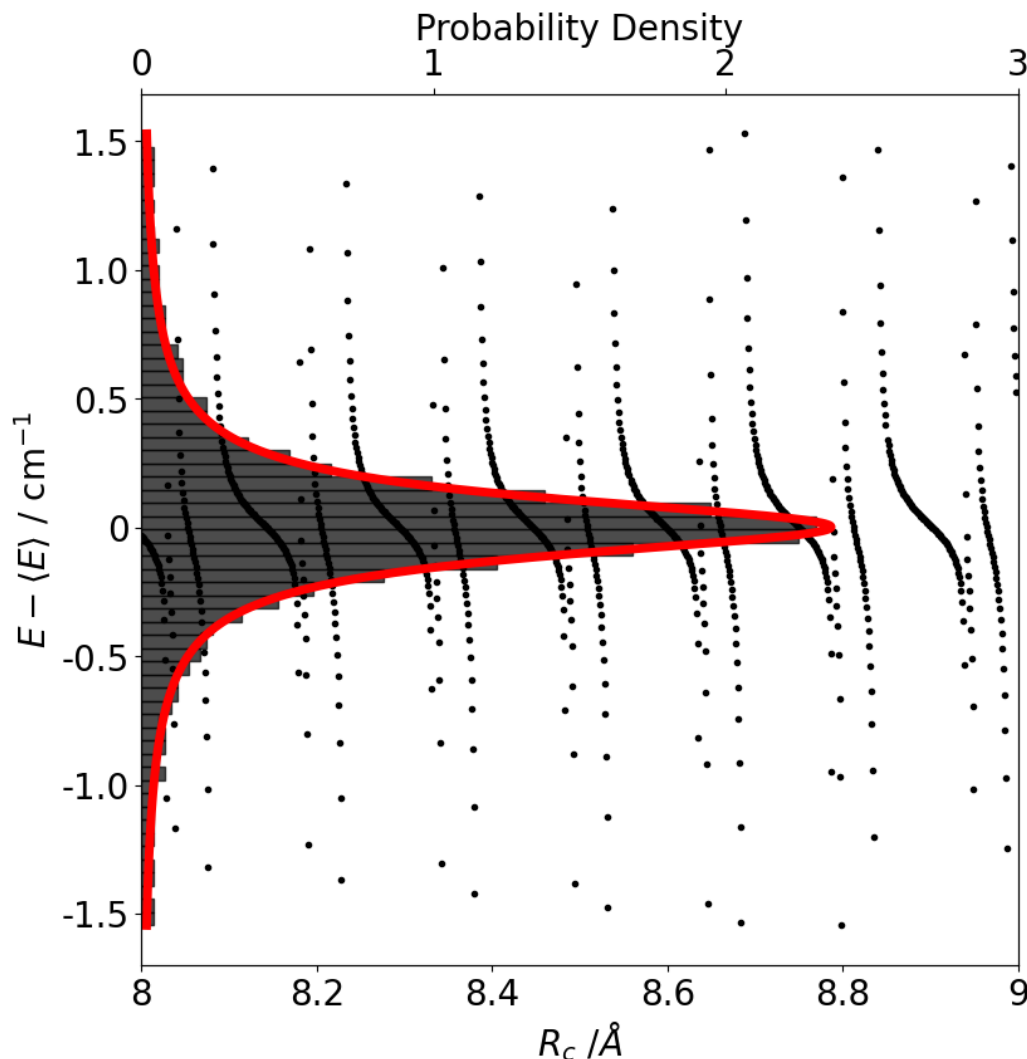


Figure 5.6: Plot of the energy against box length with the fitted histogram of energy points for the $|A^2\Sigma^+, J = 0.5, v = 4, e\rangle$ state.

$$E_c(R_c) = E_i(R_c) - \langle E_i \rangle. \quad (5.8)$$

Before this centring is performed, however, we first ensure a symmetrical distribution. We define the *cutoff* function, $C(E_i, N)$,

$$C(E_i, N) = \begin{cases} E_i & \text{if } E_i \in [\langle E_i \rangle - N\sigma, \langle E_i \rangle + N\sigma] \\ \emptyset & \text{otherwise.} \end{cases} \quad (5.9)$$

Where σ is the standard deviation of the initial dataset E_i , N is some user multiple, and $\emptyset$ is a null value, hence the data point is removed from the data set. This function essentially constrains the data set to contain only energies that are within $N\sigma \text{ cm}^{-1}$ from the centroid estimate. This, however, does not reliably remove misassigned regions like that in Figure 5.7, as it is common for $\langle E_i \rangle$ to be hundreds of cm^{-1} from region (a) due to a skewed mean. This can be somewhat remedied by considering a different measure of central tendency, like the median, however, this is unreliable as the median can fall directly in region (b).

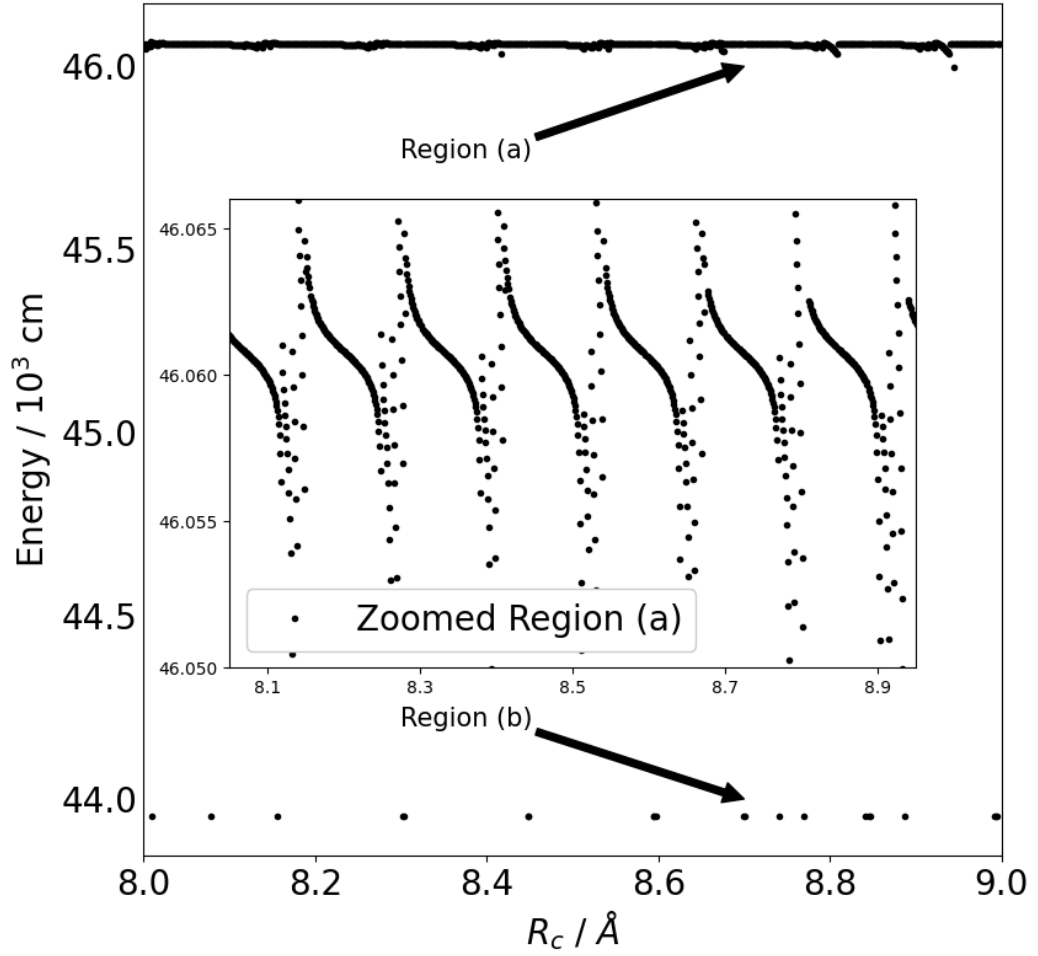


Figure 5.7: Example of misassignment in extraction of energy profile term values. Region (a) contains desired values and region (b) contains misassigned values from other local state(s).

To deal with this, we establish two datasets; the quasi-bound solution, where 1 ($^2\Sigma^-$, $^4\Sigma^-$, $^4\Pi$) and their associated couplings are present, and the bound solution, where these repulsive curves are not present. Hence, for a given rovibronic state of A $^2\Sigma^+$, $E(A, J, v, p)$ we have two solutions, E_q , and E_b , representing the quasi-bound and bound solutions respectively. The average energy of the two regions, (a) and (b) in Figure 5.7, are assumed to be well separated,

$$|\langle E_{(a)} \rangle - \langle E_{(b)} \rangle| \gg 0, \quad (5.10)$$

and it is also assumed that the centroid of the quasi-bound solution, E_{Cent} (Equation 5.19 in Section 5.3.7), is sufficiently close to the bound solution (Equation 5.11),

$$|E_{\text{Cent}} - E_b| < |\langle E_{(a)} \rangle - \langle E_{(b)} \rangle|, \quad (5.11)$$

where E_{Cent} is the energy position of the centroid. We use the reference bound solution energy to remove region (b). To do this we define the *lock* function, $L(E_i, E_b, K)$.

$$L(E_i, E_b, K) = \begin{cases} E_i & \text{if } E_i \in [E_b - K, E_b + K] \\ \emptyset & \text{otherwise,} \end{cases} \quad (5.12)$$

where K is a user defined parameter in cm^{-1} . Hence the full filtering function with respect to the bound state energies, $C_L(E_i, E_b, N, K)$ is,

$$C_L(E_i, E_b, N, K) = C(L(E_i, E_b, K), N). \quad (5.13)$$

After which the centring procedure is performed, allowing for the full resolution of region (a).

5.3.2 Initial Parameter values

Optimization of the Lorentzian parameters, P_L , was performed using a gradient descent least squares method. Initial gradients are calculated from a set of guessed parameters, $P_0 = \{E_0, \Gamma_0\}$. Bad initial guesses result in fits which are not representative of the true energy profile distributions as the algorithm may become stuck in a local minimum or the maximum allowed iterations can elapse before a stable solution is achieved. As discussed earlier, centring allows for an $E_0 = 0 \text{ cm}^{-1}$. Γ_0 is found by linearly interpolating the histogram points, $H(c, p)$, where c are the bin centers and p are the heights of the data points. We find the intersection points, $\{c_i\}$ with the line $p = \frac{\max(H)}{2}$. Over-binning the histogram results in a noisy structure at the shoulder and wings of the distribution. Under-binning results in all the term values being collected in one bin. Both of these scenarios result in $|\{c_i\}| \neq 2$ and so results for the relevant bin number are discarded and $\Gamma_0 = 0$ is used. For an appropriate bin number, $|\{c_i\}| = 2$, and $\Gamma_0 = |c_1 - c_2|$. Hence,

$$P_0 = \{0, |c_1 - c_2|\}.$$

5.3.3 Bin numbers

A further difficulty arises when calculating the histogram. The number of bins used in the approximation of the probability density function non-trivially affects the fitted value of Γ , see Figure 5.8.

A too high or too low bin number results in an over or under-description of the energy profile distribution, hence the fitted parameters in these cases are unstable solutions. The shaded area in Figure 5.8 highlights a region where the lifetimes extracted are stable within some variance. This difficulty can be overcome by treating the variance induced by the bin number statistically. The variance here is assumed to be random and hence, normal. The calculated lifetimes are binned into a histogram, $H(\tau)$, with bin number, $N_B = \left\lfloor \frac{|\{\tau\}|}{F} \right\rfloor$, where F is a user defined parameter. $H(\tau)$ is then fit to a Gaussian distribution, (equation 5.14) as demonstrated in Figure 5.8 and returns a central value for the lifetime μ_τ , and a measure of the variance in the standard deviation σ_τ . σ_τ hence becomes a consideration in the estimation of the uncertainties of the lifetimes. For a full discussion on uncertainties, see Section 5.3.6.

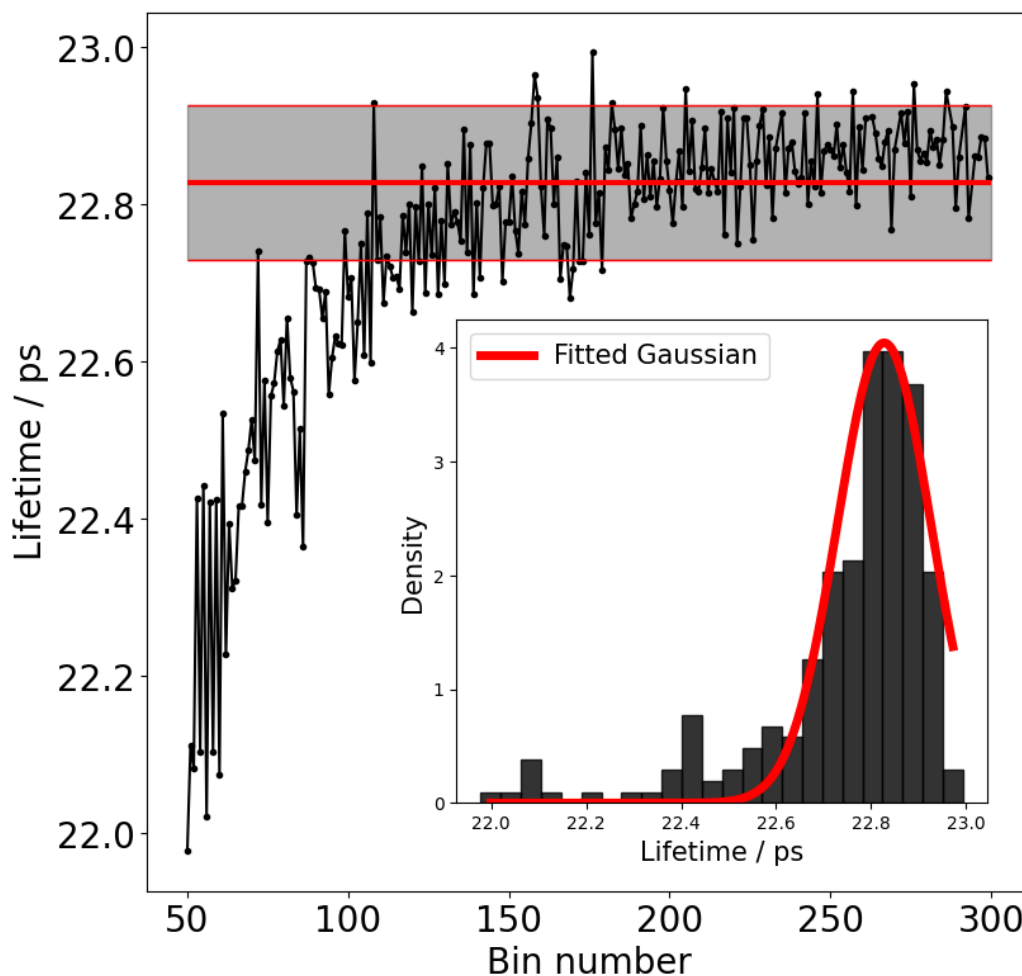


Figure 5.8: Lifetimes calculated using the stabilization method depend on the bin number of the integral normalised histogram, N_b . This relationship is detailed here. The subfigure details the procedure in Section 5.3.3 used to determine Δ_C and recovers the best estimate for the lifetime, μ_τ detailed in the shaded area. The bold red line is μ_τ with Gaussian uncertainty $\Delta_C = \sigma_\tau$.

The Gaussian distribution is given by:

$$G(\tau; \mu_\tau, \sigma_\tau) = \frac{1}{\sigma_\tau \sqrt{2\pi}} \exp \left(-\frac{1}{2} \left(\frac{\tau - \mu_\tau}{\sigma_\tau} \right)^2 \right), \quad (5.14)$$

where τ is the lifetime in ps, μ_τ is the mean lifetime in ps, and σ_τ is the standard deviation of the lifetime in ps.

5.3.4 Long lifetimes

Some predissociating rovibronic levels have a comparatively long lifetime, of the order of milliseconds relative to the nano- and pico-scale of the majority of levels. A higher lifetime means a narrower energy profile. Deviations from the central energy position are very small like in the case for $|\text{OH}, A, 18.5, 0, e\rangle$, as in Figure 5.9. The resulting histogram is sparsely populated as the variation in the energy is of the order of the numerical precision of DUO. Producing a meaningful Lorentzian profile here is unrealistic, so these levels are assigned

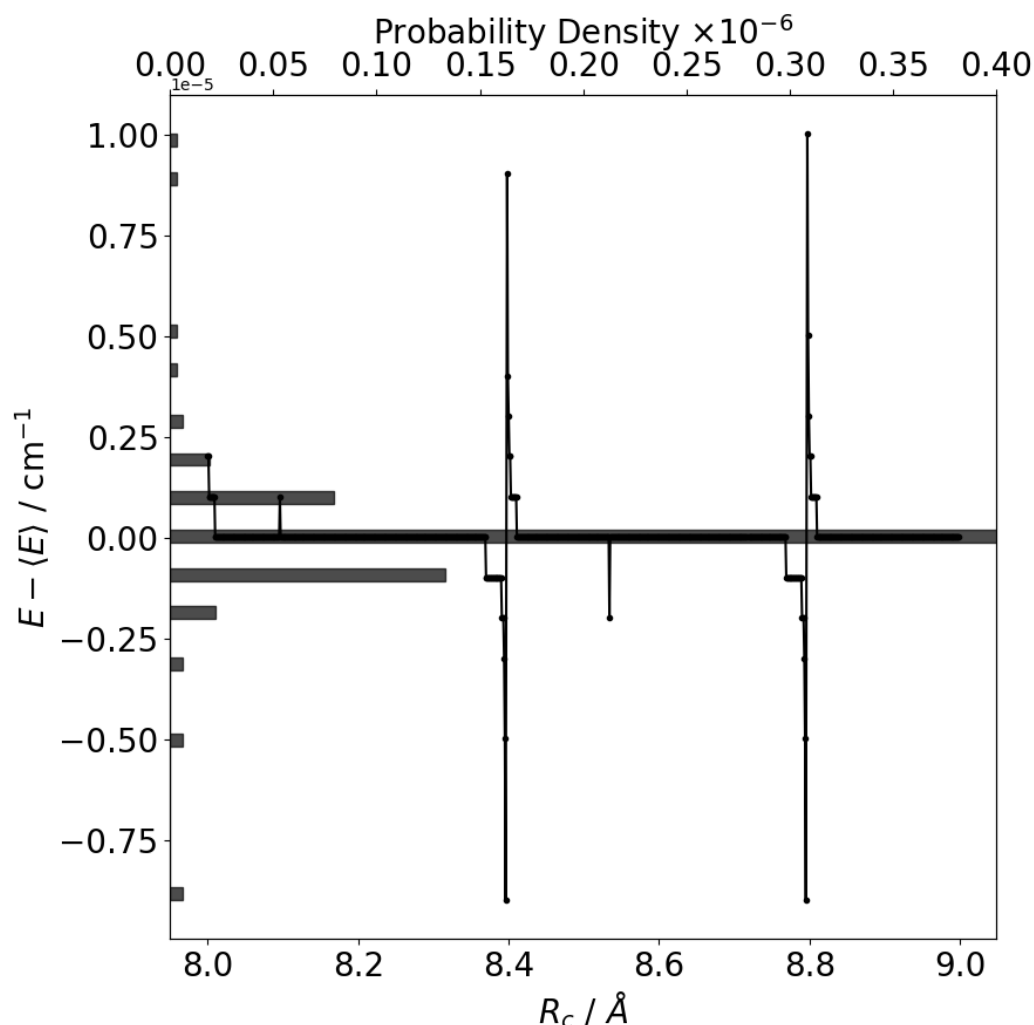


Figure 5.9: Example of a narrow energy profile resulting in a sparsely populated integral normalised histogram of the term values. This distribution results in an erroneous Lorentzian energy profile and cannot be used.

a null value for the predissociation lifetime. In these cases, it is assumed that $\tau_{\text{so}} \gg 0$, so the effect on the total lifetime upon convolution (Equation 4.47) is hence assumed to be minimal as well.

5.3.5 Skewed Energy profiles

When performing the procedure in 5.3.3, a sufficient number of bin-dependent lifetimes need to be extracted, else a distribution of values cannot be recovered and one cannot fit a meaningful Gaussian distribution. Furthermore, fitting the Lorentzian becomes more difficult when the energy profile is very skewed such as in fig 5.10. In both the cases of a discontinuous distribution and a skewed distribution, the algorithm will likely fail to return a lifetime and these must be examined individually. In these instances, energy profiles are examined individually and a lifetime is calculated case-by-case. In general, Lorentzian profiles are fit over all bin numbers previously attempted, and the fit which returns the lowest χ^2 test statistic is accepted to be the best representation of the energy profile. This does not, however, allow for the estimation of σ_τ , and so the Gaussian uncertainty is estimated

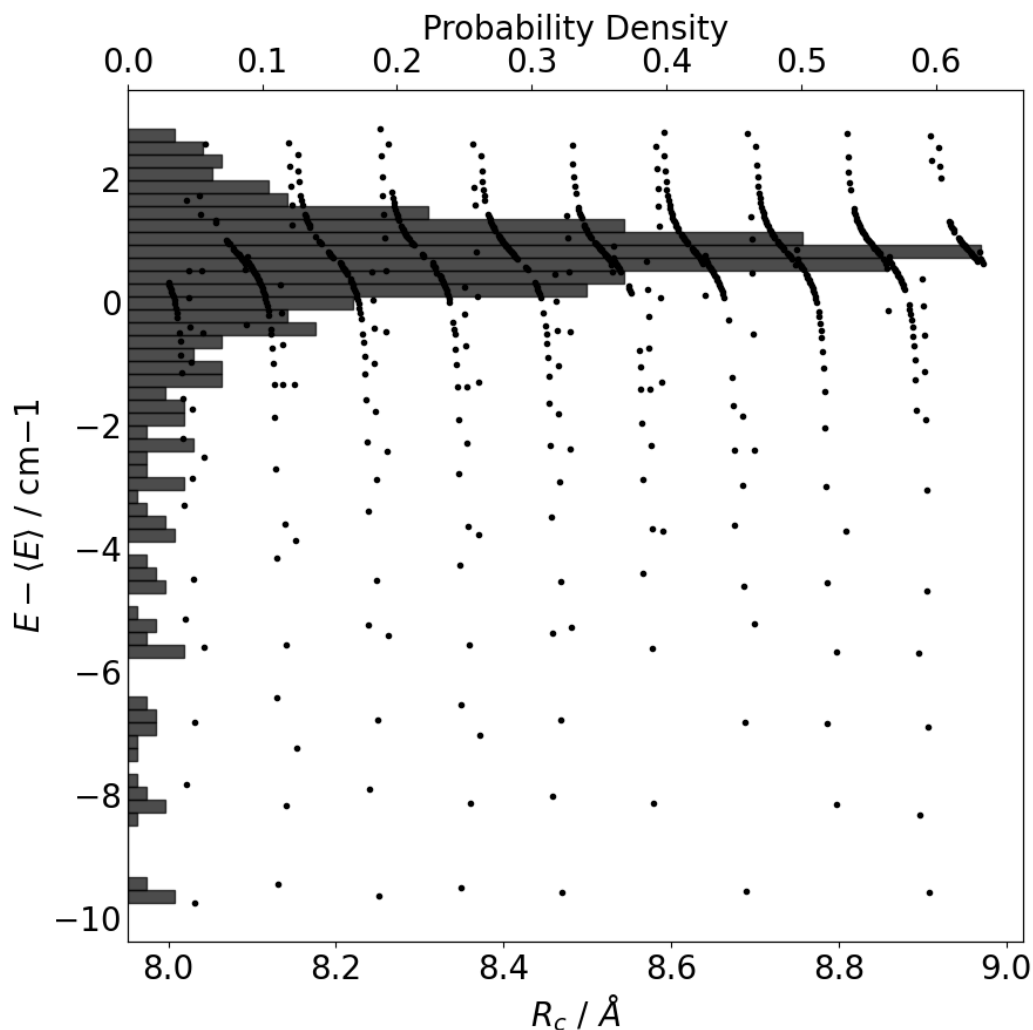


Figure 5.10: Example of a skewed energy profile. Distributions like this are harder to fit as information on the topside wings is not present. In cases such as this, an insufficient number of lifetimes are extracted to treat statistically as in Figure 5.8.

at a conservative $3\langle\sigma_\tau\rangle$.

It is important at this point to acknowledge that there are several sources of uncertainty when using this method to calculate predissociation lifetimes. Along with the Gaussian uncertainty described here, the spectroscopic model itself is a source of uncertainty. The positions of the mutually perturbed quasi-bound and continuum states impact the energy profiles. Extending this, the shapes of the $A^2\Sigma^+$ and $1(2\Sigma^-, 4\Sigma^-, 4\Pi)$ curves, their positions relative to the $X^2\Pi$ state, and the strengths of the SOCs are all variables in the lifetime calculation. A quantitative description of the uncertainty estimates is given in Section 5.3.6.

5.3.6 Uncertainty estimation

As this numerical procedure is based on a fitting routine and not a rigorous calculation, there are multiple sources of uncertainty to consider here. Typically, the largest percentage uncertainties occur with levels with longer lifetimes as the energy profiles are very narrow. In these cases, a very high point density is needed to capture fine structures. In these cases, predissociation lifetimes are on a similar scale as the radiative lifetimes, so the return on

investment for more accurate computation is not sufficient, so energy profile calculations are limited to 1000 points. Here, four components have been identified as sources of uncertainty and are assumed independent and systematic and so are added to produce a final uncertainty Δ_τ :

$$\Delta_\tau = \Delta_M + \Delta_R + \Delta_B + \Delta_C, \quad (5.15)$$

where Δ_M is the uncertainty from convergence which is defined as $1 - M$ where M is the convergence level of the lifetime for a given state. This is typically the largest uncertainty and in cases of long lifetimes ($\tau_{so} > 10^6 ps$) this can be as high as 60%. Details of how these values are estimated in section 5.3.6.1.

Δ_R and Δ_B are the uncertainties from the positions of the repulsive and bound states' energy levels respectively. Δ_B is very difficult to measure directly, as it requires that the energy level positions of the bound states can be controlled with high precision in order to establish a relationship between the energy offset and the lifetime. This is, at the moment, infeasible. This has been estimated, however, by probing the effect the repulsive energy level positions have on the lifetimes. The asymptotic energy of the continuum states go to the $O(^3P)$ level, the same as the $X\ ^2\Pi$ state. $D_0(X)$ has been experimentally measured to an uncertainty of 10 cm^{-1} by Joens (2001) (see Section 4.3.2.3). The continuum curves were set to have the same D_e as $X\ ^2\Pi$ initially and were shifted down by 20 cm^{-1} to measure the effect this has on the lifetimes. The lifetimes for the predissociative states with $J = 0.5, 1.5$ were re-computed and compared to the original model. This gives a conservative estimate on the uncertainty of the position of the continuum curves, Δ_R of about 5%. Δ_B is hence also estimated at 5%.

Δ_C is the uncertainty of the numerical procedure excluding the problem of convergence and is equal to σ_τ from Equation 5.14. This is evaluated *in situ* for each state (Section 5.3.3) and has an average value over all states of approximately 2% in the case of OH. These uncertainties are distributed exponentially as seen in Figure 5.11

5.3.6.1 Convergence uncertainty - Δ_M

For longer lifetime energy levels, the energy profile is narrower, asymptotic regions are more sparsely populated, and the available asymptotes require more points for effective description than do those in the broader energy profiles which result in shorter lifetimes. This relationship can be probed by *loading* the energy profile in from left to right, refitting the Lorentzian (Equation 5.6) at each step and seeing how it affects the lifetime calculated.

Considering that the full energy profile (see Figure 5.3) has a minimum and maximum value for R_c : R_{c_1} and R_{c_2} and a grid spacing ΔR_c , *loading* works as follows:

1. The R_c domain is restricted to some initial values,
 - (a) in this case $R_c \in [R_{c_1} = 8, R_{c_2} = 8.2]$,
2. The restricted energy profile is formed,
3. The Lorentzian distribution (Equation 5.6) of the restricted energy profile is fit, and a lifetime is calculated and stored,

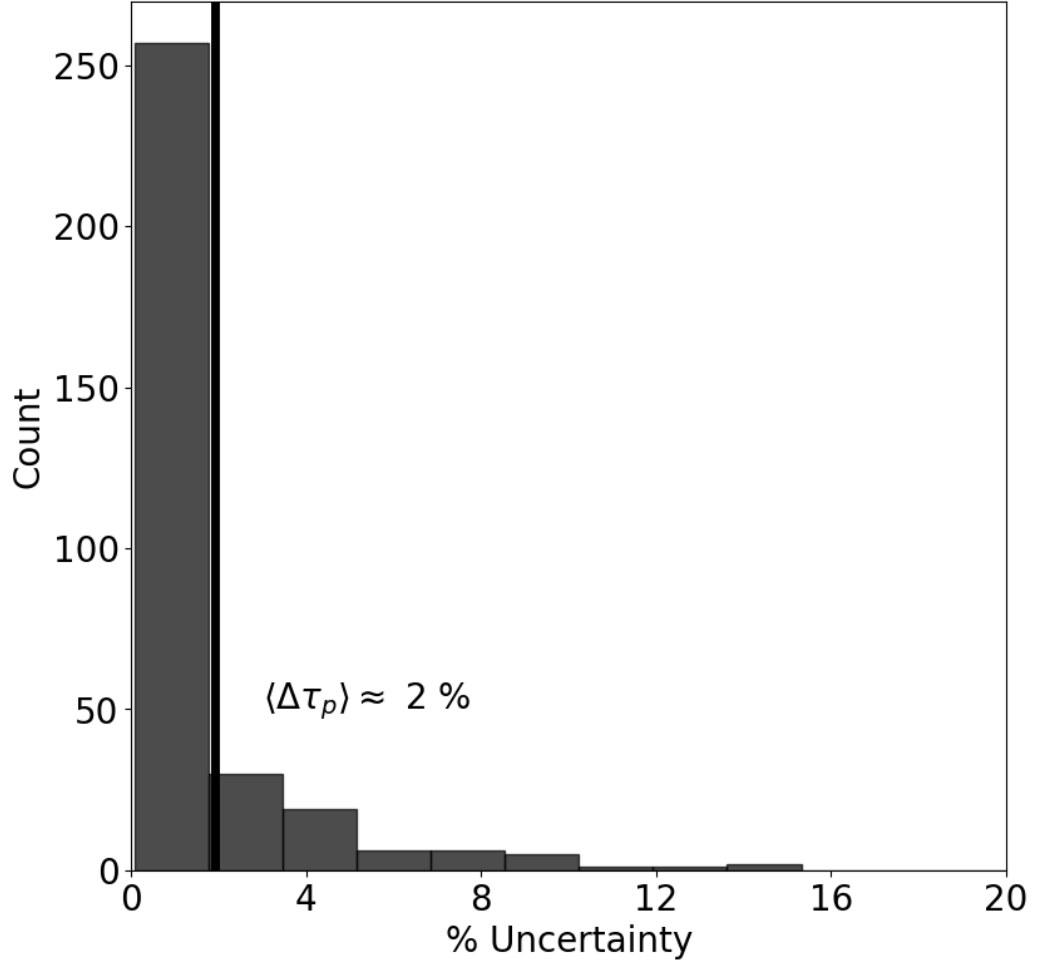


Figure 5.11: Distribution of percentage uncertainties in the lifetime induced by the computational procedure.

4. The R_c domain size is increased by increasing R_{c_2} by ΔR_c . In pseudo-code: $R_{c_2} = R_{c_2} + \Delta R_c$.
5. Steps 3 – 4 are repeated until the full domain is returned.

This forms a relationship between the domain size, i.e. the percentage of the energy profile *loaded*, and the lifetime. At each iteration, more information is supplied to the fitting algorithm and the value of the lifetime converges.

To measure the convergence, we take the moving average, $\mu(\tau_i; W)$,

$$\mu(\tau_i; W) = \frac{1}{W} \sum_{j=i-W}^i \tau_j \text{ for } j, i, W \in \mathbb{N}, \quad (5.16)$$

and the moving standard deviation, $\sigma(\tau_i; W)$,

$$\sigma(\tau_i) = \sqrt{\frac{1}{W} \sum_{j=i-W}^i (\tau_j - \mu(\tau_i))^2}, \quad (5.17)$$

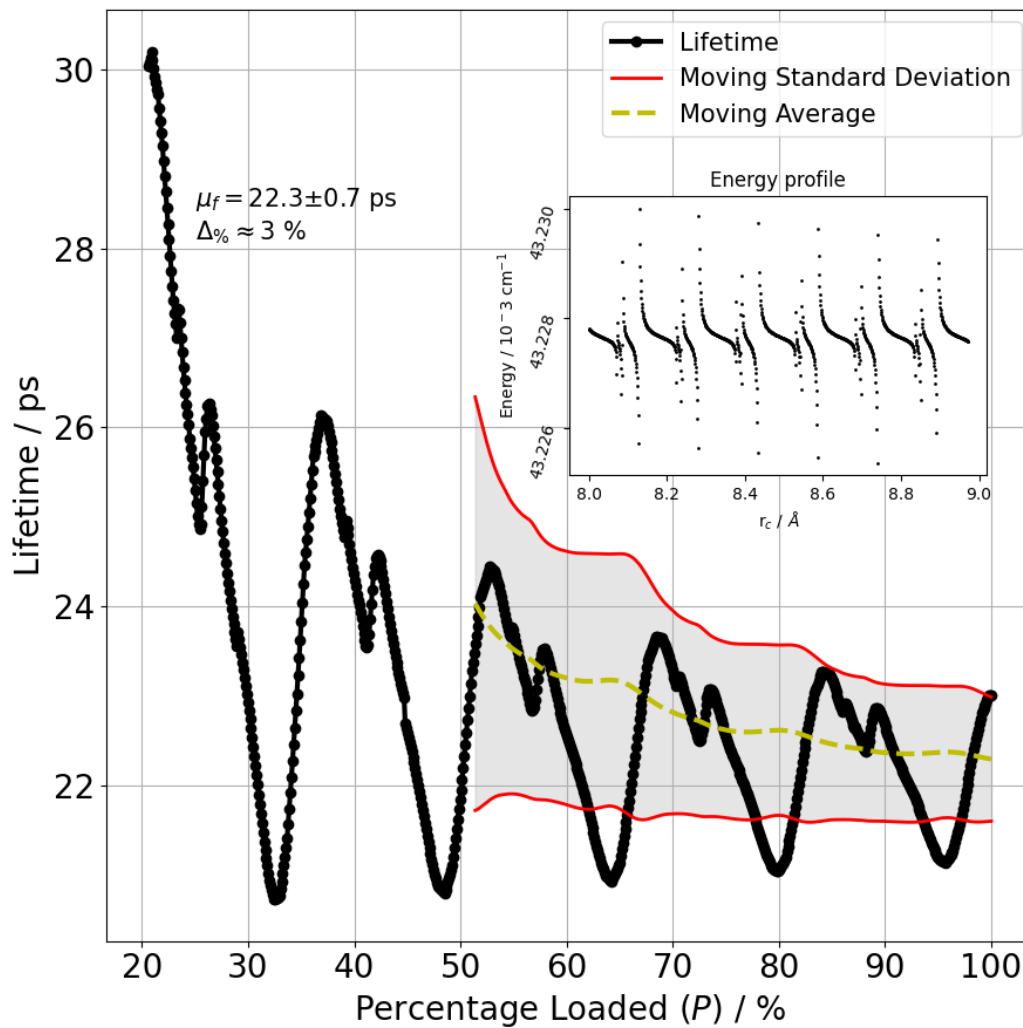


Figure 5.12: The energy profile (subplot) for $|\text{OH}, A, 0.5, 4, f\rangle$ is loaded in from left to right starting with $R_c \in [8, 8.2]$ Å. The lifetime is recomputed at each step and presented here. The lifetime converged to a $\sim 3\%$ uncertainty against the moving average at 100%.

which return the mean and standard deviation over W points preceding τ_i . Hence the convergence ratio, $\varepsilon = 1 - M$, is defined as,

$$\varepsilon = \frac{\sigma_f}{\mu_f}, \quad (5.18)$$

where μ_f and σ_f are the final values of the moving average and the moving standard deviation respectively; lower is better.

For the broader energy profile like that for the state $|\text{OH}, A, 0.5, 4, e\rangle$, one can see that the lifetime converges as more information is supplied to the algorithm, see Figure 5.12.

For a narrower energy profile, like for $|\text{OH}, A, 17.5, 1, e\rangle$ (Figure 5.13), the lifetime does not appear to converge as well. Hence, to fit meaningful Lorentzian distributions, both a sufficient range of R_c and a sufficient resolution, δ_{R_c} are required. The value of δ_{R_c} needs not be uniform over the range, and higher emphasis can be placed on asymptotic regions during the calculation of the .STATES files as has been similarly done by Tennyson & Noble (1984).

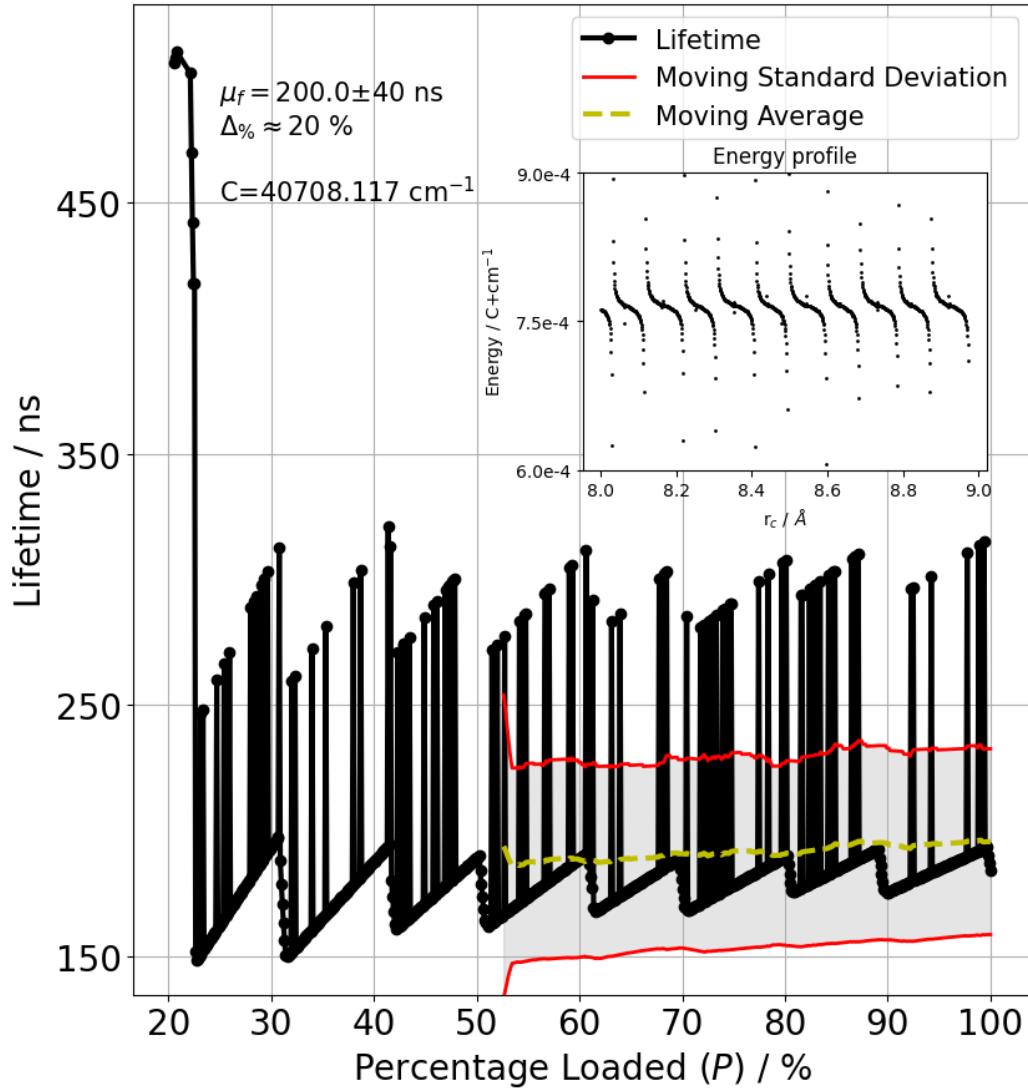


Figure 5.13: The energy profile (subplot) for $|\text{OH}, A, 17.5, 1, e\rangle$ is loaded in from left to right starting with $r_c \in [8, 8.2]$ Å. The lifetime is recomputed at each step and presented here. The lifetime converged to a $\sim 20\%$ uncertainty against the moving average at 100%.

This convergence property increases the lifetime uncertainty for longer lifetimes and has been factored in during uncertainty estimation as per Equation 5.15.

5.3.7 Stabilization Fitting

The final centroid position is determined through the fitting procedure outlined above, and the value of the centroid position, E_{Cent} , is determined as,

$$E_{\text{Cent}} = \tilde{E}_0 + \langle E_i \rangle, \quad (5.19)$$

where $\tilde{E}_0$ is the fitted parameter from Equation 5.6 and $\langle E_i \rangle$ is the average value of the initial data set. As per Equation 5.11, we make the assumption that the difference between quasi-bound and bound term values is less than the vibrational spacing. The implication of this is that these energy levels are, in fact, different to begin with. Indeed, we find that these levels are different and can differ significantly:

$$E_{\text{Cent}} \neq E_b. \quad (5.20)$$

In Chapter 4, we made the decision to neglect the effect of spin-orbit coupling to the continuum as a way to augment the positions of the A $^2\Sigma^+$ state energy levels as a matter of pragmatism. Instead, the diagonal spin-rotational coupling constant, γ , and the off-diagonal spin-orbit coupling curve, ξ_{XA} , and angular momentum coupling curve, L_{XA} , are adjusted accordingly to deal with this.

However, a fuller treatment of the coupling to the continua can be formulated where E_{Cent} is taken as the energy instead of E_b , as E_{Cent} can be interpreted as the true energy position when allowing for the inclusion of continuum states. This then allows for the implementation of stabilization fitting, whereby all energy levels are computed through the stabilization procedure as E_{Cent} .

While this may be a nice solution in theory, in practice it is tremendously expensive with the stabilization algorithm thus far described. When fitting with $E = E_b$, as in Section 4.3, a DUO run contained up to 300 iterations. After each iteration, gradients between the calculated and observed eigenvalues are computed, informing the adjustment of the model parameters. Hundreds of runs were required to achieve the OH spectroscopic model, varying different parameters at each stage in order to reach a stable solution. The amount of individual iterations considered here would hence be of the order of thousands.

This is feasible as the calculation of the set of eigenvalues, $\{E_b\}$, take on the order of seconds to minutes. Implementing stabilization fitting would extend the time taken for each individual iteration to, at the very minimum, days. Furthermore, the values of E_{Cent} are not as precisely calculated as E_b , which have a 10^{-6} cm^{-1} numerical accuracy. Determining the numerical accuracy of E_{Cent} is a problem in itself.

Stabilization fitting is a theoretically simple method to treat the continuum using the current bound-like methods from DUO. However, it would require significant optimization of the implementation outlined in this work. This is left, speculatively, as future work.

5.4 Rotational Predissociation

As outlined in Section 4.4, the assignment of vibrational quanta for levels above D_e is unreliable. This makes measuring the spin-orbit induced predissociation lifetimes in this region much more difficult because the production of energy profiles is reliant on matching energies on quantum numbers, which is already challenging as outlined in Section 5.3.1. Furthermore, in this region, there is the introduction of shape resonances which results in rotational predissociation. It was found that the stabilization method was ineffective at producing accurate estimates for shape resonances and a treatment using LEVEL (Le Roy, 2017b) was used to calculate these lifetimes for AlH (Yurchenko et al., 2018b). This method is proven to give useful results as these lifetime calculations allowed for the detection of AlH in an optically thick region of Proxima Centauri (Pavlenko et al., 2022), as is the motivation for studying predissociation in this context.

The shape resonances shift the energy levels as a function of R_c and make assignment in this region even more challenging. It is likely that the inefficacy of the stabilization method for this case is due to difficulty in assignment of the R_c -dependent energy levels. This makes it very difficult to produce useful energy profiles. Overcoming this, one still cannot

decouple the rotational and spin-orbit predissociation and instead must compute the total non-radiative lifetime in the region above D_e .

One could then extract an estimate for the spin-orbit predissociation lifetime using the relationship in Equation 5.21.

$$\tau_{\text{Spin-Orbit}}^{-1} = \tau_{\text{Rotational: LEVEL}}^{-1} - \tau_{\text{non-radiative: Stabilization}}^{-1} \quad (5.21)$$

For the time being, it appears that the stabilization method is not appropriate for use for rovibronic levels with energy above the dissociation energy of the corresponding electronic state.

5.5 Results - OH

5.5.1 Lifetime Analysis

BINSLT was used to analyse the 547 bound-labelled A $^2\Sigma^+$ rovibronic levels of OH, resulting in 475 evaluated spin-orbit induced predissociation lifetimes.

This was computed by setting the binning range (Section 5.3.3) to [30, 400] in unit steps, with K (Equation 5.12) equal to 10 cm^{-1} . As with the treatment of the binning numbers, it was found that using different N (Equation 5.9) also returned different results. The procedure outlined in Section 5.3 was performed with $N = [3, 4, 5]$, and resulting statistical lifetimes, τ_N , were averaged, and associated $\Delta_C(N)$ (Section 5.3.6), were propagated as,

$$\Delta_C = \frac{1}{|\{\Delta_C(N)\}|} \sqrt{\sum_N (\Delta_C(N)^2)}, \quad (5.22)$$

where $|\{\Delta_C(N)\}|$ is the number of resolved statistical lifetimes. A tabulation of

This procedure initially returned 436 non-null lifetimes out of the 547 rovibronic levels analysed. As stated earlier, this procedure relies on fitting distributions, which is not straightforward to do automatically without any mistakes. Initially, the full dataset was split into two subsets using the following relationship for each level,

$$\text{Category} = \begin{cases} \text{valid} & \text{if } \tau \neq \emptyset \text{ and } \tau > \Delta_C \\ \text{invalid} & \text{if } \tau = \emptyset \text{ or } \tau < \Delta_C. \end{cases} \quad (5.23)$$

The second condition tests if the value of Δ_C is overestimated and requires extra work. The valid subset contained 411 elements, and the invalid subset contained 136 elements. 25 of the invalid datasets contained non-null lifetimes but still met the condition that the uncertainty was greater than the lifetime. The remaining datasets had $\tau = \emptyset$.

All fitted Lorentzian distribution parameters for all binning and cutoff numbers are saved automatically along with all lifetimes and uncertainties in a .BLT file. For each state and cutoff number, there is an associated *FitInfos* object instance which contains Lorentzian distribution parameters for each bin number which did not fail. After the initial calculation, all energy profiles were binned with $N_B = 100$, and the fitted parameters were averaged for $N = 5$ for each rovibronic level to return a distribution used for inspection. Each rovibronic level's histogram and fitted distribution was plotted, saved, and inspected visually to assess

Table 5.1: Conditions for assigning confusion tags for visually assessed energy profile Lorentzian fits. ✓: Condition met, ✗: Condition not met

Tag	Category	C_1	C_2	C_3
True Positive (TP)	Valid	✓	✓	✓
False Positive (FP)	Valid	✗	✗	✗
True Positive - Bad Fit (TP-BF)	Valid	✗	✓	✓
True Negative (TN)	Invalid	✗	✗	✗
False Negative (FN)	Invalid	✗	✓	✓

the algorithm’s results as a sanity check. These inspection plots were assessed visually with three criteria.

- C_1 : The fitted distribution should represent the histogram reasonably,
- C_2 : The histogram should not be sparsely populated as in Section 5.3.4,
- C_3 : The histogram should have the expected shape as in Figure 5.6.

This, of course is a qualitative assessment of the results and is a significant weakness of the methods presented. At this stage, however, this serves as a reasonably effective method for calculating spin-orbit induced predissociation lifetimes, and as a proof of concept. It is not too time consuming to assess these distributions for this case, where only 547 levels are concerned, however, for polyatomic molecules, this would likely be prohibitive. This can be improved further by leveraging machine learning methods, or more sophisticated statistical treatments. However, time constraints made these difficult to implement. Furthermore, machine learning treatments would require supervision and a substantial training set for categorization, so visual inspection here would be unavoidable. This is, hence, left as future work.

Inspection resulted in a further separation of the dataset and five confusion Tags were assigned to the levels as shown in Table 5.1.

Examples of Energy profiles with the associated tag are provided in Figure 5.14 and the populations of each tag after inspection are given in Figure 5.15.

The TP-BF and FN tagged energy profiles were refit with $N_B = 100$ and good fits were extracted for these states. As the procedure to estimate Δ_C could not be implemented for these cases, an estimate of three times the average percentage uncertainty, $3\langle\Delta_{C\%}\rangle$ was taken where,

$$\Delta_{C\%}(\tau_i) = \Delta_C(\tau_i)/\tau_i. \quad (5.24)$$

This was calculated based only on TP tagged results and the average percentage uncertainty here is $\langle\Delta_{C\%}\rangle \approx 2\%$. The FP and TN predissociation lifetimes were assigned null values, and the TP predissociation lifetimes were left as calculated by BINSALT. The resulting dataset contains 475 predissociation lifetimes for the A $^2\Sigma^+$ state of OH.

The procedure outlined in Section 5.3.6.1 was performed over many levels to find a relationship between the lifetime of a state and the level of convergence. For sake of simplicity, this procedure was performed only on levels which have been tagged TP, as these levels’

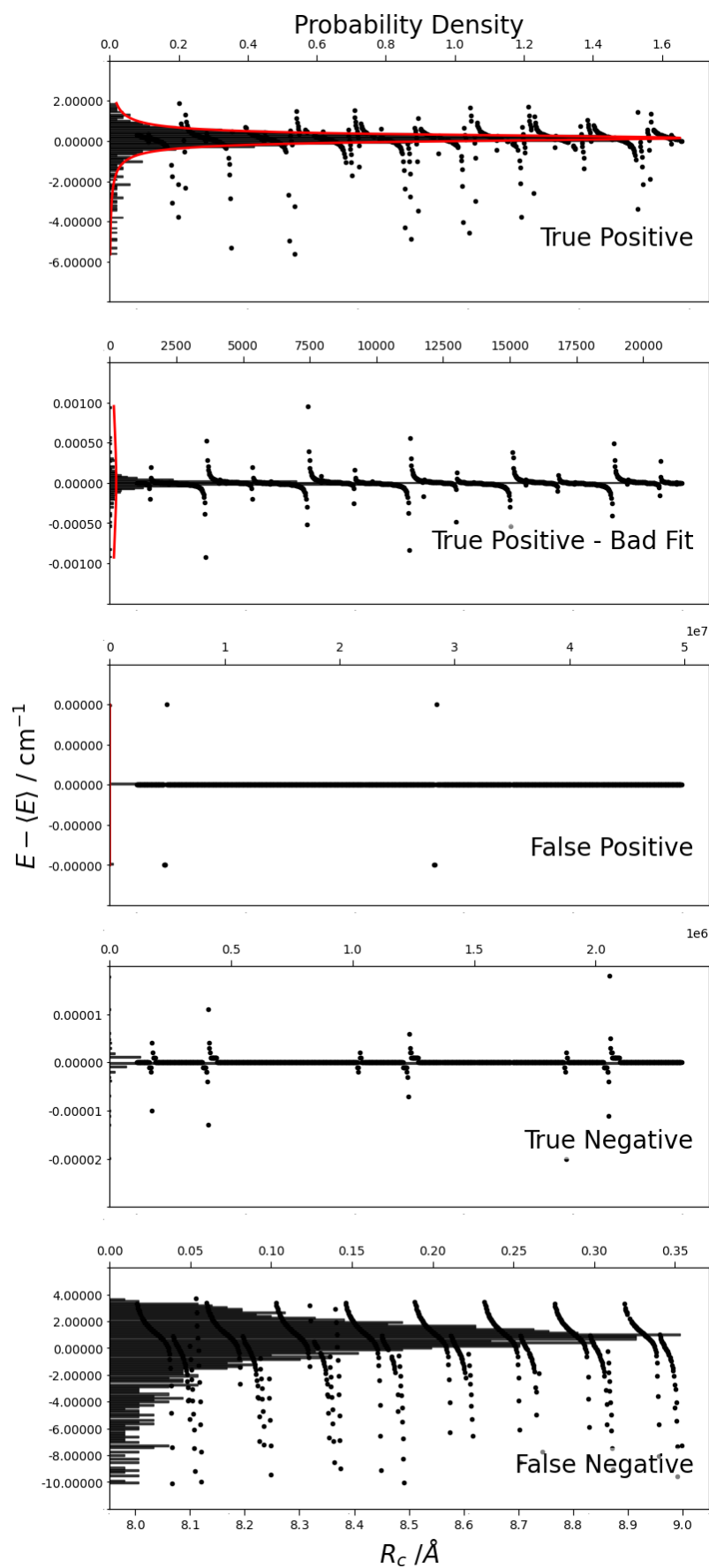


Figure 5.14: Examples of TP, TP-BF, FP, TN, and FN predissociation energy profiles of OH.

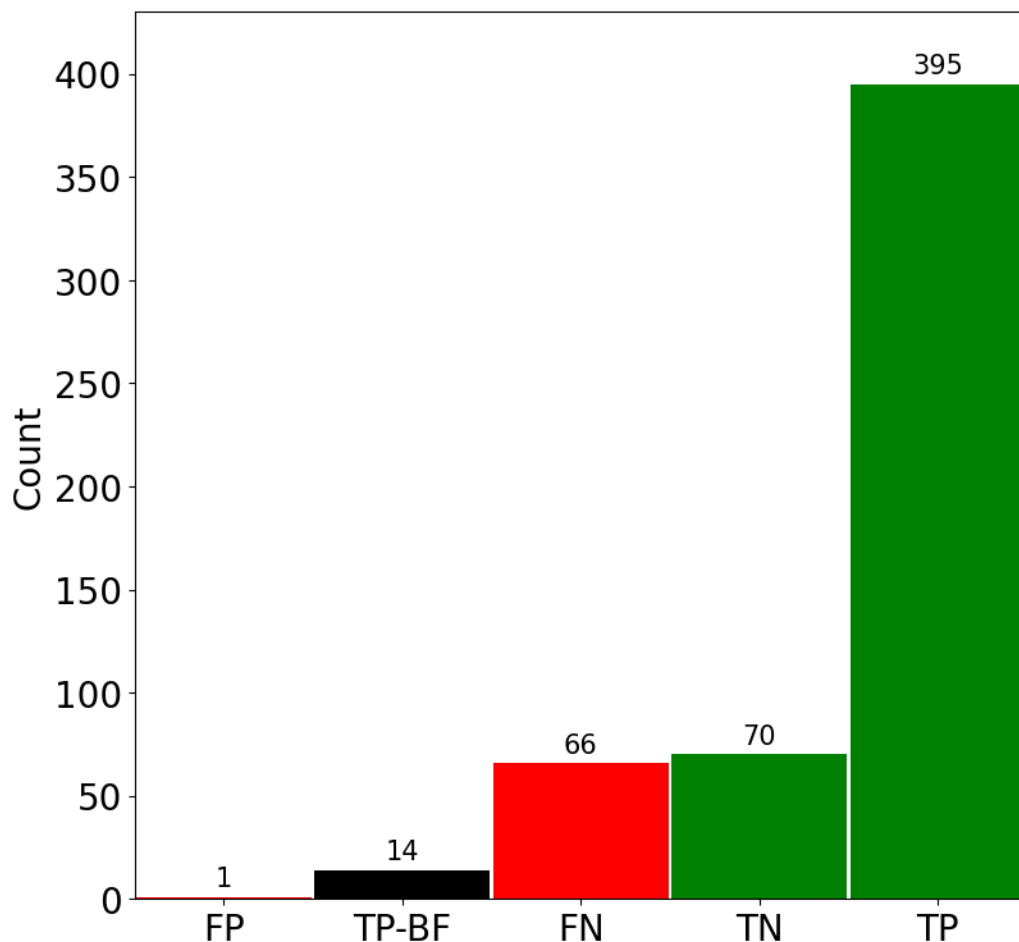


Figure 5.15: Population of OH predissociation energy profile tag datasets.

lifetimes can be more reliably modelled with the methods outlined. Furthermore, as per the discussions in Sections 5.3.7 and 5.4, the levels have further been limited to the those with $D_e(X) < E_b < D_e(A)$.

As some levels do not show a stable convergence of the fit for a given bin number as per Section 5.3.3, the convergence procedure is carried out with $N_B \in [100, 150, 200]$. Then the harmonic average (Equation 5.25) of the lifetimes and convergences (μ_f and ε from Equation 5.18 respectively) are calculated to better account for outliers.

$$\langle (x_1, x_2, \dots, x_n) \rangle_H = \frac{n}{\sum_{i=1}^n \frac{1}{x_i}}. \quad (5.25)$$

From here, it is found that for lifetimes less than 10^5 ps, convergence uncertainty is generally better than 5% with an average of $\sim 2\%$. When lifetimes are longer than this, the uncertainties increase, as it is harder to fit a Lorentzian distribution to a narrower, more sparsely populated profile. For levels with $10^5 < \tau_{so} < 10^6$ ps, the average convergence uncertainty is $\sim 9\%$ with a maximum of $\sim 53\%$. There are only two levels with $\tau_{so} > 10^6$ ps, so measuring the convergence over this range is dubious. However, the average convergence uncertainty here is $\sim 39\%$ with a maximum of $\sim 66\%$. Figure 5.16 presents the convergence ratios against the order of magnitude of the lifetime. From this we arrive at the rules in Table 5.2.

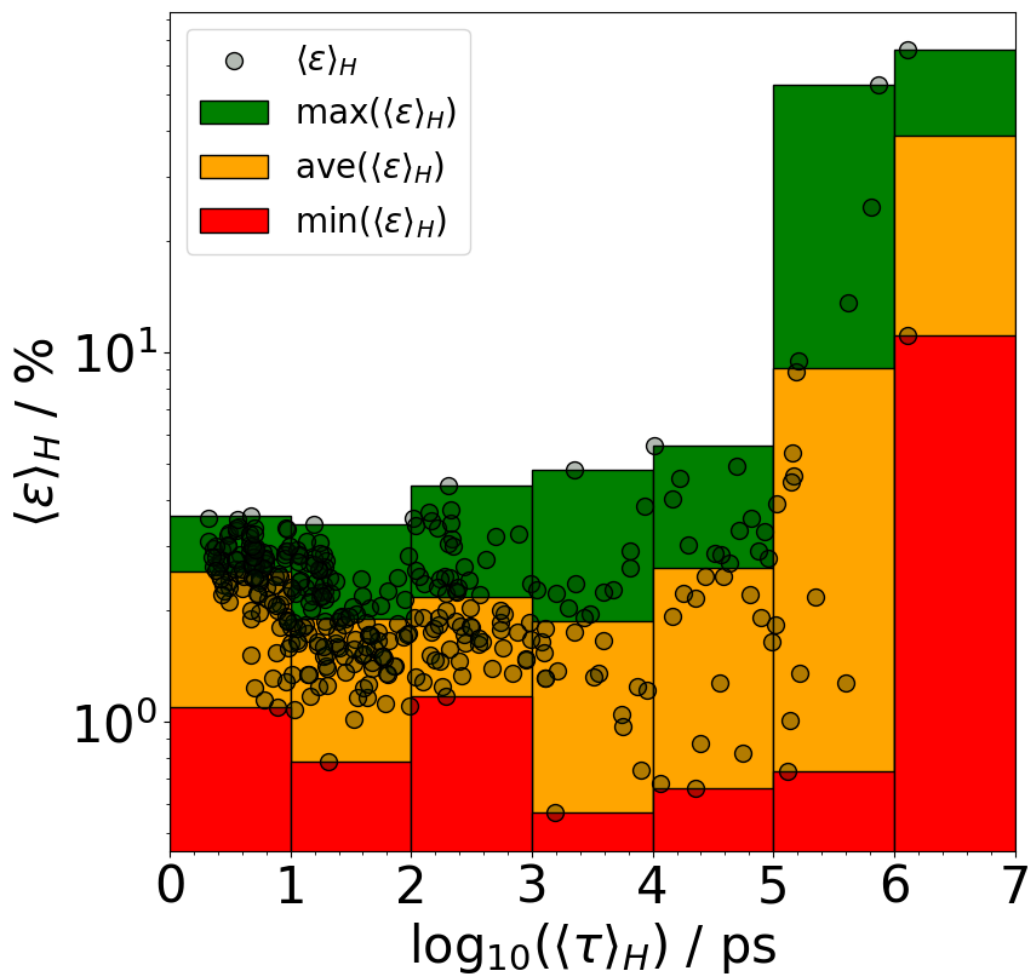


Figure 5.16: Harmonically averaged convergence ratio, $\langle \epsilon \rangle_H$ against order of magnitude of predissociation lifetimes of OH as calculated using the modified stabilization method.

Table 5.2: Rules for assigning uncertainties to predissociation lifetimes of OH as calculated using the modified stabilization method. Δ_C is calculated *in situ* for each level. $\Delta_{\tau_{so}}$ is calculated as Equation 5.15 with $\Delta_R = \Delta_B = 5\%$.

Lifetime Range / ps	Δ_M / %	$\Delta_{\tau_{so}}$
$10^0 < \tau_{so} < 10^5$	2	$\Delta_C + 12\%$
$10^5 < \tau_{so} < 10^6$	9	$\Delta_C + 19\%$
$10^6 < \tau_{so}$	39	$\Delta_C + 49\%$

The resulting lifetimes are presented in Figure 5.17. For $v > 4$ the lifetimes behave less predictably, wherein they do not decrease monotonically. The cause of this has not yet been identified with certainty however it is expected that this is due to the quasi-bound energy level falling outside of the main crossing region. This figure is separated into two panels, with the left covering the region where $E_b > D_e(A)$ and the right covering the region where $E_b \geq D_e(A)$ in light of the discussion in Sections 5.3.7 and 5.4. The predissociation lifetimes of the rovibronic levels above dissociation are unreliable, and as such are not appropriate for use in modelling the spectrum of OH. This concerns 61 rovibronic levels, hence, the final count on available predissociation lifetimes from this work is 414.

The widths, Γ (Equation 5.7) generally increase with energy as expected, and are distributed as in Figure 5.18.

5.5.2 Comparison with Literature

Predissociation lifetimes of the $A^2\Sigma^+$ state of OH have long been the subject of theoretical and experimental studies, a summary of available literature data has been provided in Table 5.3.

The data provided by Heard et al. (1992); Spaanjaars et al. (1997) are given as predissociation rates, R_p and these have been inverted to return the required predissociation lifetimes,

$$\tau_p = \frac{1}{R_p}. \quad (5.26)$$

Brzozowski et al. (1978) provides measurements of the total lifetime which is given by

$$\tau_{\text{tot}} = \frac{\tau_r \tau_n}{\tau_r + \tau_n}, \quad (5.27)$$

where τ_r and τ_n are the radiative and non-radiative lifetimes respectively. As these values include also the radiative lifetime, we expect our calculations to be greater than these values. This is compounded by the fact that the predissociation in the region of $v \in [0, 1, 2]$ is less dominant than in $v \geq 3$.

A comparison with the lifetimes available in the literature (experiment and theory) and this work is illustrated in Figure 5.19, where the lifetime values are plotted as a function of J . The corresponding J -averaged percentage errors and their standard deviations are given in Table 5.4.

Table 5.4 shows that there is satisfactory agreement between the lifetimes presented here and experiment; there is particularly good agreement for the cases where $v = 3, 4$, see Figure 5.19. For levels where the lifetimes do not agree within mutual uncertainties, the mean percentage real difference in this region is 12.5%. The percentage real difference, ${}^R\Delta\%$ and percentage difference, $\Delta\%$ here is defined as

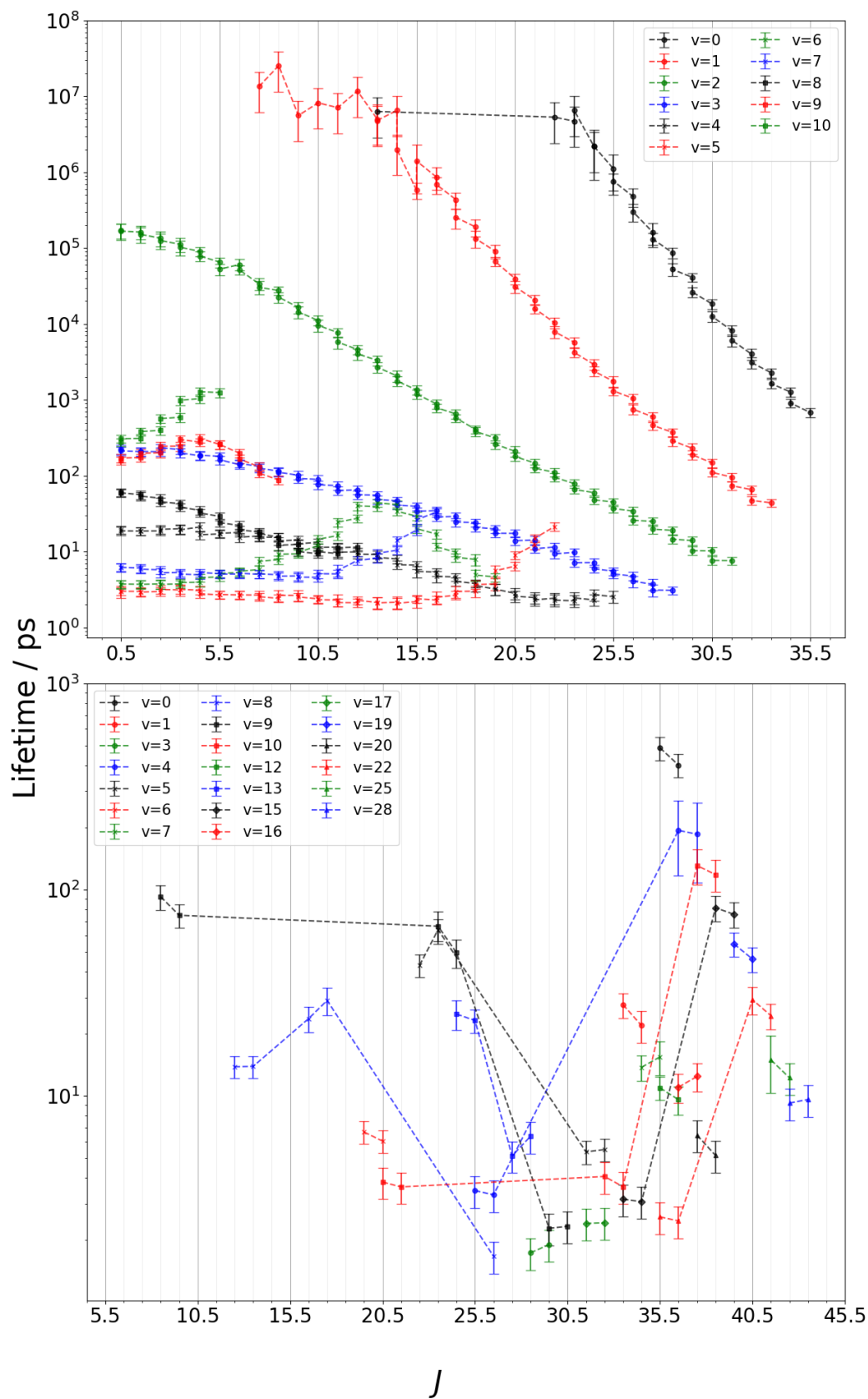


Figure 5.17: Predissociation lifetimes of OH organized by vibrational and rotational quanta. Top panel: Predissociation lifetimes for rovibronic levels with $E_b < D_e(A)$. Bottom panel: Predissociation lifetimes for rovibronic levels with $E_b \geq D_e(A)$

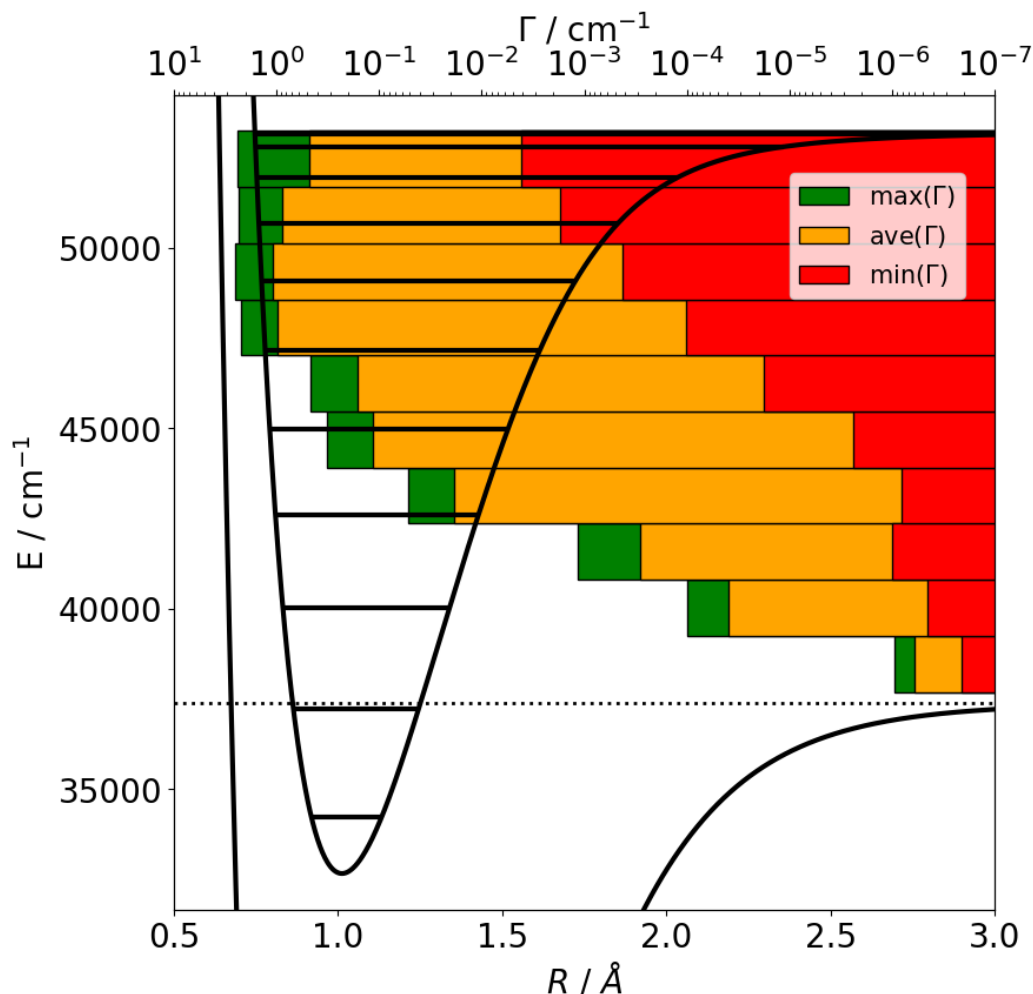


Figure 5.18: Distribution of predissociation widths, Γ of the A $^2\Sigma^+$ state of OH binned over energy. Solid horizontal lines: Positions of vibrational band centres of the A $^2\Sigma^+$ state ($J = 0.5, p = e$). Dotted line: Position of $D_e(X)$.

Table 5.3: Summary of predissociation lifetime data available from experimental and theoretical sources. Data column: τ_p represents predissociation lifetime, τ_{tot} represents total lifetimes (Equation 5.27), R_p represents predissociation rates.

	Lifetime (ps)		ν		J			
Reference	Min	Max	Min	Max	Min	Max	Number	Data
Experiment								
Derro et al. (2005)	17	23	4	4	0.5	7.5	8	τ_p
Sun et al. (2021)	14	130000	2	4	0.5	2.5	2	τ_p
Brzozowski et al. (1978)	33000	1110000	0	2	0.5	29.5	118	τ_{tot}
Gray & Farrow (1991)	73	500	3	3	0.5	9.5	17	τ_p
Heard et al. (1992)	62.89	312.50	3	3	0.5	13.5	27	R_p
Spaanjaars et al. (1997)	29	167	3	3	4.5	14.5	20	R_p
Theory								
Sink et al. (1980)	2.95	428.16	3	9	No J		7	τ_p
Kalyanaraman & Sathyamurthy (1994)	3.32	6895.10	1	7	No J		7	τ_p
Parlant & Yarkony (1999)	6000	9666000	0	4	0.5	30.5	107	τ_p
Grand Total							313	
This work	2.1	25000000	0	10	0.5	35.5	414	τ_p

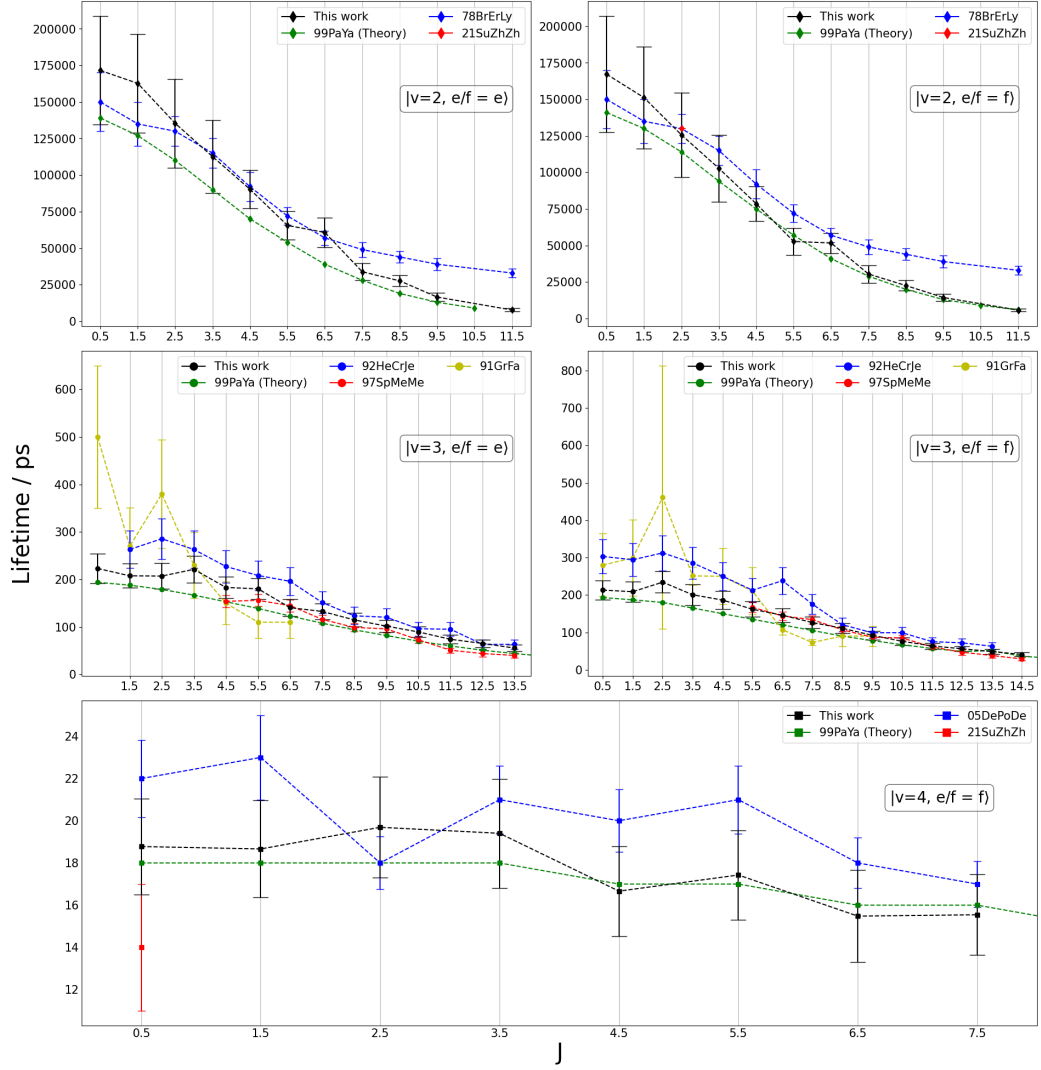


Figure 5.19: Predissociation lifetimes as calculated in this work compared to experimental values from 05DePoDe (Derro et al., 2005), 78BrErly (Brzozowski et al., 1978), 91GrFa (Gray & Farrow, 1991), 92HeCrJe (Heard et al., 1992), 97SpMeMe (Spaanjaars et al., 1997), and 21SuZhZh (Sun et al., 2021), and theoretical values from 99PaYa (Parlant & Yarkony, 1999).

$$D = \frac{|\Delta| - (\delta_{\text{calc}} + \delta_{\text{lit}})}{\tau_{\text{lit}}}, \quad (5.28)$$

$$R_{\Delta\%} = \begin{cases} D & \text{for } D > 0 \\ 0 & \text{otherwise,} \end{cases} \quad (5.29)$$

$$\Delta_{\%} = \frac{\tau_{\text{lit}} - \tau_{\text{calc}}}{\tau_{\text{lit}}} \equiv \frac{\Delta}{\tau_{\text{lit}}}, \quad (5.30)$$

where $\tau_{\text{lit, calc}}$ are the literature and calculated predissociation lifetimes respectively, Δ is the difference in those values, and $\delta_{\text{lit, calc}}$ are the uncertainties quoted in the literature and calculated values respectively.

Table 5.4: Summary of comparison between A $^2\Sigma^+$ predissociation lifetimes as calculated in this work and available literature values. Differences are averaged over J for a given v . Only rotationally resolved literature lifetimes are compared here (see Table 5.3).

Type	Ref	v	$\langle\Delta\%$	Number	C_A	$\langle^R\Delta\%$
Exp	Derro et al. (2005)	4	11.0	8	7	0.2
	Sun et al. (2021)	2	3.3	1	1	
		4	-34.1	1	1	
	Brzozowski et al. (1978)	2	20.1	22	13	33.5
	Gray & Farrow (1991)	3	3.0	17	12	17.5
	Heard et al. (1992)	3	19.5	27	18	5.0
	Spaanjaars et al. (1997)	3	-15.4	20	16	12.4
	Total			96	68	
Theory	Parlant & Yarkony (1999)	2	-18.8	23	15	11.3
		3	-18.7	35	12	7.9
		4	-2.6	21	18	6.9
	Total			79	45	
Grand Total				175	113	

The columns are as follows:

Type = Experiment or Theory

Ref = Reference

v = Vibrational quantum number

$\langle\Delta\%$

Number = number of J resolved levels

C_A = Number of levels whose lifetimes agree within uncertainty

$\langle^R\Delta\%$: Average $^R\Delta\%$ for values which do not agree within uncertainty

5.5.3 Centroids of OH

As discussed in Section 5.3.7, the centroid position E_{Cent} , is known, in general, to differ from the bound solution position, E_b , leading to the idea of stabilization fitting as a method to treat the continuum fully using DUO. The rovibronic levels of OH are briefly examined here to show the significant change in energy one can see when treating the continuum in this manner. Only levels which are tagged TP are considered here for simplicity of calculation. The centroid for each level is calculated as per Equation 5.19. The centroid shift, Δ_E , is calculated as,

$$\Delta_E = E_b - E_{\text{Cent}}. \quad (5.31)$$

As in the treatment of the predissociation widths in Figure 5.18; the minimum, maximum, and average values of Δ_E are found, binned by energy. Figure 5.20 presents the relationship between the centroid shift and the energy for OH. The key takeaway from this figure is that not including continuum curves in the formation of a spectroscopic model can significantly impact the extent to which one can control the positions of the energy levels. In the case of OH, the maximum centroid shift is $\sim 10 \text{ cm}^{-1}$. This is significant, as this results in other coupling curves needing to overcompensate for this missing contribution as discussed in Section 4.6.1. The centroid shift increases in strength as energy increases similarly to how the widths increase with energy (Figure 5.18), as the off-diagonal coupling with the

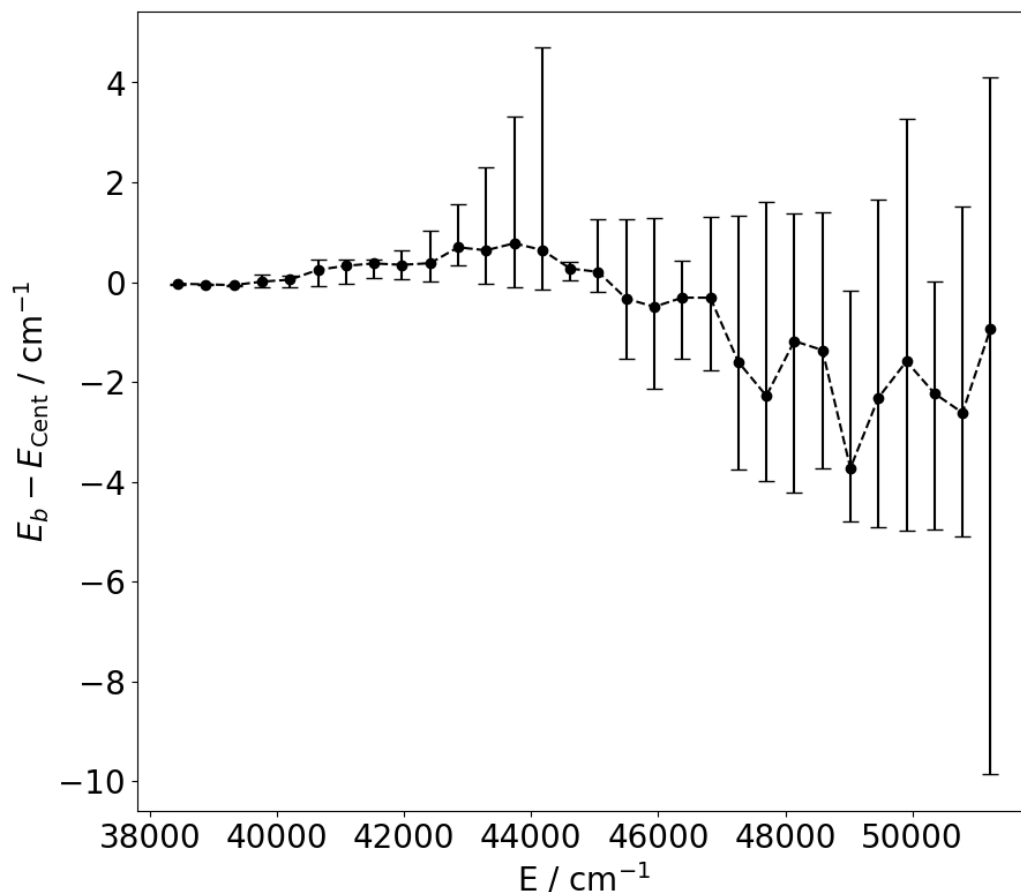


Figure 5.20: Centroid shifts of the A $2\Sigma^+$ state of OH averaged over discrete energy regions. Error bars represent minimum and maximum centroid shifts.

continuum increases in strength in this region.

5.6 Preliminary Results - SH/SD

The work done here on producing a quantitative method for extracting predissociation lifetimes from DUO .STATES files was performed concurrently with an ORBYTS (Original Research By Young Twinkle Students) project ([Sousa-Silva et al., 2018](#)) run by R. P. Brady and O. Smola, PhD students at ExoMol, Parmiters School Watford, and Kingsmead School Enfield.¹

The project was based on the current recommended ExoMol model of SH, called GYT ([Gorman et al., 2019](#); [Yurchenko et al., 2018a](#)). SH and SD are treated by changing the mass of the hydrogen, the spectroscopic model is otherwise unchanged. As sulphur and oxygen are in the same group of the periodic table, it is not surprising that they share similar curve structure, energy ordering and electronic state symmetries. Indeed the ground, first excited, and predissociation relevant repulsive states are of the same symmetry and order

¹ORBYTS is intended to widen participation of school students from disadvantaged and minority backgrounds in scientific research. Originally being primarily MARVEL based projects ([McKemmish et al. \(2017\)](#); [Chubb et al. \(2018a,b\)](#); [McKemmish et al. \(2018\)](#); [Darby-Lewis et al. \(2019\)](#)), the scope of ORBYTS has since expanded to encompass other fields of research, including astrophysics ([Francis et al. \(2020\)](#); [Edwards et al. \(2021\)](#); [Dunn et al. \(2022\)](#)) and quantum computing ([Banks et al. \(2023\)](#)).

in energy.

The bound state PECs and their associated coupling curves are taken directly from the GYT model with the repulsive $1\ (^2\Sigma^-, ^4\Sigma^-, ^4\Pi)$ PEC and coupling curves calculated *ab initio* and their dissociation energies set to $D_e(X)$. Energy profiles are calculated for SH and SD in the same fashion as with OH. The profile for SH spans $R_c \in [5, 6]$ with $\delta_{R_c} = 0.001\ \text{\AA}$ and the SD profile spans $R_c \in [10, 11]$ with $\delta_{R_c} = 0.0005\ \text{\AA}$. These energy profiles were then fit by hand, state-by-state by the ORBYTS students with supervision from Brady and Smola. There are difficulties in ensuring consistency when acquiring data this way, especially with projects like the calculations of predissociation lifetimes, as such calculations are not as established as MARVEL projects.

As this ORBYTS project is outside the remit of this thesis, the results will not be discussed here, however, the energy profiles calculated by Brady and Smola have been analysed with BINSALT to produce some preliminary results for SH. These have not gone through the full treatment as in Section 5.3, but are interesting and are briefly discussed here.

There are 539 rovibronic levels in the $A\ ^2\Sigma^+$ state of SH, of which 308 levels are in the range $E \in [T_e(A), D_e(A)]$. 263 predissociation lifetimes were recovered from running BINSALT. The energy binned widths are presented in Figure 5.21.

A key difference between OH and SH is that SH is significantly more broadened by predissociation than is OH, with SH having roughly $10\times$ the broadening of OH. The average broadening of OH over the whole dataset is $\sim 0.6\ \text{cm}^{-1}$, whereas for SH this is $\sim 5.6\ \text{cm}^{-1}$. The maximal broadening of OH is $\sim 3\ \text{cm}^{-1}$, and for SH, $\sim 30\ \text{cm}^{-1}$.

The coupling between the $A\ ^2\Sigma^+$ state and the continua in SH is stronger than OH as expected, as S is heavier than O. This indeed, translates into a stronger centroid shift, presented in Figure 5.22, where the maximal centroid shift is on the order of $60\ \text{cm}^{-1}$.

Initially, when computing the predissociation lifetimes for SH, the *lock* procedure (Equation 5.12) was used as in OH, with $K = 10\ \text{cm}^{-1}$. In light of Figure 5.22, it is clear why this was not successful and instead $K = 500\ \text{cm}^{-1}$ was used. In SH and OH, the assumption in Equation 5.11 holds fast, as the vibrational band gap is sufficiently large. It is clear, however, that in the case of SH, this assumption is being tested somewhat, and may not hold in systems with a higher density of vibrational states.

SD predissociation lifetimes have not been calculated as part of this thesis and as of yet, a thorough literature review of SH/SD predissociation lifetimes has not been carried out, so a comparison is not provided here. Furthermore, the results for the SH predissociation lifetimes are preliminary, and their veracity has not been tested with the full treatment as in Section 5.3. These results are interesting, however, and appear promising as a test for the methods outlined in this Chapter. Moreover, it shows that for systems like SH, we can resolve very significant levels of predissociation broadening, which would be important for detecting SH in optically thick environments similar to the detection of AIH in Proxima Centauri (Pavlenko et al., 2022). It must be noted that the calculations for OH and SH/SD are for very similar molecules, and more thorough testing is necessary before this procedure can be deemed reliable. A full analysis of SH and SD predissociation lifetimes will be the subject of a forthcoming paper (Mitev et al., 2024).

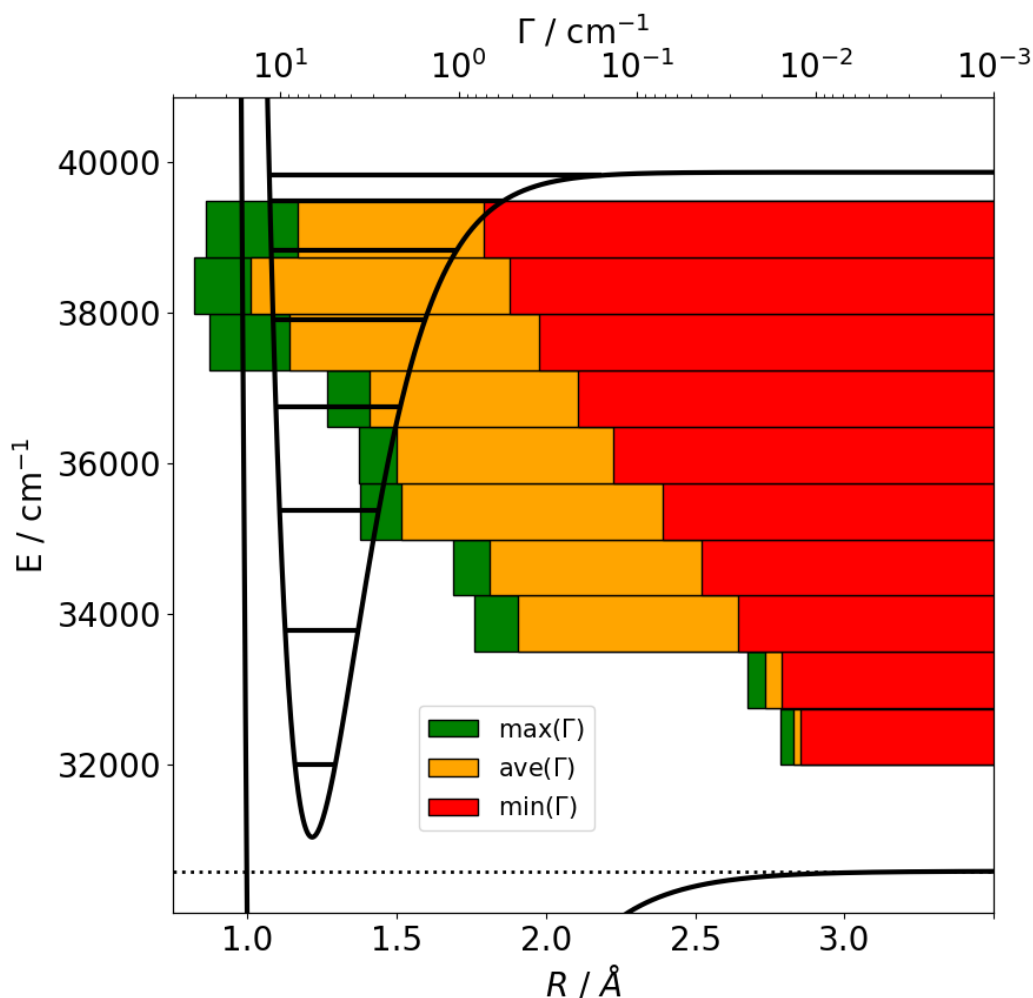


Figure 5.21: Distribution of predissociation widths, Γ of the A $2\Sigma^+$ state of SH binned over energy. Solid horizontal lines: Positions of vibrational band centres of the A $2\Sigma^+$ state ($J = 0.5, p = e$). Dotted line: Position of $D_e(X)$.

5.7 Conclusion and Future work

A method based on a modification of the stabilization method for calculating spin-orbit induced predissociation lifetimes of diatomic molecules is presented. The methods outlined in this thesis have some key benefits compared to other methods in the literature. This treatment solves the full variational problem when calculating the energy profiles. This is not the case when using the perturbation theory methods (Equation 5.1). The stabilization method here also retains real eigenvalues and is time-independent through its use of DUO. DUO is a staple program used in the ExoMol group, so integration of this method into the general workflow is not as challenging. This would not be the case if a complex absorbing potential or time-dependent method was attempted instead. Most importantly, the predissociation lifetimes computed show very good agreement with both experimental and theoretical J -resolved lifetimes from the literature.

There are also limitations and difficulties to these techniques, such as dealing with unfavourable energy profiles, misassignments, and the current inability to resolve non-radiative lifetimes for rovibronic levels lying above dissociation.

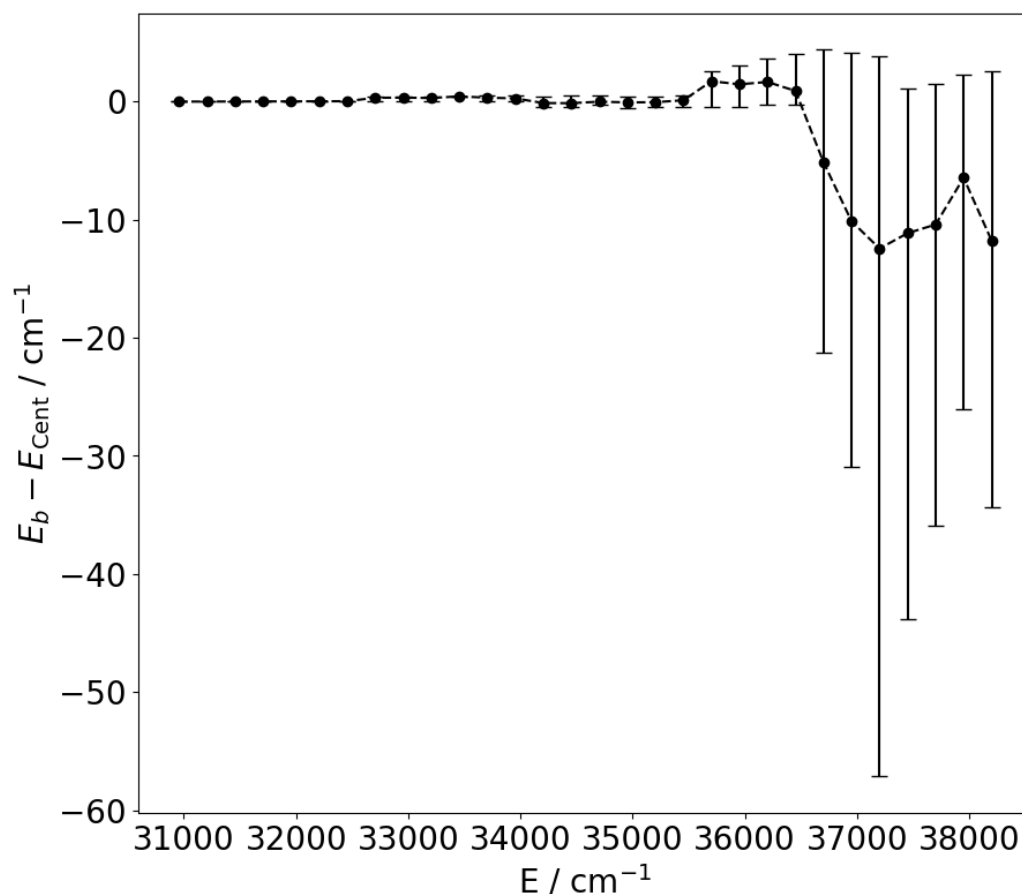


Figure 5.22: Centroid shifts of the A $^2\Sigma^+$ state of OH averaged over discrete energy regions. Error bars represent minimum and maximum centroid shifts.

547 rovibronic levels of A $^2\Sigma^+$ in OH and 308 rovibronic levels of A $^2\Sigma^+$ in SH are treated with the BINSALT program, returning 414 and 263 predissociation lifetimes respectively. This method has produced a set of predissociation lifetimes from first principles and a quantitative measure of their uncertainties, providing good agreement with available experimental values. The methods used here allow for completeness over all levels considered in a given spectroscopic model and is applicable to other systems.

OH and SH exhibit strong and complex predissociation dynamics through the interaction between the A $^2\Sigma^+$ state and three repulsive electronic states. It is, however, a streamlined example of this effect as the energetic limits of the repulsive states are the same as that of the ground state. If one ignores asymptotic fine structure effects, the dissociation products are independent of the dissociation channel. This may not be the case for other systems, however, and the study of predissociation dynamics in this manner would allow for interpretation of predissociation products and the calculation of branching ratios. Molecules with more varied predissociation channels may be of interest for future study.

For the time being, the procedures developed can be used for determining the predissociation lifetimes of other diatomic molecules and can be further optimized to remove the need for the visual inspection of energy profiles as is done in Section 5.5.1. A suggested route is to implement a machine learning model to perform the inspection instead of a user. This would require some supervision however, and a substantial training set. It is expected

that these calculations are to be extended for use in polyatomic molecules, following coordinate generalization and the aforementioned optimization. During the development of this project, we also establish a routine to fully treat the continuum using DUO in section 5.3.7 which can be used to fit continuum states as part of the curve refinement procedure. This is tentative, however, as the positions of centroids are not rigorously calculable unlike the bound model solutions.

5.7.1 Data Availability

The A $^2\Sigma^+$ state predissociation lifetimes calculated here are available at www.github.com/GBMitev/MYTHOS and the BINSLT program is available at www.github.com/ExoMol/binslt.

Chapter 6

Direct Photodissociation of OH

6.1 Introduction

In Chapter 5, predissociation, whereby the molecule dissociates through the non-radiative decay from a bound electronic state to a repulsive electronic state, is studied. When predissociation is considered, bound to bound transitions where the upper state is predissociative have an increased lifetime broadening parameter. An example of such a transition is $A^2\Sigma^+ \leftarrow X^2\Pi$ in OH and SH where a lifetime broadening parameter can be as high as 3 cm^{-1} or 30 cm^{-1} respectively. Predissociation, as it is a dissociative process, is a constituent in the temperature-dependent photodissociation cross-sections to be computed in this section. The other process that needs to be considered is direct photodissociation, which will be referred to as photodissociation hereafter.

This process is distinct from predissociation as this is due to a transition from a bound electronic state directly to the continuum. Predissociation is a two-step process, going from bound to bound to repulsive, characterised in the calculations done in this work through box size-dependent resonances. Photodissociation is an important marker not only of the abundance of photofragments like excited oxygen, but also as a marker for other hydroxyl containing molecules such as water [Dalgarno \(1987\)](#); [Tang et al. \(2021\)](#); [Wang et al. \(2017\)](#); [Schoerghofer et al. \(2021\)](#). Spectral features resulting from photodissociation are very broad, absorbant, and heavily temperature-dependent at higher wavelengths. Modelling the photochemistry of hot planetary and stellar environments requires a description of temperature-dependent photodissociation cross-sections, which are produced in this chapter.

In OH, direct photodissociation has several channels. Transitions from the ground state to the $1^2\Sigma^-$, $1^2\Delta$, and $B^2\Sigma^+$ states results in photodissociation ([van Dishoeck & Dalgarno, 1983](#); [Radenović et al., 2008](#); [Li & Zhang, 2011](#); [Nee & Lee, 1984a](#); [Kurucz et al., 1987](#)). For the $B^2\Sigma^+$ case, there is a shallow bound region with a well depth of around $2,000\text{ cm}^{-1}$. This region is modelled as such and is included in the MYTHOS linelist as described in Chapter 4. In general, however, all transitions to the $B^2\Sigma^+$ state are dissociative due to crossings with the local $2^2\Pi$ repulsive state resulting in predissociation ([Sun et al., 2020](#); [van Dishoeck & Dalgarno, 1984b](#); [van Dishoeck & Dalgarno, 1984a](#)). [Hwang et al. \(2001\)](#) experimentally found that the total lifetimes of the $v = 0$ band of $B^2\Sigma^+$ are on the order of 100 ns for $J = 0.5$ decreasing exponentially to 10 ns for $J = 4.5$, which they claim agree well with [Sappey et al. \(1989\)](#). These data are not available however, and are only given as plots, so making use of them is difficult. This predissociative effect has not been considered

in this study, and is left as future work.

OH can also directly photodissociate through the $2^2\Pi$ state (Kalyanaraman & Sathya-murthy, 1994). van Dishoeck & Dalgarno (1983) and van Dishoeck et al. (1984) calculated *ab initio* photodissociation cross-sections for transitions from $X^2\Pi$ to $1^2\Sigma^-$, $1^2\Delta$, $B^2\Sigma^+$, and $2^2\Pi$ states. The photodissociation cross-section for $2^2\Pi \leftarrow X^2\Pi$ is centered around $\sim 95,000\text{ cm}^{-1}$ and is considerably narrower than the other cross-sections. There are also many other transition bands overlapping with the $2^2\Pi \leftarrow X^2\Pi$ band in the region of $95,000\text{ cm}^{-1}$. van Dishoeck & Dalgarno (1984b) give a nice visualisation of the many potential energy curves of OH including high energy ionic and Rydberg states. This is given in Figure 6.1. As is visible here, the $2^2\Pi$ state has a significant avoided crossing with the $3^2\Pi$ state. If one is to diabatised these curves to remove this crossing, we find that the minimum of the $3^2\Pi$ state lies around the equilibrium geometry of $X^2\Pi$, meaning the Franck-Condon overlap in this region would be strong. van Dishoeck et al. (1984) showed that the photodissociation cross-section of $2^2\Pi$ is strongly affected by the presence of the $3^2\Pi$ state. The $3^2\Pi$ state predissociates through the $2^2\Pi$ state, meaning that effective modelling of the $2^2\Pi$ photodissociation cross-section would also require modelling the $3^2\Pi$ predissociation. At this stage, this has been deemed time-prohibitive and has not been attempted, so modelling of the dissociative cross-sections for electronic states above $B^2\Sigma^+$ is left for future work.

The Leiden database (Heays et al., 2017) contains photodissociation cross-sections of OH, making use of the calculations of van Dishoeck & Dalgarno (1983); van Dishoeck & Dalgarno (1984b); van Dishoeck & Dalgarno (1984a); van Dishoeck et al. (1984). These cross-sections will be used for comparison in Section 6.3.

Within the ExoMol group, studying the temperature-dependence of photodissociation cross-sections started with the work of Pezzella et al. (2021, 2022), where cross-sections for HCl, HF, NaCl, and BeH^+ were computed for temperatures up to 20,000 K. This study on diatomics made use of both a modification of the stabilization method (which was also used to study predissociation in Chapter 5) and an implementation of Gaussian smoothing, whereby a Gaussian line profile of $\text{HWHM} = \alpha$ is applied to the cross-section to smooth the discretized continuum cross-section while maintaining the integral value, and hence, the rates.

Using the stabilization method to compute photodissociation cross-sections is prohibitively expensive, so for larger molecules, this smoothing procedure is necessary and has been applied to HCN (Pezzella et al., 2024).

In this Chapter, the temperature-dependent photodissociation cross-sections for the $X^2\Pi \rightarrow (B^2\Sigma^+, 1^2\Sigma^-, 1^2\Delta)$ continuum absorption transitions are calculated. This is done by adapting the Gaussian smoothing method from Pezzella et al. (2021) in two ways. A root-finding method is presented in Section 6.2.2.1 and an energy-dependent method is presented in Section 6.2.2.2.

6.2 Methods

6.2.1 Leveraging DUO Spectroscopic Models

As with the treatment of predissociation lifetimes, here we leverage the DUO spectroscopic model constructed in Chapter 4. Starting with this model, one can compute an absorp-

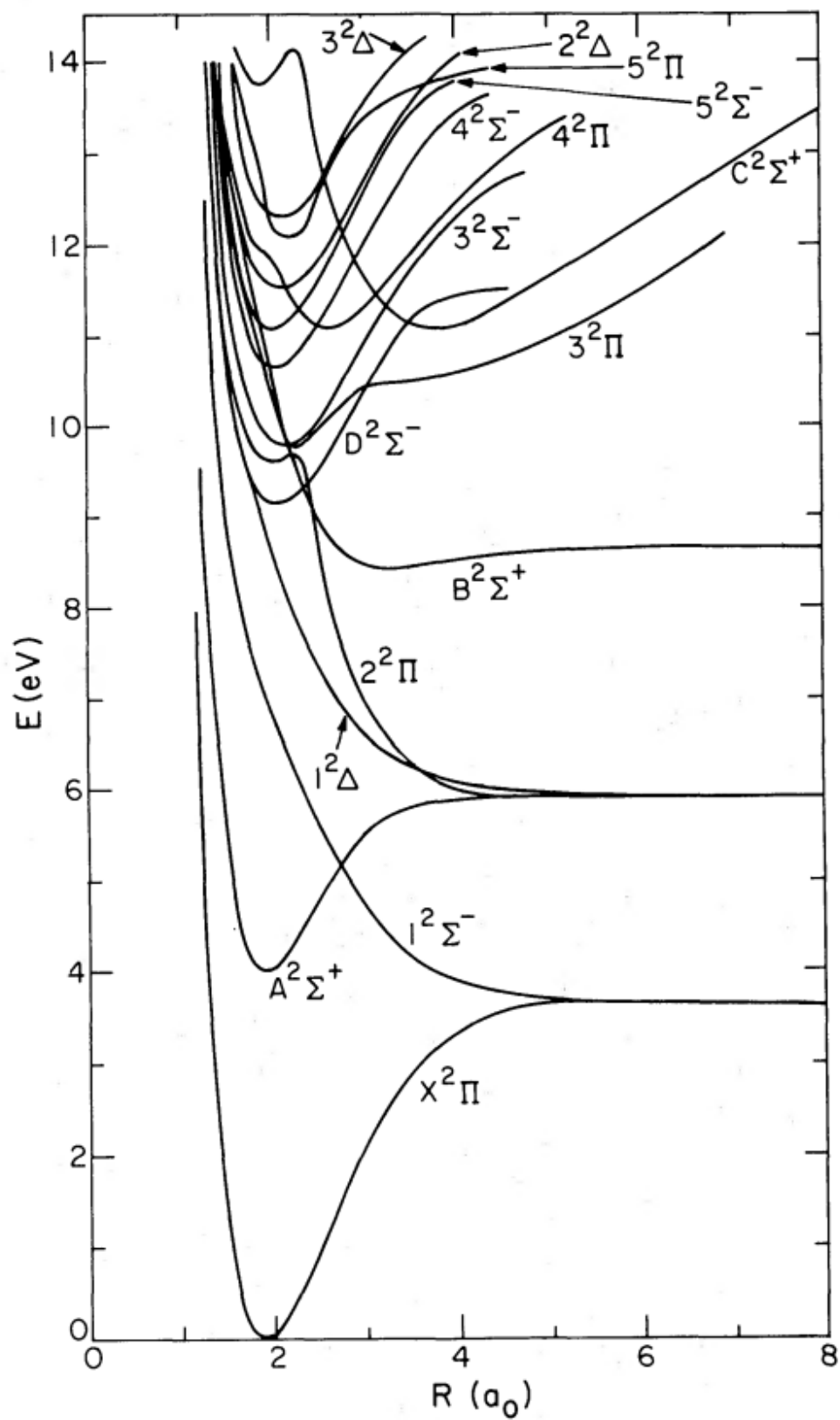


Figure 6.1: *Ab initio* doublet potential energy curves of OH from [van Dishoeck & Dalgarno \(1984b\)](#)

tion cross-section using EXOCROSS. As discussed earlier, modelling the continuum with a bound-state-like solution as is implemented in DUO results in a discretization of the continuum energy levels. This is problematic as it contradicts the expected infinite density of states for repulsive electronic states, resulting in a concentration of the absorption cross-section in finite regions where energy levels can be resolved.

The method which was applied by [Pezzella et al. \(2021\)](#) to remedy this is to apply a normalised Gaussian filter to each grid point of a pre-computed absorption cross-section with a Gaussian profile with $\alpha = 10 \text{ cm}^{-1}$. The form of the Gaussian distributed is repeated in Equation 6.1 for convenience.

$$G(\nu; \nu_0, \alpha) = \sqrt{\frac{\ln 2}{\pi}} \alpha^{-1} \exp - \frac{(\nu - \nu_0)^2 \ln 2}{\alpha^2}, \quad (6.1)$$

where ν is the wavenumber in cm^{-1} , ν_0 is the line position in cm^{-1} , and α is Gaussian half width at half maximum. Applying this filter to the cross-section has the effect of distributing the intensity over a wider region, hence lowering the maximal intensity and *smoothing* the cross-section while maintaining the integral.

The photodissociation rate, k of a molecule dissociated by a field with flux, $F(\nu)$ between the wavenumbers ν_1 and ν_2 , is given by;

$$k = \int_{\nu_1}^{\nu_2} F(\nu) \sigma(\nu) d\nu. \quad (6.2)$$

This value, assuming that ν_1 and ν_2 cover the full range of the calculated cross-section, would remain the same whether or not the cross-section is smooth. In cases when ν_1 and ν_2 do not cover the full range, giving a physical cross-section is vital in calculating accurate rates.

As discussed in Chapter 5, one can probe the continuum and find different term values for iso-numeric states by varying the calculation box's right side boundary position, R_c . Effectively, one can “fill in the gaps” using this treatment, and average the resulting cross-sections to obtain a better approximation of the continuum absorption.

This is not ideal as one must perform stabilization calculations for each dissociation channel, increasing expense. Furthermore, the smoothness of the final cross-section is dependent on the step size of R_c during said calculations. We define the following energy difference,

$$\Delta_E(Q, R_c, \delta_{R_c}) = E_Q(R_c + \delta_{R_c}) - E_Q(R_c), \quad (6.3)$$

where E_Q here is a continuum energy level with assigned quantum numbers, Q , and δ_{R_c} is the step size of R_c . In order to use this method, the step of the continuum cross-section, δ_ν , must necessarily be greater than or equal to Δ_E , otherwise, the resulting cross-section will still contain some of the discrete structure from before. As a test case, with setting $\delta_{R_c} = 0.01 \text{ \AA}$, the average Δ_E for the $1^4\Sigma^-$ state of OH is $\sim 2 \text{ cm}^{-1}$ with a maximum of $\sim 6 \text{ cm}^{-1}$. In order to meaningfully apply this method, an increase of resolution of an order of magnitude is required, making the calculation much more expensive.

In this section, two variations of the Gaussian smoothing method of [Pezzella et al. \(2021\)](#) are applied to the OH photodissociation cross-sections. A method for finding an optimum

value of α for a uniform Gaussian filter applied over a cross-section is presented in Section 6.2.2.1 and a wavenumber-dependent α implementation is presented in Section 6.2.2.2.

6.2.2 Numerical Treatment

6.2.2.1 Gaussian smoothing

The Gaussian smoothing method outlined in Pezzella et al. (2021) is largely based on trial and error, testing different values of α until a smooth cross-section is returned. This approach is fundamentally qualitative as it depends on a visual assessment on the smoothness of a specific cross-section. While this is not especially problematic, as the integral of the cross-section, and any computed photodissociation rate is conserved independent of the smoothing parameter chosen, it is a labour intensive activity. In the ExoMol database, photoabsorption cross-sections are given for temperatures ranging from 100 K to some maximum temperature $T_{\max}$ in steps of 100 K. In OH, four direct photodissociation channels are considered and must be assessed individually using this method. As $T_{\max}(\text{OH}) = 8000$ K as per the convergence of the partition function from Section 4.6.2, this would require 320 individual smoothing procedures, 80 for each channel. As discussed earlier, there are more direct dissociation channels which have not yet been considered for OH, and so, in future, including these would require an automation of the smoothing procedure. As this requires a quantitative measure of smoothness, an automation would result in quicker turnaround and more consistent results between species.

As per Pezzella et al. (2021), initial cross-sections of $X \rightarrow U$, electronic transitions are produced with an $\alpha = 10 \text{ cm}^{-1}$ using EXOCROSS. Here, U represents any given unbound electronic state. Examples of these initial cross-sections for $T = 300$ K are given in Figure 6.2.

To quantify optimum smoothness, we require that the resulting smoothed cross-section must be continuous and that the minimum value of α is used to result in a continuous cross-section so as to avoid over-distribution of intensity to the wings.

To assess the continuity of the cross-sections, one notes that at their maximum intensity, each cross-section has a single isolated turning point, and the cross-sections are bell shaped. In general, direct photodissociation to purely repulsive states appear to have this shape as found in this study and in those of Pezzella et al. (2021, 2022).

As such the smoothing of the cross-section is constrained by the number of maxima expected, N_M . The continuity condition is so defined to be that the resulting, smoothed, cross-section should have a number of roots in its first and second differential equal to N_M and $N_M + 1$ respectively, and hence, should be twice differentiable (see Figure 6.3 and discussion).

It is found that there are usually a range of α that meet this condition, and so the minimum value is taken to satisfy the condition on minimum smoothing. Formally;

$$\alpha_0 = \min \left\{ \alpha \in \mathbb{R} \left| N \left(\frac{d^2 \sigma}{dv^2}; \alpha \right) = N \left(\frac{d\sigma}{dv}; \alpha \right) + 1 = N_M + 1 \right. \right\}, \quad (6.4)$$

where $N(f)$ is the number of roots of a function f . Due to the discrete nature of this problem, one cannot implement this procedure as a standard minimization problem through

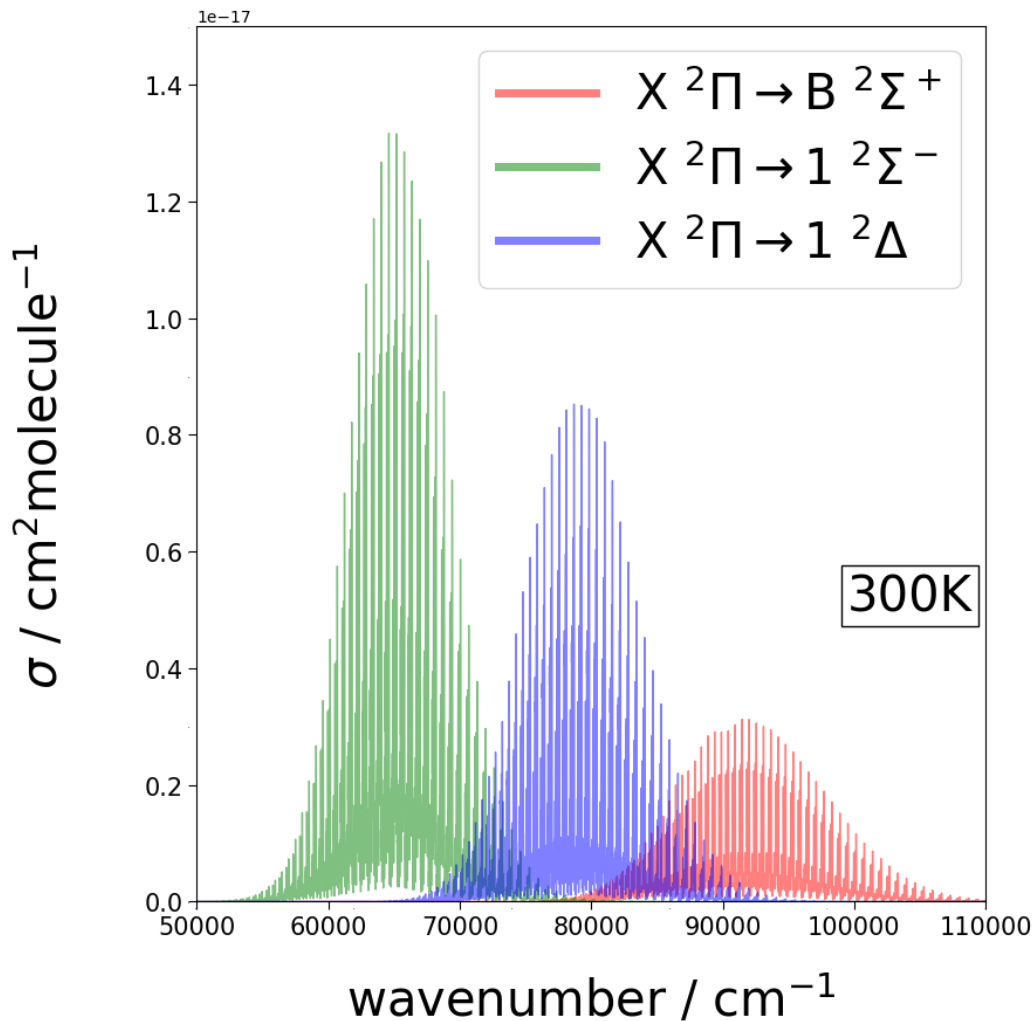


Figure 6.2: Initial photodissociation cross-sections calculated for OH using EXOCROSS with $\alpha = 10 \text{ cm}^{-1}$.

treatments like gradient descent and it must instead be solved iteratively.

The numerical method behind this is to establish a range of α values over which to test. At each iteration, first and second forward derivatives are computed as,

$$f'(x_{i+s}) = \frac{f(x_{i+s}) - f(x_i)}{x_{i+s} - x_i}, \quad (6.5)$$

where s is the sampling window. This is a necessary inclusion to deal with the numerical noise of producing these differentials. In general, a value of $s \approx \text{len}(\tilde{\nu})/100$ is found to be appropriate for both first and second derivatives.

Roots are counted by scanning the available smoothed cross-section and finding where the sign of the derivatives change. In areas of low intensity in the initial cross-section, small changes in intensity result in large changes of gradient. While roots in these regions are not false positives, it is impractical to count them. To counteract this, a threshold value, K , is imposed such that a root will only be counted if the smoothed cross-section, $\tilde{\sigma}(\nu; \alpha) > K$.

Each iteration counts the number of roots which meet the threshold condition. Upon meet-

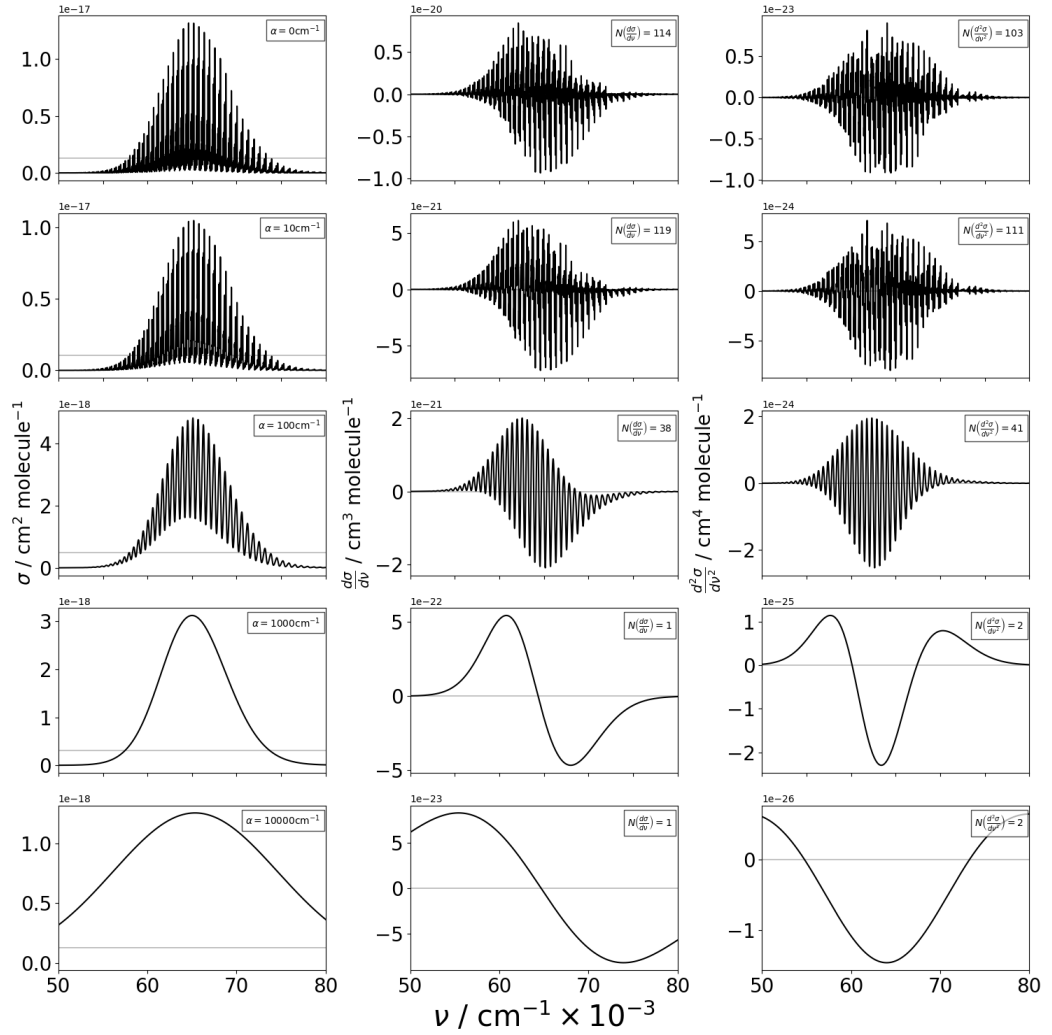


Figure 6.3: Dependence of shape of a photodissociation cross-section and its first and second derivatives (with respect to ν) on α in the smoothing procedure. Left column shows the smoothed cross-section, middle column is the first derivative, right column is the second derivative. This calculation is performed for the $1^2\Sigma^- \leftarrow X^2\Pi$ transition at 300 K

ing the continuity condition or all test values are used, the process halts. An example showing how increasing the α parameter affects the derivatives and shape of the cross-section is shown in Figure 6.3. As is visible here, both $\alpha = 1000 \text{ cm}^{-1}$ and $\alpha = 10,000 \text{ cm}^{-1}$ meet the continuity condition imposed by Equation 6.4, however, the shape of the cross-section in the $\alpha = 10,000 \text{ cm}^{-1}$ case does not faithfully represent the shape of the raw cross-section in the top left panel, therefore, one must include the requirement for minimal smoothing. In this dataset, the threshold value was estimated as, $K = \max(\sigma)/10$. The benefits of this procedure is that it is simple to implement, requires minimal computational expense, and provides good results in terms of smoothing. A limitation of this method is that upon meeting the aforementioned criteria, smoothing does not tend to be sufficient at higher ν . As ν increases, the gaps between successive vibrational bands also increases and so a minimal smoothing parameter as defined above would still allow for discrete structures to show through at high ν . One could increase α to account for this. However, this results in a slight over-smoothing in the lower ν regions and is more challenging to automate reliably. An

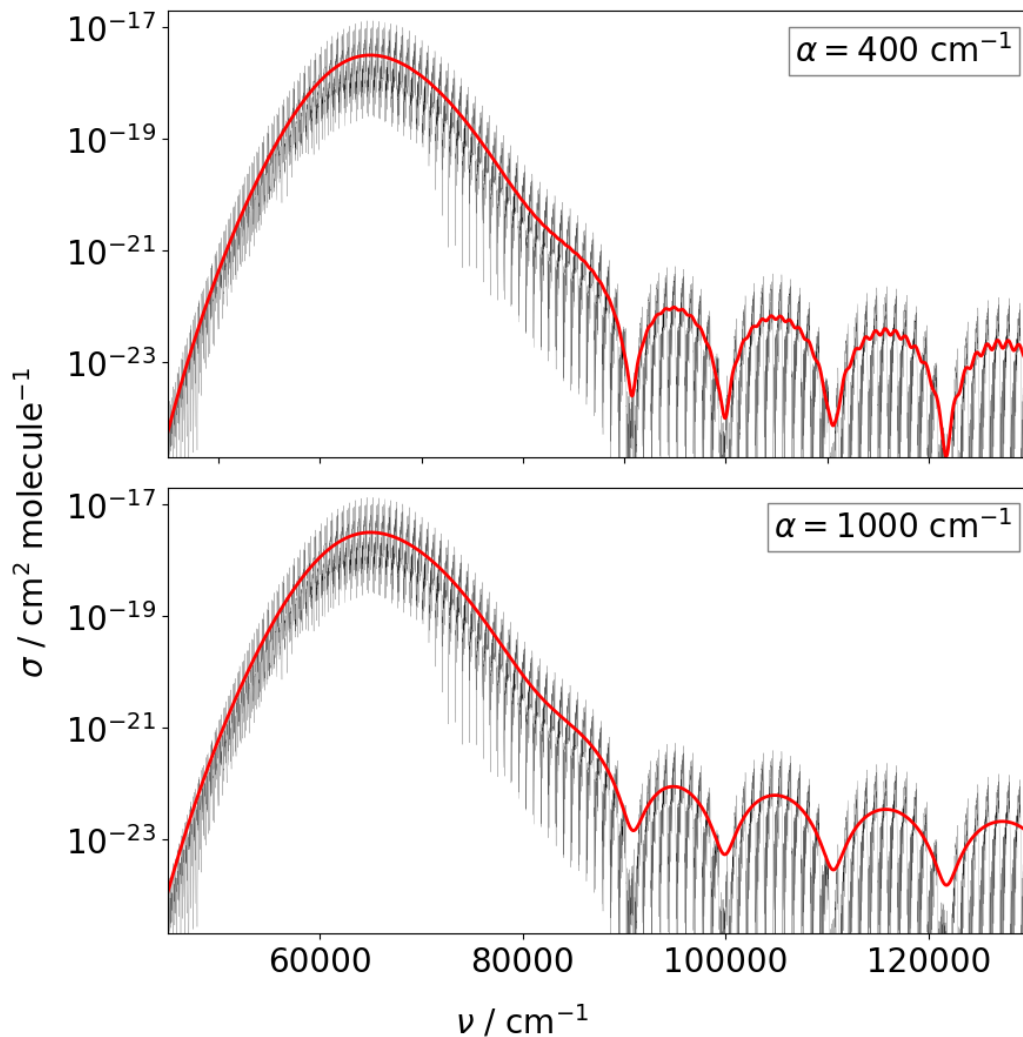


Figure 6.4: Photodissociation cross-section of the $1^2\Sigma^- \leftarrow X^2\Pi$ transitions of OH with Gaussian smoothing applied for $\alpha = 400 \text{ cm}^{-1}$ and $\alpha = 1000 \text{ cm}^{-1}$.

example of this is shown in Figure 6.4.

This is a minor limitation, however, as the temperature-dependent effects of these cross-sections will manifest themselves primarily in the lower wavenumber regions. As will be discussed later, due to other limitations in the model, this is not a limiting factor in the quality of the cross-sections.

It does, however, raise the question of whether a more thorough approximation for continuum smoothing could be made which would smooth appropriately over all regions.

6.2.2.2 Energy-Dependent Smoothing

As stated earlier, vibrational band gaps increase with energy for transitions with a repulsive upper state. Modelling the density of states in the repulsive state in the particle in a box approximation, we would expect that the term value would scale as the square of some counting number,

$$E_n = \frac{n^2 h^2}{8mL^2} = kn^2, \quad (6.6)$$

where n is the counting number, h is Planck's constant, m is the mass of the particle and L is the size of the box. As discussed in Chapter 2, the vibrational quantum number is assigned by counting within a given J, τ symmetry block. Using this as the counting number, and the approximation above, we find that the energy difference between vibrational levels,

$$\Delta E(v) = E_{v+1} - E_v \quad (6.7)$$

is approximately,

$$\Delta E(v) = k(2v + 1), \quad (6.8)$$

$$\Delta E(E) = k \left(2\sqrt{\frac{E}{k}} + 1 \right), \quad (6.9)$$

$$\Delta E(E^2) = k^{\frac{1}{2}} 2E + k. \quad (6.10)$$

And so the vibrational gap scales linearly with E^2 . It should again be noted that using the vibrational quantum number here is a convenient way to count up in energy, rather than a true vibrational state. Extending this to transitions, one can look at the energy difference between a given vibrational state in $X^2\Pi$ to a vibrational states in the repulsive states. In essence, we look at the following transition

$$|X^2\Pi, J'', \Omega'', v''\rangle \rightarrow |U, J', \Omega', v'\rangle, \quad (6.11)$$

where U is a repulsive electronic state. What we are interested in here is the energy difference from Equation 6.9, which can be found for a given v'' .

$$\Delta E_{v'', v'} = v(|X^2\Pi, J'', \Omega'', v''\rangle \rightarrow |U, J', \Omega', v' + 1\rangle) - v(|X^2\Pi, J'', \Omega'', v''\rangle \rightarrow |U, J', \Omega', v'\rangle). \quad (6.12)$$

In $X^2\Pi$, the lowest rovibrational level for a given v'' is for $J'' = 1.5, \Omega'' = -1.5$. This can be used as a reference point from which to measure the energy gap, so the reference energy for a given v'' is $E_{v''} = E(|X^2\Pi, J'' = 1.5, \Omega'' = -1.5, v''\rangle)$. Measuring from this reference point and finding the average energy for a given vibrational counting number in U , $\langle E_{v'} \rangle$, we establish the following matrix of values,

$$\tilde{V}_{v'', v'} = \langle E_{v'} \rangle - E_{v''}, \quad (6.13)$$

from which we arrive at the following extended form of Equation 6.7,

$$\Delta \tilde{V}_{v'', v'} = \tilde{V}_{v'', v'+1} - \tilde{V}_{v'', v'}, \quad (6.14)$$

and through the analogous treatment for Equation 6.9,

$$\Delta \tilde{V}_{v''}(v) = a\sqrt{v} + b, \quad (6.15)$$

where a and b are constants. This relationship is found to hold reasonably well, especially at higher v as the potential curve of the repulsive state more closely approximates a vertical

potential well as in the model of a particle in a box. Figure 6.5 shows this relationship for the case of $X^2\Pi \rightarrow 1^2\Delta$.

The relationship here is used to “fill in the gaps” between neighbouring transitions as in the method described in section 6.2.2.1. This method allows for setting a specific α for each transition based on the lower state vibrational level and the energy of the transition,

$$\alpha(v'', v) = \Delta\tilde{\nu}_{v''}(v) = a\sqrt{v} + b. \quad (6.16)$$

For each v'' , $\Delta\tilde{\nu}_{v''}(v)$ is found and squared, allowing for a linear regression model to be fit. To avoid errors induced by misassignment in v' , a Huber loss regression algorithm (Huber & Ronchetti, 2009; Bowesman et al., 2024b), which is more resistant to outliers was used in place of a least squares regression. For each v'' , a new model is made and stored. In PYEXOCROSS (Zhang et al., 2024b) one can set a Gaussian HWHM for each transition line by assigning a new column in the .TRANS file. Doing this one can produce an automated, energy-dependent smoothing of photodissociation cross-sections, avoiding the inclusion of the discretized high energy cross-sections caused by a uniform smoothing as before. The benefit of this method is that it is also simple to implement, as line-by-line profiles are built into PYEXOCROSS, furthermore, it removes the need to establish values for N_M and for K . This is a more thorough approximation of the photodissociation cross-section and requires less supervision from a practitioner to calculate. An example of this is available in Figure 6.6.

6.2.3 Photodissociation Rates

The photodissociation rate, κ , of a molecule dissociated by a field with flux dependent on wavelength $F(\lambda)$ is given by the following integral:

$$\kappa(T) = \int_{\lambda_1}^{\lambda_2} F(\lambda) \sigma(\lambda; T) d\lambda. \quad (6.17)$$

There are many standard fluxes which are used to model different environments. In the recent ExoMol photodissociation cross-section release by Pezzella et al. (2022); rates were computed for the interstellar radiation field (ISRF), Solar radiation field, two models of the Proxima Centauri field, PHOENIX (Husser et al., 2013) and MUSCLES (France et al., 2016; Youngblood et al., 2016; Loyd et al., 2016), and the Black Body radiation field (BB), $B(\lambda, T_{\text{rad}})$, defined as,

$$B(\lambda, T_{\text{rad}}) = \frac{2 \times 10^4}{4\pi\lambda^4} \frac{1}{e^{\frac{hc}{\lambda k_B T_{\text{rad}}}} - 1}, \quad (6.18)$$

where k_B is the Boltzmann constant, h is Planck’s constant, c is the speed of light and T_{rad} is the temperature of the black body.

In this study the ISRF, BB, and Solar radiation fields will be used to produce temperature-dependent rates of OH for $T \in [300, 1000, 2000, 5000]$ K as OH is known to be photodissociatively active in interstellar clouds, especially through the $1^2\Sigma^- \leftarrow X^2\Pi$ transition, which is the primary destructor of OH in this medium (Radenović et al., 2008; van Dishoeck & Dalgarno, 1983). Also as OH is known to be present in sunspots, BB and Solar flux modelling are sensible choices.

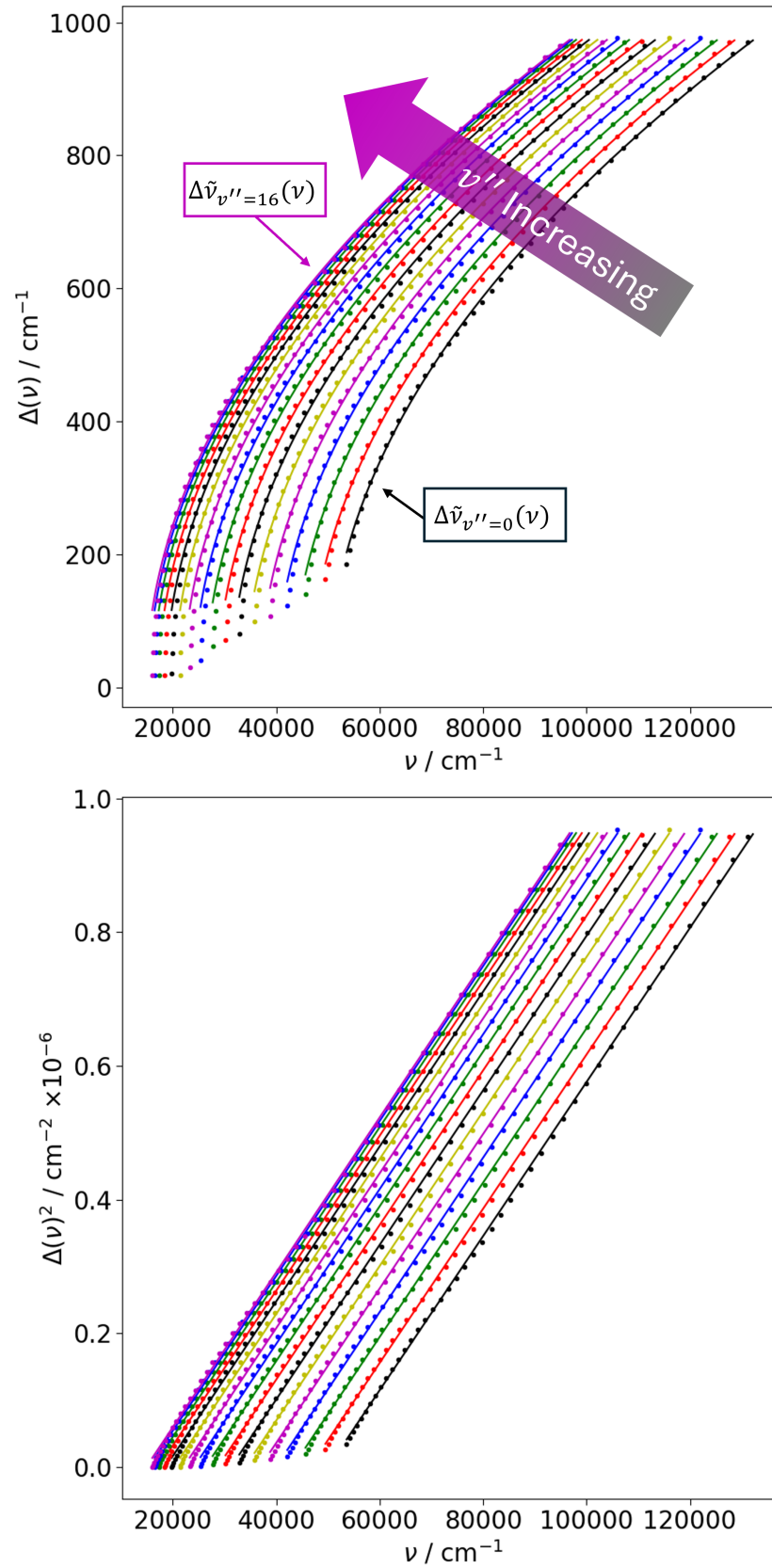


Figure 6.5: $\Delta\tilde{\nu}_{v''}(v)$ for the set of transitions, $X^2\Pi \rightarrow 1^2\Delta$ of OH. Lower panel displays that the relationship between $\Delta\tilde{\nu}$ and ν can be represented linearly as $\Delta\tilde{\nu} = a\sqrt{\nu} + b$ where a and b are constants.

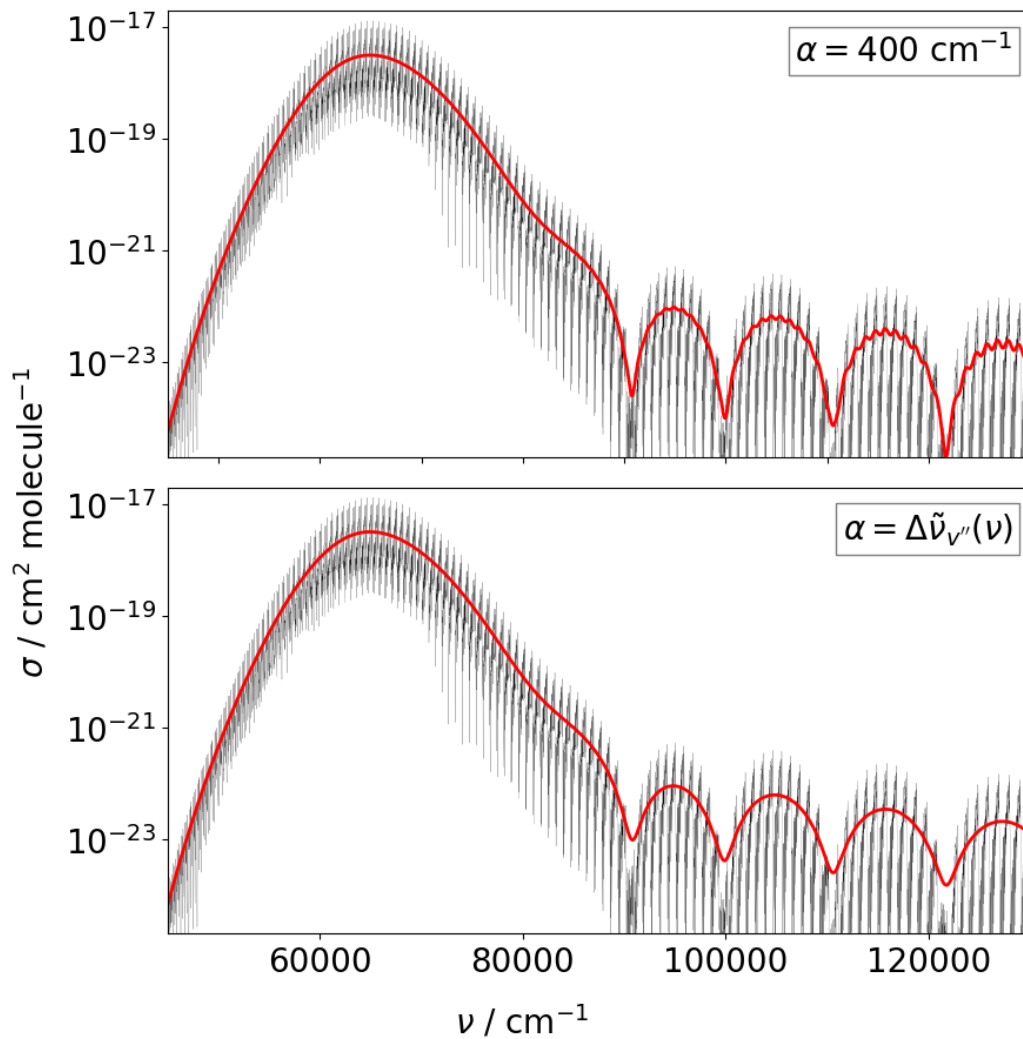


Figure 6.6: Photodissociation cross-section of the $1^2\Sigma^- \leftarrow X^2\Pi$ transitions of OH with Gaussian smoothing applied for $\alpha = 400$ (top panel) and energy-dependent smoothing applied (bottom panel)

Available OH photodissociation rates are largely computed using one or more of the first three radiation fields, (Nee & Lee, 1985; van Dishoeck & Dalgarno, 1984b). The Leiden database (Heays et al., 2017) offers rates using the ISRF radiation field using the fit from Draine (1978), which is fit from 91.2 and 200 nm using the extension to higher wavelengths from van Dishoeck & Black (1982), the Solar radiation field is compiled from the measurements of Woods et al. (1996) and Curdt, W. et al. (2001), and the Black body radiation fields are defined for $T_{\text{rad}} \in [4000, 10000, 20000]$ K. Plots of these fields are made available in Figure 6.7.

6.2.4 Non-LTE Photodissociation Cross-Sections - Preliminary Methods

The calculations here are performed for a molecule assumed to be in local thermodynamic equilibrium (LTE), so that the populations of initial states are distributed by the Boltzmann distribution. Many different processes including chemical reactions and photodissociation can result in products which are not in thermodynamic equilibrium. In these cases,

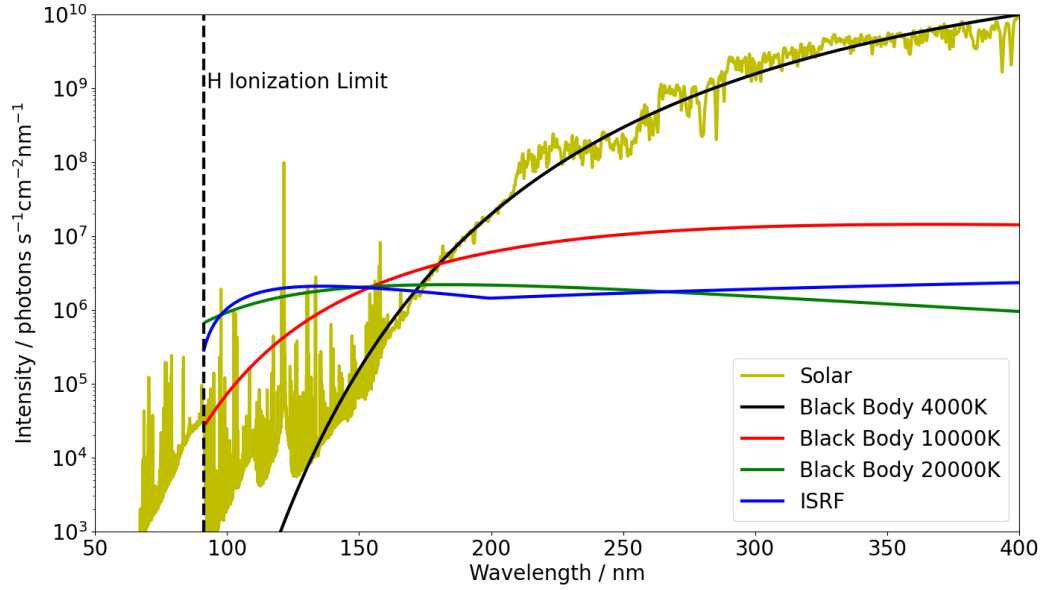


Figure 6.7: Radiation field fluxes for various environments taken from the Leiden database [Heays et al. \(2017\)](#).

their populations are not characterized by the Boltzmann distribution. These lead to non-LTE spectral features where intensity is distributed rather differently, as populations are informed by the prerequisite processes.

As such, the inclusion of non-LTE effects allows for more robust modelling of exoplanet atmospheric chemistry and chemical dynamics ([Clark & Yurchenko, 2021](#)). In radiation-rich environments, such as those in exoplanets close to their mother star where photodissociative processes are important ([Pezzella et al., 2021](#)), modelling non-LTE spectral features in photodissociation could be useful in detecting precursors of the dissociating molecule. One important example would be OH, whose non-LTE effects have been studied in ExoMol for their capacity for measuring the effective temperature of hot-Jupiter atmospheres ([Wright et al., 2023](#)). Moreover, OH is a dissociation product of water ([Zannese et al., 2023](#); [Wang et al., 2017](#)), and in environments where an OH product is likely to dissociate prior to reaching thermal equilibrium, understanding its non-LTE photodissociation spectra can be useful not only in detecting OH, but also as an indirect tool for detecting water. From discussions with Dr. Maria Bergemann from the Max-Planck Institute in Heidelberg and Prof. Ewine van Dishoeck, it is also understood that non-LTE photodissociation cross-sections are useful in studying solar and stellar abundances, leading to the following proposed methodology. The intensity of a given transition is, again,

$$I(f \leftarrow i) = \frac{g_f^{\text{tot}} A_{fi}}{8\pi c \nu_{fi}^2} \cdot \frac{e^{-c_2 E_i/T} (1 - e^{-c_2 \nu_{fi}/T})}{Q(T)}. \quad (6.19)$$

This form assumes that the initial populations are thermalized and hence Boltzmann-distributed. Except for microwave rotational transitions, the self-absorption term, $(1 - e^{-c_2 \nu_{fi}/T})$ is very close to unity, and, for the purposes of photodissociation cross-sections, can safely be neglected.

The Boltzmann population, n_B is given by,

$$n_B = \frac{g_i^{\text{tot}}}{Q(T)} e^{-c_2 E_i / T}, \quad (6.20)$$

so the intensity can be rewritten as a parametric function of the populations,

$$I(f \leftarrow i; n_B) = \frac{n_B g_f^{\text{tot}} A_{fi}}{8\pi c v_{fi}^2 g_i^{\text{tot}}}. \quad (6.21)$$

Dividing through by n_B gives an intensity independent of populations, which is “non-LTE ready” (NLTE-R),

$$I_{\text{NLTE-R}}(f \leftarrow i) = I(f \leftarrow i; n_B) / n_B. \quad (6.22)$$

Dr. Bergemann and Prof. Van Dishoeck have requested datasets containing cross-sections with $I_{\text{NLTE-R}}$ intensities for each, $v'', J'', \tau'', \Omega''$ (τ'' is the parity) of X $^2\Pi$ transitioning to each dissociative channel, 1 $^2\Sigma^-$, 1 $^2\Delta$, and B $^2\Sigma^+$.

Defining the initial states, $\{i\}$, as a state in X $^2\Pi$ with some $v'', J'', \tau'', \Omega''$, we have a set of transitions going to the set of upper states, $\{f\}$. The upper states, $\{f\}$ include all possible upper states for a given dissociative channel. This leaves us with a set of possible transitions for a given $i = |X \ ^2\Pi, v'', J'', \tau'', \Omega''\rangle$ and dissociation channel:

$$\mathbf{T}_i = (f_1 \leftarrow i, f_2 \leftarrow i, \dots, f_n \leftarrow i), \quad (6.23)$$

and so,

$$\mathbf{T} = \begin{pmatrix} f_1 \leftarrow i_1 & \dots & f_n \leftarrow i_1 \\ \vdots & \ddots & \vdots \\ f_1 \leftarrow i_m & \dots & f_n \leftarrow i_m \end{pmatrix}, \quad (6.24)$$

which has matrix elements,

$$T_{ab} = f_b \leftarrow i_a, \quad (6.25)$$

where a and b are the unique enumerators (see Section 2.1.3) of the upper (f) and lower (i) states, we can define the intensities matrix to have matrix elements,

$$I_{ab} = I_{\text{NLTE-R}}(f_b \leftarrow i_a), \quad (6.26)$$

and hence adjust the populations by scaling the intensities for a given initial state i_a by P_a , returning scaled intensities with matrix elements,

$$S_{ab} = P_a I_{ab}. \quad (6.27)$$

Each combination of a and b has a line center $\nu_{ab} = E_{f_b} - E_{i_a}$ and some line-broadening parameter, Γ_{ab} as per Section 6.2.2.2. So we can write the full cross-section of the population adjusted transitions with a line profile, π as,

$$\sigma(\nu) = \sum_a \sum_b \pi(\nu; \nu_{ab}, \Gamma_{ab}) S_{ab}. \quad (6.28)$$

But since $S_{ab} = P_a I_{ab}$,

$$\sigma(\nu) = \sum_a P_a \sum_b \pi(\nu; \nu_{ab}, \Gamma_{ab}) I_{ab} \quad (6.29)$$

$$\sigma(\nu) = \sum_a P_a \sigma_a(\nu) \quad (6.30)$$

So we can give cross-sections σ_a , for each initial state, i_a , and form the population scaled cross-section $\sigma(\nu)$ from there. It is clear however, that there is no mapping which can take an already formed $\sigma(\nu)$ with populations $\mathbf{P}$, to another $\tilde{\sigma}(\nu)$ with populations $\tilde{\mathbf{P}}$. So if one gives the full cross-section $\sum_a \sigma_a(\nu)$ containing all lower states with $I_{\text{NLTE-R}}$ intensities, one cannot then unpack this in terms of σ_a and introduce the populations in post, so the result is meaningless.

Separating out the datasets by initial state quantum numbers allows for the imposition of population conditions before combining cross-sections. Computing cross-sections is computationally time consuming, especially for a fine grid spacing; so pre-computed cross-sections separated out by initial quantum numbers with intensities independent of thermal effects give flexibility to the end user, as problem-specific populations can be used to produce full cross-sections at low cost. This allows for the use of sophisticated, expensive fitting algorithms, which would otherwise be limited by the time-consuming cross-section calculations.

Efforts are underway to produce such cross-sections which has required the development of some new code to produce them efficiently along with the formulation of a new data format to contain them. This project is as of yet incomplete and final results are not available. It has therefore been left for (near) future work.

6.3 Results

6.3.1 Photodissociation cross-sections

Temperature-dependent photodissociation cross-sections for the hydroxyl radical are produced in the range of $T \in [100, 8000]$ K in steps of 100 K. Table 6.1 summarises the transitions which are included in the total photoabsorption spectrum of OH, and the types of transitions they are. Transitions which exhibit direct photodissociation or predissociation are included in the photodissociation cross-sections.

The direct photodissociation cross-sections were smoothed using both the uniform Gaussian smoothing method outlined in section 6.2.2.1 and the energy-dependent smoothing outlined in section 6.2.2.2. An outline of smoothing parameters used for uniform Gaussian smoothing is available in Table 6.2.

The resulting photodissociation cross-sections contain smoothed direct photodissociation cross-sections and unsmoothed, appropriately broadened predissociation cross-sections as per Chapter 5. Figure 6.8 presents the photodissociation cross-section of OH plotted in units of wavelength.

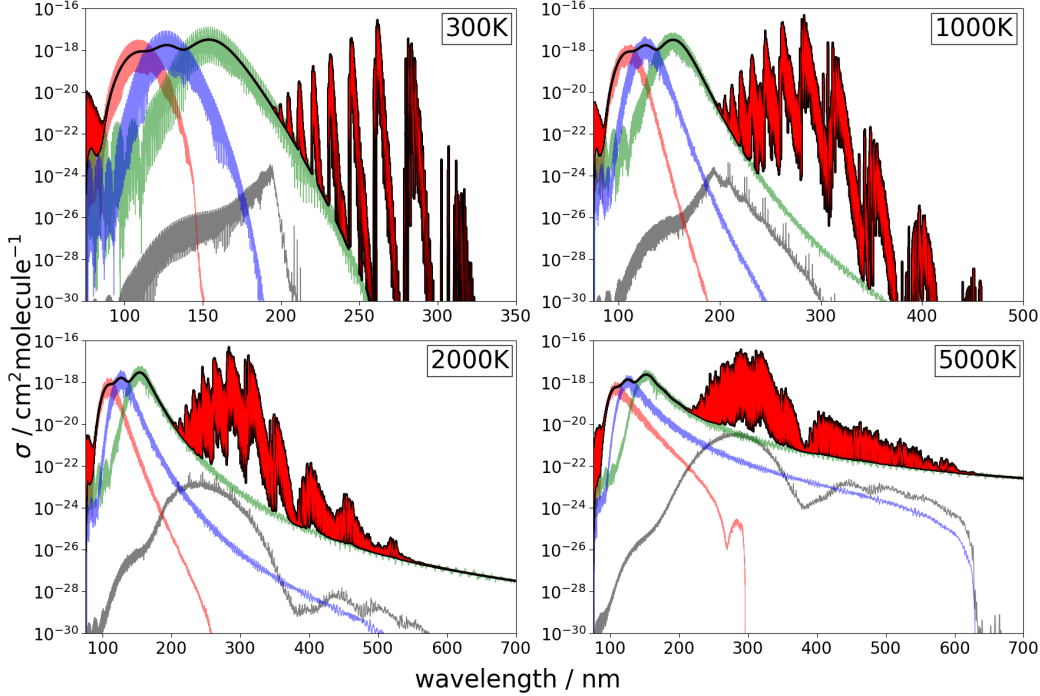
As discussed in Section 4.6.4, the Leiden cross-sections do not consider temperature. A 1 K calculation was performed, and Figure 6.9 presents a comparison between the cross-sections from this work and from Leiden.

Table 6.1: Transitions of OH included in the photoabsorption spectrum and their associated dissociative properties.

Transition	Bound-to-Bound	Direct Photodiss.	Prediss.	Smoothed
$X^2\Pi \leftarrow X^2\Pi$	✓			
$A^2\Sigma^+ \leftarrow X^2\Pi$	✓	✓	✓	✓
$B^2\Sigma^+ \leftarrow X^2\Pi$	✓	✓	✓	✓
$C^2\Sigma^+ \leftarrow X^2\Pi$	✓		✓	
$1^2\Sigma^- \leftarrow X^2\Pi$		✓		✓
$1^2\Delta \leftarrow X^2\Pi$		✓		✓
$A^2\Sigma^+ \leftarrow A^2\Sigma^+$	✓	✓	✓	
$B^2\Sigma^+ \leftarrow B^2\Sigma^+$	✓	✓	✓	
$C^2\Sigma^+ \leftarrow C^2\Sigma^+$	✓		✓	

Table 6.2: Summary of uniform Gaussian smoothing parameters of direct photodissociation transitions in OH.

Transition	$\alpha(300\text{ K})$	$\alpha(1000\text{ K})$	$\alpha(2000\text{ K})$	$\alpha(5000\text{ K})$
$A^2\Sigma^+ \leftarrow X^2\Pi$	500	1200	1200	1200
$1^2\Sigma^- \leftarrow X^2\Pi$	400	300	300	300
$1^2\Delta \leftarrow X^2\Pi$	400	400	400	400
$B^2\Sigma^+ \leftarrow X^2\Pi$	400	300	300	300

**Figure 6.8:** Photodissociation cross-section of OH at $T = 300, 1000, 2000, 5000\text{ K}$. The black line represents the flat Gaussian smoothed cross-section, the red line is the energy-dependent smoothing cross-section, the magenta line is the Leiden database cross-section [Heays et al. \(2017\)](#), and the other colored lines are the raw cross-sections pre-smoothing, see Figure 6.2.

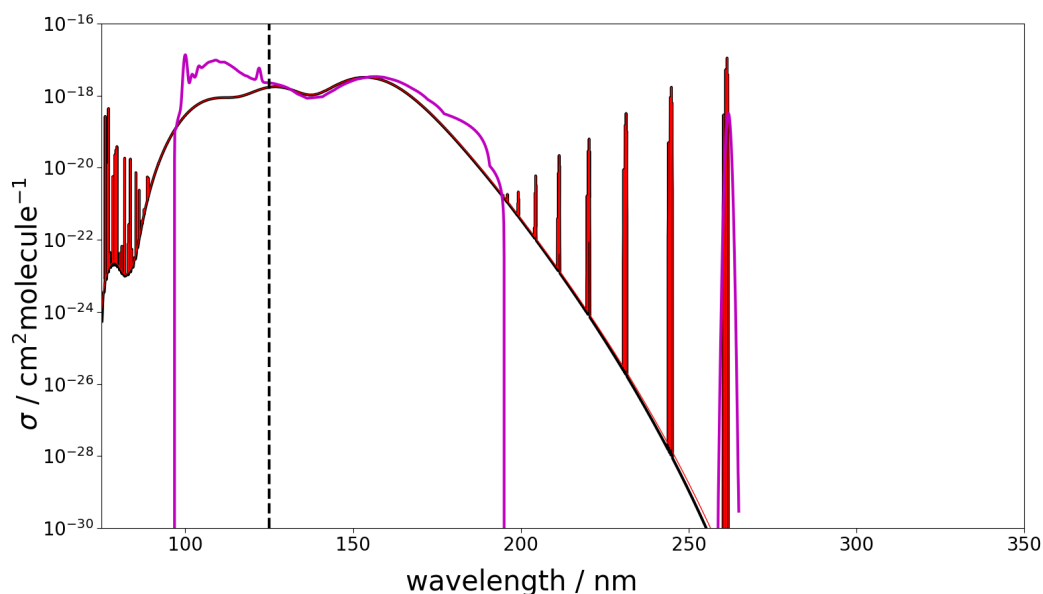


Figure 6.9: Comparison between photodissociation cross-section of OH computed in this work at 1 K with $\alpha = \alpha(300 \text{ K})$ from Table 6.2 and cross-section given by Leiden database (Heays et al., 2017).

There is generally good agreement in the position of transition lines and cross-section intensities with the cross-section produced by Heays et al. (2017). Notably the higher wavelength cross-section is much sparser in the reference curve, and is likely due to an insufficient treatment of the predissociative effects of the $A^2\Sigma^+$ state. Below 125 nm, however, agreement is poor and this is because this work’s model does not include the higher energy Rydberg states of OH. The Leiden cross-sections appear to be based on the work of van Dishoeck & Dalgarno (1983) and van Dishoeck & Dalgarno (1984b) which include these higher energy states, notably the $2^2\Pi$, $3^2\Pi$, and $D^2\Sigma^-$ states. These states were not included in the model produced in Chapter 4 and so the cross-section for wavelengths below 125 nm is not complete and is hence, inaccurate.

Attempts were made to produce the necessary potential energy, spin-orbit coupling, and transition dipole moment curves, however it was found to be infeasible at this time due to complex avoided crossings with Rydberg states, orbital swappings with local $^2\Phi$ states and $^2\Sigma^\pm$ states. The extension of the OH photodissociation cross-section to these higher frequencies is hence left as future work and for astronomical applications, the Leiden cross-section remains recommended for the region below 125 nm.

The benefit of this model, however, is the more thorough modelling of the lower frequency regions with the inclusion of a complete set of predissociative lines of the $A^2\Sigma^+$ state. The Leiden results on the other hand appear to concentrate all predissociative intensity into the v_2^A absorption band. Also this work includes temperature-dependence, which impacts the cross-section mostly in the lower frequency regions where accuracy is good.

6.3.2 Rates

Photodissociation rates for OH are calculated using the energy-dependent smoothed model of OH from Figure 6.8 and the standard fluxes taken from the Leiden database (Heays et al., 2017). The photodissociation cross-section of Heays et al. (2017) are also complete down

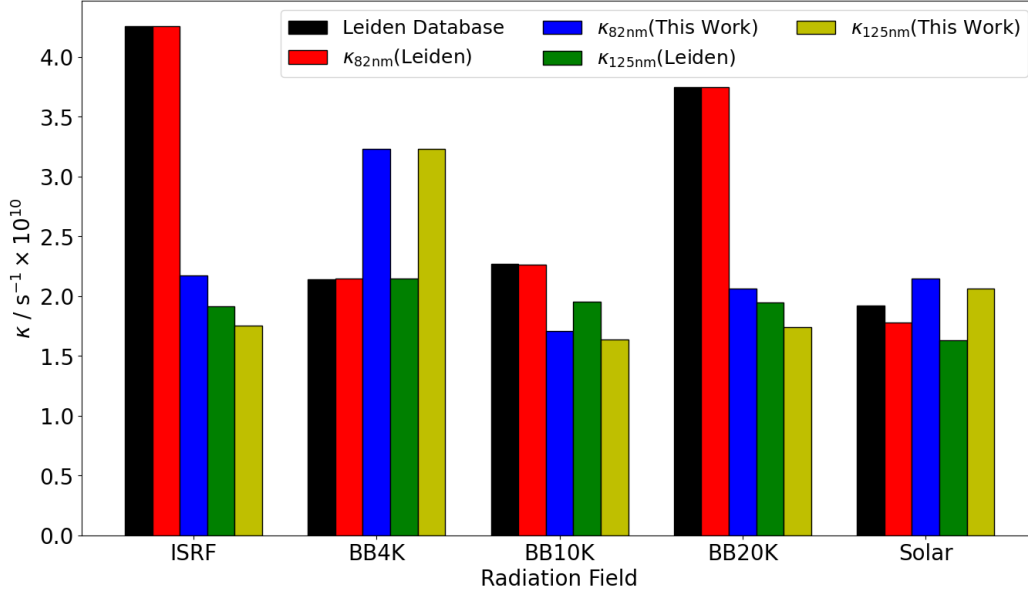


Figure 6.10: Comparison of photodissociation rates between those of [Hrodmarsson & van Dishoeck \(2023\)](#) and this work.

to 82 nm. As such it was expected that the following rate,

$$\kappa_{82\text{nm}}(T) = \int_{\lambda=82\text{nm}}^{\lambda_{\text{max}}} F(\lambda) \sigma(\lambda; T) d\lambda \quad (6.31)$$

would be larger in the reference material than in the rate calculated by this work. This is true except for the cases where the incident flux is from a black-body at 4000 K or from the Sun. The rate calculated in this work is larger for these two fluxes as the majority of their intensity is above 125 nm.

For the sake of comparison, $\kappa_{82\text{nm}}$ is found for both the Leiden cross-section and our cross-section, along with $\kappa_{125\text{nm}}$ which is analogously defined as in Equation 6.31. Figure 6.10 presents a comparison between photodissociation rates calculated for the ISRF, Solar radiation field, and BB field at 4000 K, 10,000 K, and 20,000 K (see equation 6.18).

As expected, the Leiden database's photodissociation rates are higher when considering the full range ($\kappa_{82\text{nm}}$) except for the aforementioned $B(\lambda, 4000\text{K})$ and Solar radiation fields. In other fields, $\kappa_{125\text{nm}}$ appears to agree reasonably well, although it was expected that this work's $\kappa_{125\text{nm}}$ would always be higher than that of the Leiden calculation due to the more complete description of the predissociation of $\text{A } ^2\Sigma^+$.

Temperature-dependent $\kappa_{125\text{nm}}$ values are computed for $T \in [1, 300, 1000, 2000, 5000]$ K and are presented in Figure 6.11. Despite quite the stark difference between the rates computed in this work and those of the Leiden calculations in Figure 6.10, with calculated rates lower by up to around a factor of two for some fields, Figure 6.11 shows that this discrepancy becomes negligible when temperature-dependence is considered. The rates for cross-sections computed at various temperatures span a range of around 3-4 orders of magnitude. Considering this, the Leiden database's photodissociation cross-sections and rates are likely inadequate for the modelling of exoplanetary atmospheres.

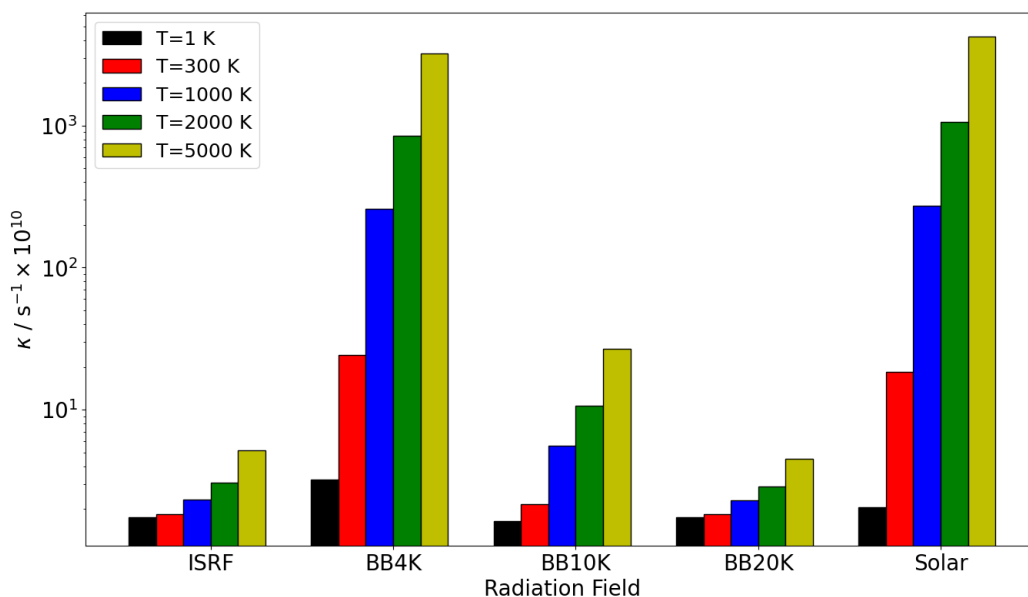


Figure 6.11: Temperature-dependent photodissociation rates of OH for the wavelength region above 125 nm for various standard fluxes from [Hrodmarsson & van Dishoeck \(2023\)](#).

6.4 Conclusion and Future Work

Uniform Gaussian smoothing and energy-dependent smoothing are presented as fast, easy to implement and pragmatic methods for producing these cross-sections, leveraging pre-existing DUO models. The photodissociation cross-sections and rates are largely in line with the available data from the Leiden database ([Heays et al., 2017](#)) in the region above 125nm. A rate roughly 50% higher than that of the Leiden calculation is reported for the $B(\lambda, 4000 \text{ K})$ and Solar radiation fields; a much higher photodissociation rate than previously expected. This is likely due to the increased level of description of the predissociative region in $A^2\Sigma^+$ and increases dramatically when temperature effects are considered. Due to the increased rate for these fluxes, it is likely that these calculations would be particularly useful for studying OH photodissociation in sunspots and other similar main-sequence stars.

Furthermore, in diffuse, optically thin interstellar clouds, the primary channel for the destruction of OH through direct photodissociation is $1^2\Sigma^- \leftarrow X^2\Pi$, followed closely by $3^2\Pi \leftarrow X^2\Pi$ and $1^2\Delta \leftarrow X^2\Pi$, with relative rates in the ratio of $\sim 1 : 0.9 : 0.4$ respectively ([van Dishoeck & Dalgarno, 1983](#)). The $1^2\Sigma^- \leftarrow X^2\Pi$ cross-section is of good quality, as the energy levels of $X^2\Pi$ are experimental and the predissociation lifetimes of $A^2\Sigma^+$ presented in Chapter 5 show good agreement with experiment. As the continuum states' curves have not been refined like those of the bound states, one can base their accuracy on the quality of the *ab initio* calculations. Additional evidence is given by the demonstrated accuracy of the $A^2\Sigma^+$ state predissociation lifetimes, which rely heavily on *ab initio* curves. These results indicate that the theoretical curves should be sufficiently accurate for modelling continuum absorption cross-sections. As such, the produced data can be applied to studies of optically thin interstellar clouds for wavelengths above 125 nm.

OH is a very complex dissociation-prone molecule, with some sort of dissociative mechanism available for all excited electronic states. The notable exception to this is the small fully bound region in $A^2\Sigma^+$ below $D_e(X)$. Above this energy, all transitions are at least

predissociative or photodissociative. Some mechanisms that have not been considered fully here are rotational predissociation, indirect predissociation, and spontaneous radiative dissociation. The latter effect has been studied by [van Dishoeck & Dalgarno \(1984b\)](#); [van der Loo & Groenenboom \(2005\)](#), and [Greenslade et al. \(2005\)](#) in D $^2\Sigma^-$ and is a logical extension to studying dissociation dynamics of OH and extending the energy coverage of the cross-sections. Extending further to include other Rydberg states like higher energy $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ states would fill in the picture and allow for the production of an energy-complete set of temperature-dependent cross-sections, returning agreement with [Heays et al. \(2017\)](#) for radiation fields outside of Solar-like fields. The photodissociation of OD has also seen much study ([van Dishoeck & Dalgarno, 1984a](#); [Nee & Lee, 1984b, 1985](#); [Radenović et al., 2003](#)). After work in extending modelling to more dissociation mechanisms and including higher energy electronic states, including the OD and ^{18}OH isotopologues are sensible extensions. As of now, the uniform Gaussian smoothing algorithm has been applied for HCN by [Pezzella et al. \(2024\)](#) and has been found to be a robust treatment. Further testing of energy-dependent smoothing is required and new implementations will be needed to extend treatment to polyatomics. In the near future - in collaboration with Dr. Maria Bergemann and Prof. Ewine van Dishoeck - it is expected that non-LTE photodissociation cross-sections for OH are to be produced with the methodology described in Section 6.2.4 for use in the characterization of Solar and stellar molecular abundances.

6.4.1 Data Availability

The calculated temperature-dependent photodissociation cross-sections for $T \in [100, 200, \dots, 8000]$ K are available at www.exomol.com.

Chapter 7

Conclusion

7.1 Summary

Chapter 3 detailed the formation of a new line list, NaOUCMe, refining novel *ab initio* potential energy curves and corresponding diagonal and off-diagonal coupling curves from Prof. A. V. Stolyarov and Prof. A. A. Buchachenko against experimental transitions from Yamada et al. (1989) and Joo et al. (1999). The model reproduces the experimental transitions with an average root mean square error of $\sim 0.006 \text{ cm}^{-1}$ for rovibrational transitions in the X $^2\Pi$ state, and $\sim 0.35 \text{ cm}^{-1}$ for rovibronic transitions between the X $^2\Pi$ and A $^2\Sigma^+$ states, with particularly strong agreement for the $v''_X = 0 \rightarrow v'_A = 0$ band of $\sim 0.023 \text{ cm}^{-1}$. The lifetimes produced in this line list are a constituent of the LiDB database (Owens et al., 2023b) and have seen use in a photodissociation cross-section study of NaO (Bai et al., 2023). The full line list has since been used to produce new low temperature gas opacities by Marigo et al. (2022) and has been used in atmospheric retrievals of low-density lava world atmospheres by Piette et al. (2023).

In Chapter 4, an update to the current MolList line list for the hydroxyl radical is described. This new line list, MYTHOS, extends the current line list to include the high-lying B $^2\Sigma^+$ and C $^2\Sigma^+$ states. A novel MARVEL dataset was released by Furtenbacher et al. (2022), making use of 45 different sources for transitions, resulting in a highly accurate, self-consistent spectroscopic network for OH transitions and hence, MARVEL energy levels. These were used to refine the *ab initio* spectroscopic model produced in 4.2, and were later supplemented in place of the model's calculated levels where possible. This was done following the *predicted shifts* methodology (Bowesman et al., 2021, 2024b; McKemmish et al., 2024) producing the first trihybrid line list for OH containing MARVEL, calculated, and interpolated energies, with Einstein-A coefficients calculated using the theoretical (transition) dipole moment curves from earlier. A framework for characterising bound and unbound rovibronic states using the individual levels' wavefunctions is applied in this chapter.

Furthermore, the spectroscopic model produced here was combined with the 1 ($^2\Sigma^-$, $^4\Sigma^-$, $^4\Pi$) states and their corresponding spin-orbit coupling curves with the A $^2\Sigma^+$ state to calculate spin-orbit-induced predissociation lifetimes for A $^2\Sigma^+$ quasi-bound rovibronic levels in Chapter 5. These were used to inform the total lifetime of each A $^2\Sigma^+$ state level, and hence the Lorentzian lifetime broadening of these levels. This was combined with the Doppler broadening for each level using the Voigt profile implemented in PYEXOCROSS (Zhang et al., 2024b) to produce the photoabsorption spectrum. On top of this, continuum

absorption transitions between the $X^2\Pi$ and $B^2\Sigma^+$, $1^2\Delta$, and $1^2\Sigma^-$ electronic states were treated with two separate automated methodologies in Chapter 6, and were added to the photoabsorption spectrum.

A rough summary of the transitions included in each data product is given in Table 7.1

Table 7.1: Summary of transitions included in each data product.

Transitions		Data Product		
Upper State	Lower State	MYTHOS	Photodissociation	Photoabsorption
$X^2\Pi$	$X^2\Pi$	✓		✓
$A^2\Sigma^+$	$A^2\Sigma^+$	✓		✓
$B^2\Sigma^+$	$B^2\Sigma^+$	✓		✓
$C^2\Sigma^+$	$C^2\Sigma^+$	✓		✓
$A^2\Sigma^+$	$X^2\Pi$	✓	✓	✓
$B^2\Sigma^+$	$X^2\Pi$	✓	✓	✓
$C^2\Sigma^+$	$X^2\Pi$	✓	✓	✓
$1^2\Sigma^-$	$X^2\Pi$		✓	✓
$1^2\Delta$	$X^2\Pi$		✓	✓

7.2 Future Work

In the current iteration of the NaO line list, the main limiting factor is the lack of experimental data. Following this, the quality and breadth of *ab initio* calculations can also be improved by, for example, computing with a larger basis set as has been done for OH to produce more accurate dipole moments. Recently, Bai et al. (2023) produced new PECs and dipole moment curves for NaO, including many additional states including the bound electronic state, $C^2\Pi$. These calculations were done in order to produce new photodissociation cross-sections of NaO. This, and the work done here can be extended by producing new, high quality *ab initio* PECs, coupling curves, and (transition) dipole moments to extend the current line list with *ab initio* energy levels. This also indicates interest for alkali metal oxide photodissociation cross-sections in general, so future studies into species such as LiO and KO are well deserved, both in a line list and photodissociation capacity. Should new experimental datasets regarding the spectroscopy of NaO be produced, a MARVEL project could also be warranted.

If studies aim to observe OH in the vacuum UV region above $80,000\text{ cm}^{-1}$, further calculations could be performed to extend the spectroscopic model to include the high lying Rydberg states present in Figure 6.1. Including these states would require extensive work in electronic structure calculations. These states are prone to exhibit pronounced avoided crossings, making them difficult to diabitize, but also often suffer from orbital swapping and contamination from differently symmetric local states. This makes it especially difficult to resolve coupling curves and dipole moments. Furthermore, to rigorously include these states, one must also perform new spin-orbit predissociation calculations, and develop methods to treat the $D^2\Sigma^-$ state's spontaneous radiative decay.

Studying the spin-orbit predissociation of OH and SH has opened a lot of doors for future research, primarily in the optimization of the algorithm itself to deal with atypical, but useful, energy profiles such as those in Figure 5.10, which seemingly must be resolved

manually as in Section 5.5.1. A possible trajectory for this project would be to use machine-learning techniques (which are already in use in ExoMol for the purpose of line broadening (Guest et al., 2024)) to perform line profile inspection instead of the manual approach taken here. This would, however, require human supervision during training, and a substantial training set. This could be possible however, as thus far 677 “good” energy profiles have been produced for OH (414 lifetimes) and SH (263 lifetimes). After SH and SD lifetimes are finalized and the methods are tested on other molecules, the training set should be sufficient for preliminary testing of such a model.

Extending these calculations for use in polyatomic molecules is also an avenue for future research. Difficulties here would lie in developing a highly optimized code to detect resonances, due to the lengthy calculations needed to solve the nuclear motion problem even for smaller polyatomics, as one could not take the same brute force approach due to the increased degrees of freedom polyatomics have. A logical place to would be with water, given the well established importance of this molecule in a wide variety of environments, and as a related molecule to OH.

Section 5.3.7 proposed a procedure to fully treat and refine continuum curves using the stabilization method. By leveraging the centroid energy levels in place of the calculated nuclear motion energy levels, one could approximate the perturbative effects of the continuum and hence fit the continuum states. This is, however, a very expensive procedure, and further optimizations and/or approximations would be necessary. An example of this could be to consider only a limited range for J and v to speed up calculations.

The ExoMol photodissociation cross-section database is, in general, underpopulated relative to the line list database. cross-sections for CH, NH, SH, OH⁺, H₂O, H₂S, and isotopologues of OH such as ¹⁸OH and OD are contenders for exploration, with some of these already in the works. Methods have already seen extension to triatomics, with HCN being the first to receive some of the treatments outlined in this work (Pezzella et al., 2024).

Finally, the to-do list of molecules requiring study by the ExoMol group is ever growing with an increasing rate. Transition metal oxides and hydrides are of particular interest to astronomers for their presence in stellar spectra (McDonald et al., 2010; Martin et al., 2010; Wende et al., 2010; Hargreaves et al., 2010; Wende et al., 2009) and meteors (Popov et al., 2021). Modelling these is very difficult however, due to their highly correlated and dense potential energy structure (Sakellaris et al., 2011), requiring the development of new techniques to accommodate them. An example of this complex structure which has been tackled at ExoMol is VO (Bowesman et al., 2022, 2024a,b), which required the use of 15 electronic states and many more coupling curves to properly characterise.

For examples like FeH, NiH, and FeO, which have been requested for study by the group, one would also have to consider a more thorough modelling of their complex Zeeman splitting effects (Harker et al., 2013; Shulyak et al., 2010; Crozet et al., 2014), given that stellar environments can also exhibit strong magnetic fields (Shulyak et al., 2010), for which the weak-field Landé- g factors (Semenov et al., 2017) currently in use would not be valid.

The continued influx of new experimental spectroscopic data, detections of astronomically important species, and the development of novel computational techniques to deal with increasingly difficult molecular structures will keep researchers busy well into the future.

Bibliography

- Al-Refaie A. F., Changeat Q., Waldmann I. P., Tinetti G., 2021, [Astrophys. J.](#), 917, 37
- Bacic Z., Simons J., 1982, [J. Phys. Chem.](#), 86, 1192
- Bai T., Yang X., Qin Z., Liu L., 2023, [Monthly Notices of the Royal Astronomical Society](#), 527, 3847
- Banks R. J., et al., 2023, Continuous-Time Quantum Walks for MAX-CUT Are Hot ([arXiv:2306.10365](#)), <https://doi.org/10.48550/arXiv.2306.10365>
- Barklem P. S., Collet R., 2016, [Astron. Astrophys.](#), 588, A96
- Bauschlicher Jr. C. W., Langhoff S. R., 1987, [J. Chem. Phys.](#), 87, 4665
- Berdugina S. V., Solanki S. K., 2001, [Astron. Astrophys.](#), 380, L5
- Berezhnoy A. A., Borovicka J., Santos J., Rivas-Silva J. F., Sandoval L., Stolyarov A. V., Palma A., 2018, [Planet Space Sci.](#), 151, 27
- Bernath P. F., 2020, [Journal of Quantitative Spectroscopy and Radiative Transfer](#), 240, 106687
- Bernath P. F., Colin R., 2009, [J. Mol. Spectrosc.](#), 257, 20
- Berning A., Schweizer M., Werner H.-J., Knowles P. J., Palmieri P., 2000, [Mol. Phys.](#), 98, 1823
- Birkby J. L., 2018, Exoplanet Atmospheres at High Spectral Resolution ([arXiv:1806.04617](#)), <https://arxiv.org/abs/1806.04617>
- Bowesman C. A., Shuai M., Yurchenko S. N., Tennyson J., 2021, [Mon. Not. Roy. Astron. Soc.](#), 508, 3181
- Bowesman C. A., Akbari H., Hopkins S., Yurchenko S. N., Tennyson J., 2022, [J. Quant. Spectrosc. Radiat. Transf.](#), 289, 108295
- Bowesman C. A., Yurchenko S. N., Tennyson J., 2024a, [Mol. Phys.](#), 122, e2255299
- Bowesman C. A., Qu Q., McKemmish L. K., Yurchenko S. N., Tennyson J., 2024b, [Mon. Not. Roy. Astron. Soc.](#), 529, 1321
- Boys S. F., Bernardi F., 1970, [Mol. Phys.](#), 19, 553

- Brady R. P., Yurchenko S. N., Tennyson J., Kim G.-S., 2023, [Monthly Notices of the Royal Astronomical Society](#), 527, 6675
- Brandl B. R., et al., 2010, Instrument concept and science case for the mid-IR E-ELT imager and spectrograph METIS, [doi:10.1117/12.857346](#)
- Brasseur G., Offermann D., 1986, [J. Geophys. Res.-Atmos.](#), 91, 10818
- Brooke J. S. A., Bernath P. F., Western C. M., Sneden C., Afsar M., Li G., Gordon I. E., 2016, [J. Quant. Spectrosc. Radiat. Transf.](#), 168, 142
- Brown J. M., Cheung A. S. C., Merer A. J., 1987, [J. Mol. Spectrosc.](#), 124, 464
- Brzozowski J., Erman P., Lyyra M., 1978, [Phys. Scr.](#), 17, 507
- Buenker R. J., Liebermann H.-P., 2009, [J. Chem. Phys.](#), 131, 114107
- Cafiero M., Bubin S., Adamowicz L., 2003, [Phys. Chem. Chem. Phys.](#), 5, 1491
- Chang C.-W., Chen I.-Y., Fittschen C., Luo P.-L., 2023, [J. Chem. Phys.](#), 159, 184203
- Chapman S., 1939, [The Astrophysical Journal](#), 90, 309–316
- Chen Q., Hu X., Guo H., Xie D., 2021, [J. Phys. Chem. Lett.](#), 12, 1822
- Chu X., Dalgarno A., 2004, [J. Chem. Phys.](#), 121, 4083
- Chubb K. L., et al., 2018a, [J. Quant. Spectrosc. Radiat. Transf.](#), 204, 42
- Chubb K. L., et al., 2018b, [J. Quant. Spectrosc. Radiat. Transf.](#), 218, 178
- Chubb K. L., et al., 2021, [Astron. Astrophys.](#), 646, A21
- Clancy R. T., et al., 2013, [Icarus](#), 226, 272
- Clark V. H. J., Yurchenko S. N., 2021, [Phys. Chem. Chem. Phys.](#), 23, 11990
- Colin R., Coheur P. F., Kiseleva M., Vandaele A. C., Bernath P. F., 2002, [J. Mol. Spectrosc.](#), 214, 225
- Coxon J. A., Sappey A. D., Copeland R. A., 1991, [J. Mol. Spectrosc.](#), 145, 41
- Crozet P., Dobrev G., Richard C., Ross A. J., 2014, [J. Mol. Spectrosc.](#), 303, 46
- Curdt, W. Brekke, P. Feldman, U. Wilhelm, K. Dwivedi, B. N. Schühle, U. Lemaire, P. 2001, [A&A](#), 375, 591
- Currie T., Biller B., Lagrange A.-M., Marois C., Guyon O., Nielsen E., Bonnefoy M., Rosa R. D., 2023, Direct Imaging and Spectroscopy of Extrasolar Planets ([arXiv:2205.05696](#)), <https://arxiv.org/abs/2205.05696>
- Czarny J., Felenbok P., Lefebvre-Brion H., 1971, [J. Phys. B-At. Mol. Opt. Phys.](#), 4, 124
- Dalgarno A., 1987, [International Journal of Mass Spectrometry and Ion Processes](#), 81, 1
- Darby-Lewis D., et al., 2019, [J. Mol. Spectrosc.](#), 362, 69

- Delahaye T., et al., 2021, [J. Mol. Spectrosc.](#), 380, 111510
- Derro E. L., Pollack I. B., Dempsey L. P., Greenslade M. E., Lei Y., Radenović D. Č., Lester M. I., 2005, [J. Chem. Phys.](#), 122, 244313
- Dmitri G. Fedorov Shiro Koseki M. W. S., Gordon M. S., 2003, [International Reviews in Physical Chemistry](#), 22, 551
- Draine B. T., 1978, [Astrophys. J. Suppl. Ser.](#), 36, 595
- Dulieu O., Kosloff R., Masnou-Seeuws F., Pichler G., 1997, [The Journal of Chemical Physics](#), 107, 10633
- Dunn W. R., et al., 2022, [Geophysical Research Letters](#), 49, e2021GL097390
- Edwards B., et al., 2021, [Monthly Notices of the Royal Astronomical Society](#), 504, 5671
- Endres C. P., Schlemmer S., Schilke P., Stutzki J., Müller H. S., 2016, [J. Mol. Spectrosc.](#), 327, 95
- France K., et al., 2016, [Astrophys. J.](#), 820, 89
- Francis A., et al., 2020, [Data](#), 5, 70
- Franzen C., Espy P. J., Hofmann N., Hibbins R. E., Djupvik A. A., 2019, [Atmosphere](#), 10, 637
- Furtenbacher T., Császár A. G., Tennyson J., 2007, [J. Mol. Spectrosc.](#), 245, 115
- Furtenbacher T., Hegedus S. T., Tennyson J., Császár A. G., 2022, [Phys. Chem. Chem. Phys.](#), 24, 19287
- Gamache R. R., et al., 2017, [J. Quant. Spectrosc. Radiat. Transf.](#), 203, 70
- Gardner J. P., et al., 2006, [Space Sci. Rev.](#), 123, 485
- Garmash O., et al., 2020, [Atmos. Chem. Phys.](#), 20, 515
- Goldman A., Schoenfeld W. G., Goorvitch D., Chackerian C., Dothe H., Melen F., Abrams M. C., Selby J. E. A., 1998, [J. Quant. Spectrosc. Radiat. Transf.](#), 59, 453
- Gordon I., et al., 2022, [J. Quant. Spectrosc. Radiat. Transf.](#), 277, 107949
- Gorman M. N., Yurchenko S. N., Tennyson J., 2019, [Mon. Not. Roy. Astron. Soc.](#), 490, 1652
- Gould T., Bučko T., 2016, [J. Chem. Theory Comput.](#), 12, 3603
- Gray J. A., Farrow R. L., 1991, [J. Chem. Phys.](#), 95, 7054
- Greenslade M. E., Lester M. I., Radenović D. C., van Roij A. J. A., Parker D. H., 2005, [J. Chem. Phys.](#), 123, 074309
- Guardiola R., Ros J., 1982, [J. Comp. Phys.](#), 45, 374
- Guest E. R., Tennyson J., Yurchenko S. N., 2024, [J. Mol. Spectrosc.](#), 401, 111901

- Gyamfi J. A., Jagau T.-C., 2024, [Journal of Chemical Theory and Computation](#), 20, 1096
- Hargreaves R. J., Hinkle K. H., Bauschlicher Jr. C. W., Wende S., Seifahrt A., Bernath P. F., 2010, [Astron. J.](#), 140, 919
- Harker H., Richard C., Tourasse G., Crozet P., Ross A. J., 2013, [J. Mol. Spectrosc.](#), 292, 28
- Hartmann J.-M., Boulet C., Robert D., 2008, Collisional effects on molecular spectra. Laboratory experiments and models, consequences for applications. Elsevier, Amsterdam
- Hazi A. U., Taylor H. S., 1970, [Phys. Rev. A](#), 1, 1109
- Heard D. E., Crosley D. R., Jeffries J. B., Smith G. P., Hirano A., 1992, [J. Chem. Phys.](#), 96, 4366
- Heays A. N., Bosman A. D., van Dishoeck E. F., 2017, [Astron. Astrophys.](#), 602, A105
- Herbig G. H., 1974, [Astrophys. J.](#), 189, 75
- Herzberg G., 1989, Spectra of diatomic molecules. Krieger Publ, pp 223,257
- Hougen J., Wiersma G., 2001, The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules, [doi:https://doi.org/10.6028/NBS.MONO.115](https://doi.org/10.6028/NBS.MONO.115)
- Hrodmarsson H. R., van Dishoeck E. F., 2023, [Astron. Astrophys.](#), 675, A25
- Huang X., Schwenke D. W., Freedman R. S., Lee T. J., 2017, [J. Quant. Spectrosc. Radiat. Transf.](#), 203, 224
- Huber K. P., Herzberg G., 1979, Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules. Van Nostrand Reinhold Company, New York, [doi:10.1007/978-1-4757-0961-2](https://doi.org/10.1007/978-1-4757-0961-2), <https://doi.org/10.1007/978-1-4757-0961-2>
- Huber P., Ronchetti E., 2009, Robust statistics. Wiley Series in Probability and Statistics, John Wiley
- Husser T.-O., Wende-von Berg S., Dreizler S., Homeier D., Reiners A., Barman T., Hauschildt P. H., 2013, [Astron. Astrophys.](#), 553, A6
- Hwang E. S., Lipson J. B., Field R. W., Dodd J. A., 2001, [J. Phys. Chem. A](#), 105, 6030
- Islampour R., Miralinaghi M., 2015, [Int. J. Quantum Chem.](#), 115, 510
- Joens J. A., 2001, [J. Phys. Chem. A](#), 105, 11041
- Jones T. J., Hyland A. R., Fix J. D., Cobb M. L., 1988, [Astron. J.](#), 95, 158
- Joo S., Worsnop D. R., Kolb C. E., Kim S. K., Herschbach D. R., 1999, [J. Phys. Chem. A](#), 103, 3193
- Kalyanaraman C., Sathyamurthy N., 1994, [Chem. Phys.](#), 187, 219
- Kaufmann M., Lehmann C., Hoffmann L., Funke B., López-Puertas M., Savigny C., Riese M., 2008, [Advances in Space Research](#), 41, 1914

- Kefala K., Boudon V., Yurchenko S. N., Tennyson J., 2024, *J. Quant. Spectrosc. Radiat. Transf.*, 316, 108897
- Knowles P. J., Werner H.-J., 1992, *Theor. Chem. Acc.*, 84, 95
- Kokoouline V., Dulieu O., Kosloff R., Masnou-Seeuws F., 2000, *Phys. Rev. A*, 62, 032716
- Kolb C. E., Elgin J. B., 1976, *Nature*, 263, 488–490
- Komasa J., Puchalski M., Czachorowski P., Łach G., Pachucki K., 2019, *Phys. Rev. A*, 100, 032519
- Kozin I. N., Roberts R. M., Tennyson J., 1999, *J. Chem. Phys.*, 111, 140
- Kozlov S. V., Pazyuk E. A., Stolyarov A. V., 2024, *Russian Journal of Physical Chemistry A*
- Kozłowski P. M., Adamowicz L., 1993, *Chem. Rev.*, 93, 2007
- Kramida A., Ralchenko Y., Reader J., NIST ASD Team 2021, NIST Atomic Spectra Database (ver. 5.9), [Online]. Available: <http://physics.nist.gov/asd> [2021, October 31]. National Institute of Standards and Technology, Gaithersburg, MD., doi:10.18434/T4W30F
- Kristiansson M. K., et al., 2022, *Nat. Commun.*, 13, 5906
- Kurucz R. L., van Dishoeck E. F., Tarafdar S. P., 1987, *Astrophys. J.*, 322, 992
- Lamperti M., et al., 2023, *Communications Physics*, 6, 67
- Landman R., Sanchez-Lopez A., Molliere P., Kesseli A. Y., Louca A. J., Snellen I. A. G., 2021, *Astron. Astrophys.*, 656, A119
- Langhoff S. R., Davidson E. R., 1974, *Int. J. Quantum Chem.*, 8, 61
- Langhoff S. R., van Dishoeck E. F., Wetmore R., Dalgarno A., 1982, *J. Chem. Phys.*, 77, 1379
- Langhoff S. R., Partridge H., Bauschlicher C. W., 1991, *Chem. Phys.*, 153, 1–12
- Lapôtre M. G. A., O'Rourke J. G., Schaefer L. K., Siebach K. L., Spalding C., Tikoo S. M., Wordsworth R. D., 2020, *Nat. Rev. Earth & Env.*
- Le Roy R. J., 2017a, *J. Quant. Spectrosc. Radiat. Transf.*, 186, 179
- Le Roy R. J., 2017b, *J. Quant. Spectrosc. Radiat. Transf.*, 186, 167
- Le Roy R. J., Henderson R. D. E., 2007, *Mol. Phys.*, 105, 663
- Le Roy R. J., Huang Y., 2002, *J. Molec. Struct. (THEOCHEM)*, 591, 175
- Le Roy R. J., Huang Y., Jary C., 2006, *J. Chem. Phys.*, 125, 164310
- Le Roy R. J., Dattani N. S., Coxon J. A., Ross A. J., Crozet P., Linton C., 2009, *J. Chem. Phys.*

- Lee S., 1995a, *J. Phys. Chem.*, 99, 13380
- Lee S., 1995b, *J. Chem. Phys.*, 103, 3501
- Lee S., 1995c, *Chem. Phys. Lett.*, 240, 595
- Lee S., 1995d, *Chem. Phys. Lett.*, 243, 250
- Lee S., 1996, *J. Chem. Phys.*, 104, 1912
- Lee S., Freed K. F., 1987, *J. Chem. Phys.*, 87, 5772
- Lee E. G., Seto J. Y., Hirao T., Bernath P. F., Le Roy R. J., 1999, *J. Mol. Spectrosc.*, 194, 197
- Lefebvre-Brion H., Field R. W., 2004, *The Spectra and Dynamics of Diatomic Molecules*, revised and enlarged edition edn. Elsevier, Amsterdam
- Levine I., 2013, *Quantum Chemistry*. Advanced Chemistry Series, Pearson, <https://books.google.ca/books?id=2rEPAQAAMAAJ>
- Li Y., Zhang P.-Y., 2011, *J. Theor. Comp. Chem.*, 10, 747
- Little D. A., Tennyson J., 2014, *J. Phys. B-At. Mol. Opt. Phys.*, 47, 105204
- Little D. A., Tennyson J., Plummer M., Sunderland A., 2017, *Comput. Phys. Commun.*, 215, 137
- Lodi L., Tennyson J., 2010, *J. Phys. B-At. Mol. Opt. Phys.*, 43, 133001
- Loyd R. O. P., et al., 2016, *Astrophys. J.*, 824, 102
- Lund J. R., Riley B. V., 1984, *IMA J. Numer. Anal.*, 4, 83
- MacDonald R. J., Batalha N. E., 2023, *Research Notes of the AAS*, 7, 54
- Mandelstam V. A., Ravuri T. R., Taylor H. S., 1993, *Phys. Rev. Lett.*, 70, 1932
- Marigo P., Aringer B., Girardi L., Bressan A., 2022, *The Astrophysical Journal*, 940, 129
- Martin E. L., et al., 2010, *Astron. Astrophys.*, 517, A53
- Matthews E. C., et al., 2024, *Nature*
- Mayor M., Queloz D., 1995, *Nature*, 378, 355
- McDonald I., Sloan G. C., Zijlstra A. A., Matsunaga N., Matsuura M., Kraemer K. E., Bernard-Salas J., Markwick A. J., 2010, *Astrophys. J. Lett.*, 717, L92
- McKemmish L. K., Yurchenko S. N., Tennyson J., 2016, *Mol. Phys.*, 114, 3232
- McKemmish L. K., et al., 2017, *The Astrophysical Journal Supplement Series*, 228, 15
- McKemmish L. K., et al., 2018, *The Astrophysical Journal*, 867, 33
- McKemmish L. K., Bowesman C. A., Kefala K., Perri A. N., Syme A. M., Yurchenko S. N., Tennyson J., 2024, *RAS Tech. Instr.*

- Medvedev E. S., Ushakov V. G., 2022, [Journal of Quantitative Spectroscopy and Radiative Transfer](#), 288, 108255
- Medvedev E. S., Meshkov V. V., Stolyarov A. V., Ushakov V. G., Gordon I. E., 2016, [J. Mol. Spectrosc.](#), 330, 36
- Medvedev E. S., Ermilov A. Y., Ushakov V. G., 2024, [Mol. Phys.](#), 0, e2395439
- Meinel I. A. B., 1950, [Astrophys. J.](#), 111, 555
- Melendez J., Barbuy B., Spite F., 2001, [Astrophys. J.](#), 556, 858
- Meuwly M., Hutson J. M., 1999, [J. Chem. Phys.](#), 110, 8338
- Mitev G. B., Brady R. P., Smola O., Tennyson J., Yurchenko S. N., 2024, *Phys. Chem. Chem. Phys.*
- Mizus I. I., Lodi L., Tennyson J., Zobov N. F., Polyansky O. L., 2022, [J. Mol. Spectrosc.](#), 368, 111621
- Morse P. M., 1929, [Phys. Rev.](#), 34, 57
- Mulliken R. S., Christy A., 1931, [Physical Review](#), 38, 87–119
- Munoz-Romero C. E., et al., 2024, [Astrophys. J.](#), 964, 36
- Nee J. B., Lee L. C., 1984a, [J. Chem. Phys.](#), 81, 31
- Nee J. B., Lee L. C., 1984b, [J. Chem. Phys.](#), 81, 3811
- Nee J. B., Lee L. C., 1985, [Astrophys. J.](#), 291, 202
- Nugroho S. K., et al., 2021, [Astrophys. J. Lett.](#), 910, L9
- O'Hare P. A. G., Wahl A. C., 1972, [J. Chem. Phys.](#), 56, 4516–4525
- Osséni R., Dulieu O., Raoult M., 2009, [Journal of Physics B: Atomic, Molecular and Optical Physics](#), 42, 185202
- Owens A., He T., Hanicinec M., Hill C., Mohr S., Tennyson J., 2023a, [Plasma Sources Sci. Technol.](#), 32, 085015
- Owens A., He T., Hanicinec M., Hill C., Mohr S., Tennyson J., 2023b, [Plasma Sources Science and Technology](#), 32, 085015
- Parlant G., Yarkony D. R., 1999, [J. Chem. Phys.](#), 110, 363
- Patrascu A. T., Hill C., Tennyson J., Yurchenko S. N., 2014, [J. Chem. Phys.](#), 141, 144312
- Pavlenko Y., Tennyson J., Yurchenko S. N., Schmidt M. R., Jones H. R. A., Lyubchik Y., Suárez Mascareño A., 2022, [Mon. Not. Roy. Astron. Soc.](#), 516, 5655
- Pazyuk E., Stolyarov A., Pupyshev V., 1994, *Chem. Phys. Lett.*, 228, 219
- Pellegrini P., Dulieu O., Masnou-Seeuws F., 2002, [Eur. Phys. J. D](#), 20, 77

- Pezzella M., Yurchenko S. N., Tennyson J., 2021, [Phys. Chem. Chem. Phys.](#), 23, 16390
- Pezzella M., Yurchenko S. N., Tennyson J., 2022, [Mon. Not. Roy. Astron. Soc.](#), 514, 4413
- Pezzella M., Mitev G. B., Yurchenko S. N., Tennyson J., Mitrushchenkov A. O., 2024, [Phys. Chem. Chem. Phys.](#)
- Pfeifer J., Gole J. L., 1984, [J. Chem. Phys.](#), 80, 565
- Piccioni G., et al., 2008, [Astron. Astrophys.](#), 483, L29
- Pickett H. M., Poynter R. L., Cohen E. A., Delitsky M. L., Pearson J. C., Müller H. S. P., 1998, [J. Quant. Spectrosc. Radiat. Transf.](#), 60, 883
- Piette A. A. A., Gao P., Brugman K., Shahar A., Lichtenberg T., Miozzi F., Driscoll P., 2023, [Astrophys. J.](#), 954, 29
- Plane J. M. C., 2003, [Chem. Rev.](#), 103, 4963–4984
- Plane J., Oetjen H., Miranda M. D., Saiz-Lopez A., Gausa M., Williams B., 2012, [J. Atmos. Solar-Terrestrial Phys.](#), 74, 181–188
- Polyansky O. L., Zobov N. F., Tennyson J., Lotoski J. A., Bernath P. F., 1997a, [J. Mol. Spectrosc.](#), 184, 35
- Polyansky O. L., Tennyson J., Bernath P. F., 1997b, [J. Mol. Spectrosc.](#), 186, 213
- Popov A. M., Berezhnoy A. A., Borovicka J., Labutin T. A., Zaytsev S. M., Stolyarov V A., 2021, [Mon. Not. Roy. Astron. Soc.](#), 500, 4296
- Prinn R. G., et al., 1995, [Science](#), 269, 187
- Pugh J. V., Shen K. K., Winstead C. B., Gole J. L., 1996, [Chem. Phys.](#), 202, 129
- Qin X., Zhang S. D., 2014, [J. Korean. Phys. Soc.](#), 65, 2017
- Radenović D. Č., et al., 2003, [J. Chem. Phys.](#), 119, 9341
- Radenović D. Č., van Roij A. J., Wu S.-M., Meulen J. T., Parker D. H., van der Loo M. P., Janssen L. M., Groenenboom G. C., 2008, [Mol. Phys.](#), 106, 557
- Reiher M., Wolf A., 2004, [J. Chem. Phys.](#), 121, 10945
- Rey M., Nikitin A. V., Babikov Y. L., Tyuterev V. G., 2016, [J. Mol. Spectrosc.](#), 327, 138
- Rivlin T., McKemmish L. K., Spinlove K. E., Tennyson J., 2019, [Mol. Phys.](#), 117, 3158
- Robert J. Le Roy Carl C. Haugen J. T., Li H., 2011, [Mol. Phys.](#), 109, 435
- Rosen B. R., Moran J. M., Reid M. J., Walker R. C., Burke B. F., Johnston K. J., Spencer J. H., 1978, [Astrophys. J.](#), 222, 132
- Rothman L. S., et al., 2010, [J. Quant. Spectrosc. Radiat. Transf.](#), 111, 2139
- Sakellaris C. N., Miliordos E., Mavridis A., 2011, [J. Chem. Phys.](#), 134, 234308

- Sappey A. D., Crosley D. R., Copeland R. A., 1989, *J. Chem. Phys.*, 90, 3484
- Sarkhel S., Sekar R., Chakrabarty D., Narayanan R., S. S., 2009, *Adv. Ear. Space. Sci.*, 114
- Sarkhel S., Sekar R., Chakrabarty D., Sridharan S., 2010, *J. Geophys. Res.*, 115, A10306
- Sauval A. J., Tatum J. B., 1984, *Astrophys. J. Suppl. Ser.*, 56, 193
- Scheidegger S., Merkt F., 2024, *Phys. Rev. Lett.*, 132, 113001
- Schoerghofer N., et al., 2021, *Space Sci. Rev.*, 217, 74
- Semenov M., Yurchenko S. N., Tennyson J., 2017, *J. Mol. Spectrosc.*, 330, 57
- Shulyak D., Reiners A., Wende S., Kochukhov O., Piskunov N., Seifahrt A., 2010, *Astron. Astrophys.*, 523, A37
- Silva B. C., Barletta P., Munro J. J., Tennyson J., 2008, *J. Chem. Phys.*, 128, 244312
- Sink M., Bandrauk A., 1979, *Chem. Phys. Lett.*, 65, 246
- Sink M. L., Bandrauk A. D., Lefebvre R., 1980, *J. Chem. Phys.*, 73, 4451
- Skokov S., Peterson K. A., Bowman J. M., 1999, *Chem. Phys. Lett.*, 312, 494
- Slanger T. G., et al., 2005, *J. Geophys. Res.*, 110, D23302
- Slater J. C., Kirkwood J. G., 1931, *Phys. Rev.*, 37, 682
- Slipher V. M., 1929, *Publ. Astron. Soc. Pacific*, 41, 262–263
- Smith F. T., 1960, *Phys. Rev.*, 118, 349
- Snellen I., 2014, *Phil. Trans. Royal Soc. London A*, 372, 20130075
- Soldán P., Lee E. P. F., Gamblin S. D., Wright T. G., 1999, *Phys. Chem. Chem. Phys.*, 1, 4947–4954
- Sousa-Silva C., McKemmish L. K., Chubb K. L., Baker J., Barton E. J., Gorman M. N., Rivlin T., Tennyson J., 2018, *Phys. Educ.*, 53, 015020
- Spaanjaars J. J. L., ter Meulen J. J., Meijer G., 1997, *J. Chem. Phys.*, 107, 2242
- Srivastava S., Sathyamurthy N., 2014, *J. Phys. Chem. A*, 118, 6343
- Sulakshina O. N., Borkov Y. G., 2023, *Mol. Phys.*
- Sun G., Zheng X.-F., Qin Y., Song Y., Zhang J., Amero J. M., Vázquez G. J., 2020, *Chinese J. Chem. Phys.*, 33, 129
- Sun G., Zhou W., Zheng X., Qin Y., Song Y., Yuan Y., Zhang J., 2021, *Mol. Phys.*, 119, e1837974
- Šurkus A. A., Rakauskas R. J., Bolotin A. B., 1984, *Chem. Phys. Lett.*, 105, 291
- Sutcliffe B. T., Woolley R. G., "2005", *Phys. Chem. Chem. Phys.*, "7", "3664

- Tang K. T., 1969, [Phys. Rev.](#), 177, 108
- Tang N., et al., 2021, [Astrophys. J. Suppl. Ser.](#), 252, 1
- Tennyson J., Noble C. J., 1984, *Comput. Phys. Commun.*, 33, 421
- Tennyson J., Yurchenko S. N., 2012, [Mon. Not. Roy. Astron. Soc.](#), 425, 21
- Tennyson J., Yurchenko S. N., 2021, [Astron. Geophys.](#), 62, 6.16
- Tennyson J., Hill C., Yurchenko S. N., 2013, in 6th international conference on atomic and molecular data and their applications ICAMDATA-2012. AIP, New York, pp 186–195, [doi:10.1063/1.4815853](#)
- Tennyson J., et al., 2014, [Pure Appl. Chem.](#), 86, 1931
- Tennyson J., Lodi L., McKemmish L. K., Yurchenko S. N., 2016a, [J. Phys. B-At. Mol. Opt. Phys.](#), 49, 102001
- Tennyson J., et al., 2016b, [J. Mol. Spectrosc.](#), 327, 73
- Tennyson J., et al., 2020, [J. Quant. Spectrosc. Radiat. Transf.](#), 255, 107228
- Tennyson J., Pezzella M., Zhang J., Yurchenko S. N., 2023, [RAS Tech. Instr.](#), 2, 231
- Tennyson J., et al., 2024, [J. Quant. Spectrosc. Radiat. Transf.](#), 326, 109083
- Thorsbro B., et al., 2023, [Astrophys. J. Lett.](#), 958, L18
- Tinetti G., Liang M.-C., Vidal-Madjar A., Ehrenreich D., des Etangs A. L., Yung Y. L., 2006, [The Astrophysical Journal](#), 654, L99
- Tinetti G., Encrenaz T., Coustenis A., 2013, [Astron. Astrophys. Suppl.](#), 21
- Tinetti G., et al., 2018, [Experimental Astronomy](#), pp 135–209
- Tkatchenko A., Scheffler M., 2009, [Phys. Rev. Lett.](#), 102, 073005
- Unterguggenberger S., Noll S., Feng W., Plane J. M. C., Kausch W., Kimeswenger S., Jones A., Moehler S., 2016, [Atmos. Chem. Phys. Discuss.](#), 2016, 1
- Upadhyay A., et al., 2024, [J. Quant. Spectrosc. Radiat. Transf.](#)
- van Dishoeck E. F., Black J. H., 1982, [Astrophys. J.](#), 258, 533
- van Dishoeck E. F., Dalgarno A., 1983, [J. Chem. Phys.](#), 79, 873
- van Dishoeck E. F., Dalgarno A., 1984a, [Icarus](#), 59, 305
- van Dishoeck E. F., Dalgarno A., 1984b, [Astrophys. J.](#), 277, 576
- van Dishoeck E. F., Langhoff S. R., Dalgarno A., 1983, [J. Chem. Phys.](#), 78, 4552
- van Dishoeck E. F., van Hemert M. C., Allison A. C., Dalgarno A., 1984, [J. Chem. Phys.](#), 81, 5709

- van der Loo M. P. J., Groenenboom G. C., 2005, *J. Chem. Phys.*, 123, 074310
- Vogiatzis K. D., Ma D., Olsen J., Gagliardi L., de Jong W. A., 2017, *J. Chem. Phys.*, 147, 184111
- Wampfler, S. F. et al., 2010, *Astron. Astrophys.*, 521, L36
- Wang Z., et al., 2017, *Astron. J.*, 154, 249
- Wang Y., Owens A., Tennyson J., Yurchenko S. N., 2020, *Astrophys. J. Suppl. Ser.*, 248, 9
- Wang R., Balciunaite U., Chen J., Yuan C., Owens A., Tennyson J., 2023, *J. Quant. Spectrosc. Radiat. Transf.*, 306, 108617
- Weinreb S., Barrett A. H., Henry J. C., Meeks M. L., 1963, *Nature*, 200, 829
- Wende S., Reiners A., Ludwig H.-G., 2009, *Astron. Astrophys.*, 508, 1429
- Wende S., Reiners A., Seifahrt A., Bernath P. F., 2010, *Astron. Astrophys.*, 523, A58
- Werner H.-J., Knowles P. J., 1985, *J. Chem. Phys.*, 82, 5053
- Werner H. J., Knowles P. J., Lindh R., Manby F. R., Schütz M., 2010, MOLPRO, a package of ab initio programs
- Werner H.-J., Knowles P. J., Knizia G., Manby F. R., Schütz M., 2012, *WIREs Comput. Mol. Sci.*, 2, 242
- Werner H. J., et al., 2015, MOLPRO, version 2015.1, a package of ab initio programs, <http://www.molpro.net>
- Werner H.-J., et al., 2020, *J. Chem. Phys.*, 152, 144107
- Western C. M., 2017, *J. Quant. Spectrosc. Radiat. Transf.*, 186, 221
- Woods T. N., et al., 1996, *Journal of Geophysical Research: Atmospheres*, 101, 9541
- Wright S. O. M., et al., 2023, *Astron. J.*, 166, 41
- Xiang Y., Sun D., Fan W., Gong X., 1997, *Phys. Lett. A*, 233, 216
- Yamada C., Fujitake M., Hirota E., 1989, *J. Chem. Phys.*, 90, 3033–3037
- Yarkony D. R., 1992, *J. Chem. Phys.*, 97, 1838
- Youngblood A., et al., 2016, *Astrophys. J.*, 824, 101
- Yousefi M., Bernath P. F., Hodges J., Masseron T., 2018, *J. Quant. Spectrosc. Radiat. Transf.*, 217, 416
- Yurchenko S. N., Lodi L., Tennyson J., Stolyarov A. V., 2016a, *Comput. Phys. Commun.*, 202, 262
- Yurchenko S. N., Blissett A., Asari U., Vasilios M., Hill C., Tennyson J., 2016b, *Mon. Not. Roy. Astron. Soc.*, 456, 4524

- Yurchenko S. N., Bond W., Gorman M. N., Lodi L., McKemmish L. K., Nunn W., Shah R., Tennyson J., 2018a, [Monthly Notices of the Royal Astronomical Society](#), 478, 270
- Yurchenko S. N., Williams H., Leyland P. C., Lodi L., Tennyson J., 2018b, [Mon. Not. Roy. Astron. Soc.](#), 479, 1401
- Yurchenko S. N., Al-Refaie A. F., Tennyson J., 2018c, [Astron. Astrophys.](#), 614, A131
- Yurchenko S. N., Szajna W., Hakalla R., Semenov M., Sokolov A., Tennyson J., Pavlenko Y., Schmidt M. R., 2024, [Mon. Not. Roy. Astron. Soc.](#), 527, 9736
- Zannese M., Tabone B., Habart E., Le Petit F., van Dishoeck E. F., Bron E., 2023, [Astron. Astrophys.](#), 671, A41
- Zare R. N., 1988, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics*, 1st edn. Wiley
- Zhang J., Hill C., Tennyson J., Yurchenko S. N., 2024a, *Astrophys. J. Suppl. Ser.*
- Zhang J., Tennyson J., Yurchenko S. N., 2024b, [RAS Tech. Instr.](#), 3, 257
- Zhou W., Yuan Y., Zhang J., 2003, [J. Chem. Phys.](#), 119, 9989