

High Resolution Theoretical Spectroscopy of The Ozone Molecule

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

Abstract

Ozone is one of the important molecules in the Earth's atmosphere which requires accurate spectroscopic data to monitor its concentration. Towards this goal, detailed electronic structure calculations on the X^1A' ground electronic state of ozone have been performed to produce a new empirically refined potential energy surfaces (PES) for $^{16}O_3$, two new dipole moment surfaces (DMSs) and a new PES for the $^{18}O_3$ isotopologue using diagonal Born Oppenheimer correction functions. An accurate spectroscopic model of ozone in the microwave and infra-red region is developed. Tests of several physical quantities calculated from the spectroscopic model (such as molecular energies, transition intensities and line positions) against high accuracy measurements and calculations from literature show good agreement.

MARVEL analysis of measured ozone line positions is performed to derive empirical MARVEL energy levels of ozone that improve the accuracy of line position calculations [153].

Through the calculations performed in this thesis, the manifestation of the so called normal intensity distribution (NID) is observed in overtone transitions of ozone [102]. This result informs us on how to achieve better accuracy of weak transition intensities in particular. It is hoped that data from this thesis can contribute towards helping to resolve the ozone atmospheric retrieval problem.

Impact statement

The data produced from calculations performed in this thesis could contribute to the monitoring of ozone concentrations in the atmosphere. In the past, molecular data calculated using the methodology of this thesis (for example CO_2 [162]), has been accepted in international standard databases such as HITRAN [73, 72]. Some parts of the MARVEL analysis (Chapter 5) was performed by students of Parmiter's school as part of the ORBYTS education program (citizen science).

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List of publications

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- S.N. Yurchenko, J. Tennyson, A.-M. Syme, A.Y. Adam, V.H.J. Clark, B. Cooper, C.P. Dobney, S.T.E. Donnelly, M.N. Gorman, A.E. Lynas-Gray, T. Meltzer, A. Owens, Q. Qu, M. Semenov, W. Somogyi, **A. Upadhyay**, S. Wright and J.C. Zapata Trujillo, ExoMol line lists - XLIV. IR and UV line list for silicon monoxide ($^{28}\text{Si}^{16}\text{O}$), Mon. Not. R. astr. Soc., 510, 903-919 (2022)
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Chapter 1

Introduction

1.1 Importance of ozone

Ozone ($^{16}\text{O}_3$) is a radiatively and chemically important molecule in the Earth's atmosphere [57, 158, 104]. Ozone is also a pollutant in the troposphere, formed by reactions with emissions from cars and industry. In the study performed by Worden et al [158] tropospheric ozone was found to be an important factor affecting climate change. Even trace concentrations of ozone is harmful to humans, animals and plants. Equally ozone in the stratosphere, the ozone layer, provides an extremely important shield of solar ultraviolet radiation. Ozone is also considered an important bio-marker in our search for habitable exoplanets [76].

In the Earth's atmosphere, human activity such as chlorofluorocarbons (CFCs) emissions has resulted in a significant reduction in stratospheric ozone and this loss has led to depleted concentrations of ozone over regions of the Earth's poles, known as "ozone holes". Encouragingly the situation seems to have improved since the implementation of the Montreal Protocol, but concerns remain, not only over Antarctica but also over the Arctic circle in the north pole [97, 116].

Ozone in the Earth's stratosphere is formed by the ozone-oxygen cycle (commonly known as the Chapman cycle). Remote sensing techniques utilizing spectroscopic methods are used to determine ozone concentrations in the Earth's atmosphere. These techniques are employed both from ground based apparatus as well as from satellites in space. There are however long-standing inconsistencies between retrieval concentrations based on laboratory intensity measurements performed in the

infrared (IR) and ultraviolet (UV) wavelengths of the electromagnetic spectrum (Smith et al 2012 [125]; Worden et al 2007 [160]; Landgraf and Hasekamp 2007 [87]; Fu et al 2013 [62]; Worden et al 2013 [159]; Cuesta et al, 2013 [46]).

Hence studying the spectroscopy of ozone is crucial to understanding its impact in the Earth's atmosphere and the wider natural environment.

1.2 Ozone retrieval problem

Measurement of ozone concentrations in the atmosphere using remote sensing techniques involves analysing absorption spectra in IR and UV wavelengths via satellite and ground based equipment. This analysis requires reference data (line intensities) usually from laboratory experiments to interpret the observed spectra. We expect retrieval analysis at each wavelength region to give the same concentration of ozone in the atmosphere. However, there are major longstanding disagreements between retrievals of ozone concentrations at different wavelengths using experimental intensities as reference data. Major inconsistencies exist between several measurements of the strong $10\text{ }\mu\text{m}$ absorption IR bands, which differ by around 4%. Some of these measurements give atmospheric retrievals in line with the UV observation of the Hartley band at 254 nm and some of them do not (Smith et al 2012 [125]; Gratien et al 2010 [74]). Due to inconsistent retrievals particularly from the IR region, the retrievals based on UV wavelengths are considered the benchmark.

It was shown by Janssen et al (2016) [82] that the concentration of ozone determined by a retrieval based on data for the $10\text{ }\mu\text{m}$ band is around 2 to 3% different from that based on the $5\text{ }\mu\text{m}$ band. For the $3\text{ }\mu\text{m}$ region analysis by Toon (2017) [144] suggests that here too there are systematic differences with line intensities when compared with results for other wavelengths, in this case in the region of 9%.

The discrepancy between ozone retrievals obtained via line intensity data from different regions of the electromagnetic spectrum suggests that the measured line intensity data is suffering from inaccuracies particularly in the IR region. It is well known that ozone intensities in particular have a large uncertainty of measurement because ozone is a relatively weakly bound molecule with a low dissociation threshold and so it readily dissociates into diatomic oxygen. Hence it is difficult

to know the concentration of ozone in the sample while intensity measurements are being made [81, 72].

Theoretical calculations of line intensities have been shown to resolve disputes between conflicting experimental measurements of line intensities as shown in Figure 7 of Gordon et al [73] where calculations from Zak et al [162] are used as the benchmark for that particular band. To this end, Tyuterev et al [147] published theoretical calculations on ozone showing excellent sub 1% agreement between theory and experiment [79] for the strong intensity transitions in the microwave (MW), 5 μm and 10 μm wavelengths of the infra-red (IR) region. These calculations [147], which utilise a purely ab-initio theoretical model for intensities, were subsequently used to update the intensities for 31 bands in the latest release of the HITRAN 2020 database [72]. However, the accuracy of intensity calculations of weak transitions remains a problem with Gordon et al [72] saying that the target accuracy of line intensities is 1% for strong transitions and about 3 or 5% for weak transitions. Although weak bands have smaller values of intensities by orders of magnitude in some cases, they are important because they occupy large regions of the spectrum and are important for overtone transitions [102].

1.3 Line positions of ozone

While the previous section outlined the ozone retrieval problem related to inaccurate intensities, the focus of this section is on issues concerning ozone line position calculations and measurements. It is well known that theoretical calculations are not able to match the accuracy of experimentally measured line positions [72, 12]. Effective Hamiltonian (EH) models, usually known for predicting line positions very accurately, struggle to predict line positions of some bands because EH models are not able to completely account for resonance interactions of vibrational states especially at energies close to the dissociation threshold where the density of states is high and also because EH models do not extrapolate very well to energy regions other than what they are fitted to.

On the other hand, purely ab-initio theoretical models for many electron molecules, are also unable to generate accurate energy levels from which line positions are calculated. Another approach is to refine the purely ab-initio theoretical model by fitting to empirical or EH energy levels (such

models are designated semi-empirical). Attempts at refining the ab-initio model by fitting the model to empirical energy levels have been made by Polyansky et al [119] with good success as illustrated by excellent agreement of vibrational energies in Table 1 of their paper (mean difference between observed and calculated value being 0.001 cm^{-1}). Fitting the ab-initio theoretical model to empirical energy levels has the added advantage that it not only improves line position predictions, but also improves the accuracy of intensity predictions via more accurate wavefunctions of the molecule. However, it is not possible to refine the ab-initio model to perfection using this approach of fitting to empirical or EH energy levels, because the EH energy levels themselves are not exactly accurate and often the complete set of all empirical energy levels of ozone are not available because they have not been measured especially at high energies close to dissociation.

1.4 Literature review

Spectroscopy of ozone has been extensively studied in recent decades. This section summarizes recently published (and relevant) experimental and theoretical papers on ozone in the scientific literature and explains why they are important for the calculations that are performed as part of this thesis.

1.4.1 Experimental studies of ozone

The HITRAN [73, 72] and the S&MPO database [3] both contain extensive data on the spectroscopic properties of ozone. These compilations of spectroscopic data are critical to testing the theoretical models and comparing and validating calculations.

Birk et al [25] have published several rotational transition intensities in the microwave region. They performed these measurements to resolve a disagreement between rotational intensities that existed between the JPL database [114] and HITRAN database since 2004. Birk et al measurements [25] validate the JPL rotational intensities and the authors remark that the HITRAN rotational intensities were inadvertently scaled in 2004.

Drouin et al [53] initially published an article in validation of $10\text{ }\mu\text{m}$ intensities in the HITRAN database. However this validation is in doubt as they used the inadvertently scaled rotational

intensities from HITRAN2012 (the 2012 release) to deduce the ozone mixing ratio based on which they determined the 10 μm intensities. Birk et al [25] remark that the 10 μm values in the current HITRAN database could be in error by roughly 3%.

New measurements in the 10 and 5 μm bands by two groups are mentioned in the theoretical paper of Tyuterev et al [147]. Tyuterev et al also report Stark effect measurements (Lichtenstein et al [91]; Mack et al [96]; Meerts et al [103]) in the microwave region.

A critical phase of the MARVEL analysis (Furtenbacher et al [69, 68]) involves compiling a database of experimental line positions. To this end a large bibliography has been compiled of these experimental sources from literature. The data from them will be processed through the MARVEL program to determine the empirical energy levels of ozone (see chapter 6).

More recently very accurate measurements of ozone intensities have been performed by Jacquemart et al [79, 81]

1.4.2 Theoretical studies of Ozone

Several theoretical studies of the ozone molecule have been performed (Tyuterev et al [151, 150, 147]; Polyansky et al [119]). A good review is given by Flaud et al [61].

The paper published by Tyuterev et al [147] gives ozone intensity calculations for the microwave, 10 μm and 5 μm bands in which they report sub 1% agreement with recent LERMA, GSMA and Stark effect measurements. However they do not publish their intensities for the weak bands of ozone in the 9 and 3 μm regions.

An accurate ground state potential energy surface (PES) of ozone was initially determined by Tyuterev et al [148]. This PES was then further improved by the same authors (Tyuterev et al [149]). More recently Tyuterev et al [150] have calculated an ab initio dipole moment surface (DMS) and used it to compute intensities of the 10 μm infrared band belonging to the ν_1 and ν_3 bands.

Polyansky et al [119] have computed a high-accuracy ab initio dipole moment surface of ozone. Using an ab initio PES as a starting point, and by fitting to experimentally determined energy levels, several fitted potential energy surfaces have been determined. Intensities for the 10 μm and 5 μm were determined to within the experimental uncertainties by performing nuclear motion

calculations using their PES and DMS. Polyansky et al [119] also publish their intensity comparisons with HITRAN for the weak bands of ozone (9 μm and 3 μm).

In the theoretical study performed by Polyansky et al [119], in the 10 μm band (for which different laboratory measurements yield results which differ by up to 4 percent) their calculations coincide within 1 percent with the measurements selected by HITRAN and confirmed by simultaneous microwave and infrared measurements made by Drouin et al [53]. Although the recent paper by Birk et al [25] casts some doubts about the validation of 10 μm intensities by Drouin et al [53]. Furthermore, the calculations in the 5 μm band using the same surfaces gives results within the experimental accuracy of about 2 percent. The results for 3 μm suggest that a significant lowering of the intensities given by HITRAN in this region is needed; this result would appear also to be in line with recent atmospheric observations where a decrease in concentrations is inferred by the analysis of Toon (2017)[144]. A decrease in intensities within the 3 μm is predicted which appears consistent with atmospheric retrievals. More recently a hybrid line list of Jacquemart et al [80] combines ab-initio line intensities and effective Hamiltonian line positions. The ab-initio intensities in [80] are calculated using PES of Polyansky et al [119] and DMS (DMS F2) of Tyuterev et al [150].

1.5 Motivation and thesis structure

The aim of this thesis is to work towards building an ab-initio (or semi-empirical) theoretical spectroscopic model of ozone that improves on the accuracy of predicted strong and weak transition intensities as well as line positions of ozone in the MW and IR regions.

Towards this aim, Chapter 2 explains the general theoretical concepts, techniques and approximations used to build the spectroscopic model of ozone. It begins with a discussion of the Born-Oppenheimer approximation which separates electronic and nuclear motions in a molecule. The variational principle, a method used to calculate electronic and rotation-vibrational (ro-vibrational) energies and wavefunctions of atoms and molecules, is described. Key concepts from group theory, heavily used throughout this thesis, are outlined. Our entire methodology of computing ro-vibrational line lists (the ExoMol methodology) is defined.

Chapter 3 details the theory of electronic structure of polyatomic molecules and its subsequent application to perform state of the art MOLPRO [157] calculations to obtain a new potential energy surface and dipole moment surfaces of ozone. Details of the parameters used for ozone calculations are described and linked back to how they relate to the electronic structure methods. Details of how linear algebra and matrix mechanics methods are used to computationally solve the electronic structure equations are described.

Chapter 4 describes the theory of nuclear motion of tri-atomic molecules. The theory in this chapter is implemented in the DVR3D programs [139] which is used to perform highly accurate state of the art calculations of rotation-vibrational (ro-vibrational) transition intensities and line positions of ozone. Particular focus is given to explaining the need for different coordinate systems and how transforming between them changes the form of the ro-vibrational Hamiltonian. The ro-vibrational basis set used to construct the Hamiltonian matrix is detailed along with the solution procedure.

Chapter 5 is dedicated to MARVEL analysis of ozone line positions. The theory of how MARVEL energy levels are derived is explained along with the quantum mechanical description of ozone energy levels. MARVEL energies are compared to ozone energy levels derived from other methods. How MARVEL energy levels help to improve the accuracy of line positions of ozone is explained.

Chapter 6 is dedicated to line list calculations of $^{16}\text{O}_3$ and $^{18}\text{O}_3$ isotopologues. Details of MOLPRO calculations of the dipole moment surfaces (DMSs) are described along with different test results that justify the inclusion of effects (e.g. relativistic effects). The DMSs are fitted to a functional form and subsequently used as an input into the DVR3D program to compute transition intensities. A new empirically refined potential energy surface is built for $^{16}\text{O}_3$ and tested for its accuracy. Details of DVR3D parameters that generate the ro-vibrational line list of ozone are given. The resulting intensities of strong and weak transitions from DMSs of this work and those published in literature are compared to latest measurements. A new PES is constructed for $^{18}\text{O}_3$ using diagonal Born Oppenheimer correction (DBOC) functions and used to calculate a line list for $^{18}\text{O}_3$ and compare with data in literature.

The conclusion is presented in Chapter 7 which also includes descriptions of some current ongoing work and discussions of possible future work.

Chapter 2

General theory

This chapter covers some basic concepts from the theory of quantum mechanics that are essential to subsequent chapters of this thesis.

2.1 Born-Oppenheimer approximation

The total energy of a molecule is given by the following expression, the so called time independent non-relativistic Hamiltonian $\hat{H}$ operator:

$$\begin{aligned} \hat{H} = & \frac{-\hbar^2}{2} \sum_{\alpha} \frac{\nabla_{\alpha}^2}{M_{\alpha}} - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} \\ & + \sum_i \sum_{j > i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \end{aligned} \quad (2.1)$$

In Equation 2.1, the first term is the kinetic energy of the nuclei, the second term is the kinetic energy of the electrons, the third term is the inter nuclear repulsion term, the fourth term represents the electrostatic interaction between nuclei and electrons and the last term is the inter electronic repulsion term [24]. The eigenvalue equation which, upon solving, gives the energies and wave-functions of the molecule is the so called time independent Schrodinger equation and is given by:

$$\hat{H}\Phi = E\Phi \quad (2.2)$$

Under the Born-Oppenheimer approximation, the molecular wavefunction Φ is written as a product of the electronic Φ_{el} and nuclear part Φ_N , as in Equation 2.3.

$$\Phi \approx \Phi_{el}(\mathbf{r}_i; \mathbf{r}_\alpha) \Phi_N(\mathbf{r}_\alpha) \quad (2.3)$$

where $\mathbf{r}_i$ and $\mathbf{r}_\alpha$ are coordinates of electrons and nuclei respectively. After we insert Equation 2.3 into the time independent Schrodinger equation we get [24]

$$\begin{aligned} & \frac{-\hbar^2}{2} \sum_{\alpha} \Phi_N \frac{\nabla_{\alpha}^2 \Phi_{el}}{M_{\alpha}} - \hbar^2 \sum_{\alpha} \frac{(\nabla_{\alpha} \Phi_{el}) \cdot (\nabla_{\alpha} \Phi_N)}{M_{\alpha}} - \frac{-\hbar^2}{2} \sum_{\alpha} \Phi_{el} \frac{\nabla_{\alpha}^2 \Phi_N}{M_{\alpha}} \\ & - \frac{-\hbar^2}{2m_e} \sum_i \Phi_N \nabla_i^2 \Phi_{el} + V \Phi_{el} \Phi_N = E \Phi_{el} \Phi_N \end{aligned} \quad (2.4)$$

We neglect the first two terms of Equation 2.4, the remaining terms are separable into two eigenvalue equations, one representing the motion of the electrons and the other the motion of nuclei:

$$\begin{aligned} & \left[-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{\alpha} \sum_{\beta>\alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 r_{\alpha\beta}} \right] \Phi_{el}(\mathbf{r}_i; \mathbf{r}_{\alpha}) \\ & = U(\mathbf{r}_{\alpha}) \Phi_{el}(\mathbf{r}_i; \mathbf{r}_{\alpha}) \end{aligned} \quad (2.5)$$

$$\left[\frac{-\hbar^2}{2} \sum_{\alpha} \frac{\nabla_{\alpha}^2}{M_{\alpha}} + U(\mathbf{r}_{\alpha}) \right] \Phi_N(\mathbf{r}_{\alpha}) = E_N \Phi_N(\mathbf{r}_{\alpha}) \quad (2.6)$$

where the collections of first three terms in the square bracket of Equation 2.5 is called the electronic Hamiltonian $\hat{H}_{el}$. The eigenvalue equation 2.5 is called the electronic Schrodinger equation and is solved for different inter nuclear geometries $\mathbf{r}_{\alpha}$ by programs such as MOLPRO [157] to give us the potential energy surface $U(\mathbf{r}_{\alpha})$ for different electronic states of a molecule, as well as other properties such as the dipole moment surface. The eigenvalue equation 2.6, which is called the nuclear Schrodinger equation, is solved by programs such as DVR3D [139] and accounts for the rotational and vibrational motion of the molecule. The terms in the square brackets of equation 2.6 is called the ro-vibrational Hamiltonian $\hat{H}_{ro-vib}$. As can be seen, the nuclear Schrodinger equation requires the potential energy function (PES) $U(\mathbf{r}_{\alpha})$ as an input, after which it can be solved for the rotation-vibrational energies of the molecule. The Born-Oppenheimer approximation essentially

states that the molecular wavefunction is approximately equal to the product of the nuclear and electronic parts. This approximation is based on the fact that the nuclei are much more massive than electrons which means they move slowly in comparison to the electrons i.e. the electronic wavefunction does not change very much in response to the motion of the nuclei [24].

2.2 Variational method

The variational method is an approximate method of solving the time independent Schrodinger equation. If the lowest eigenvalue of a time independent Hamiltonian operator $\hat{H}$ is denoted as E_1 , then the variational principle states that E_1 is approximately given by [89]:

$$E_1 \leq \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \quad (2.7)$$

where ϕ is called a trial wavefunction (un-normalised) and the expression in equation 2.7 is called the variational integral (denoted as Δ). The aim is to find the best trial wavefunction ϕ that minimises Δ . The trial wavefunction is parametrised by a number of variational parameters c_i which are varied to minimise Δ [89].

A special form of the trial wavefunction is called linear trial wavefunction which take the following form:

$$\phi = \sum_i^n c_i f_i \quad (2.8)$$

where c_i are n number of variational parameters and f_i are n number of basis functions. Substituting equation 2.8 into the variational integral and then partially differentiating the expression with respect to each c_i leads us to obtain a system of n linear equations. Since Δ is a function of the variational parameters $\Delta(c_i)$ it should be necessary that

$$\frac{\partial \Delta}{\partial c_i} = 0 \quad i = 1, 2, \dots, n \quad (2.9)$$

in order to ensure we get the best possible approximation to the eigenvalues E_n of $\hat{H}$. Using the condition of equation 2.9, our system of n equations takes the form of n linear homogeneous

equations [89]:

$$\sum_{j=1}^n (H_{ij} - S_{ik}\Delta) c_j = 0 \quad i = 1, 2, \dots, n \quad (2.10)$$

where

$$H_{ij} \equiv \langle f_i | \hat{H} | f_j \rangle \quad S_{ij} \equiv \langle f_i | f_j \rangle \quad (2.11)$$

The c_j are the n unknowns in the system of equations 2.10 which are also the variational parameters of our linear trial wavefunction. For a non-trivial solution of the system of equations 2.10 the following condition must be met:

$$\det(H_{ij} - S_{ik}\Delta) = 0 \quad (2.12)$$

Equation 2.12 is called the characteristic polynomial of degree n in the unknown Δ . Solving the characteristic polynomial (finding the roots) gives us n number of solutions $(\Delta_1, \Delta_2, \dots, \Delta_n)$, each of which is an approximation to the eigenvalues $E_1, E_2, \dots, E_n$. For each eigenvalue E_i we can then solve for the set of variational parameters $c_1^{(i)}, c_2^{(i)}, \dots, c_n^{(i)}$ which define the linear trial wavefunction ϕ_i that is an approximation to the true wavefunction of that state [89].

Concepts from this section will be used later in chapter 3 to understand several methods of electronic structure calculations.

2.3 Group theory and symmetry

Group theory is arguably an abstract theory, but it is a very powerful and useful tool, when applied to spectroscopy of molecules. To list a few benefits, we can use group theory to classify or label molecular energy levels and wavefunctions; predict whether a spectroscopic transition between molecular states is allowed or not; speed up calculations of molecular energies and wavefunctions.

A group comprises a list or collection of symmetry operators. Operators in general act on objects which can be solid objects (e.g. an equilateral triangle based pyramid), vectors, wavefunctions, basis functions, Hamiltonian or even other operators. An operator is called a symmetry operator if it acts to transform the object and leave some property (e.g. total energy) of the object unchanged. There are two types of groups: point groups and complete nuclear permutation inversion (CNPI)

group. Point groups are restricted to analysing molecules at their equilibrium geometry, whereas CNPI groups do not have this constraint.

In the CNPI framework, a symmetry operation is a transformation (e.g. change in the coordinates of the particles of the molecule), via an operator $\hat{O}$, that leaves the Hamiltonian unchanged [31]. This is equivalent to the symmetry operator $\hat{O}$ commuting with the Hamiltonian $\hat{H}$:

$$[\hat{O}, \hat{H}] = 0 \quad (2.13)$$

Hence both operators $\hat{O}$ and $\hat{H}$ share a common set of eigenfunctions and the quantum numbers that define those eigenfunctions can be used to label energy eigenstates of $\hat{H}$. For example, the angular momentum operators $\hat{J}^2$, $\hat{J}_Z$ and $\hat{J}_z$ (square of rotational angular momentum and its projections onto the space-fixed Z and molecule fixed z axes respectively) commute with the Hamiltonian of a symmetric top polyatomic molecule, hence quantum numbers J, k, m that define eigenvalues of $\hat{J}^2$, $\hat{J}_Z$ and $\hat{J}_z$ can be used to label the symmetric top rotational eigenfunctions $\Phi_{rot} = |J, k, m\rangle$ which are eigenfunctions of $\hat{H}$ along with $\hat{J}^2$, $\hat{J}_Z$ and $\hat{J}_z$ [31].

As described earlier in this section, a group is a collection of symmetry operators obeying a number of group axioms [31]. The collection of symmetry operators $\{E, (12), E^*, (12)^*\}$ form the $C_{2v}(M)$ CNPI group. If a non-degenerate molecular wavefunction Φ transforms as:

$$\hat{O}\Phi = c^{\hat{O}}\Phi \quad (2.14)$$

where $c^{\hat{O}}$ is a constant called the character of the operator and $\hat{O}$ is a symmetry operator from $C_{2v}(M)$ group. For example the character of operator (12) is $c^{(12)} = \pm 1$. Hence a character table for the group $C_{2v}(M)$ can be constructed and molecular wavefunctions can be labelled according to how the wavefunctions transform with respect to each symmetry operator [31].

Table 2.1: Character table of $C_{2v}(M)$ CNPI group

$\Gamma[C_{2v}(M)]$	E	(12)	E^*	$(12)^*$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

Each row of the character table of $C_{2v}(M)$ tells us how the molecular wavefunction Φ transforms with respect to each symmetry operator so each Φ can be labelled by a row which is labelled by the four labels A_1 , A_2 , B_1 , B_2 called symmetry species, irreducible representations (irreps) or just simply symmetry of the wavefunction. Ro-vibrational states of ozone are labelled according to the symmetry species of either $C_{2v}(M)$ CNPI or the C_{2v} point group.

Basis functions can also be labelled according to the symmetry species of groups. Doing so helps us to evaluate integrals of the type:

$$I = \int \Phi''^* \hat{O} \Phi' d\tau \quad (2.15)$$

which occur in the expression for the transition dipole moment (proportional to intensities) or to evaluate matrix elements of the Hamiltonian operator. The vanishing integral rule, rooted in group theory, predicts whether these integrals will be zero or not without having to evaluate the integral [31]. Vanishing integral rule states that for the case $\Gamma(\hat{O}) = A_1$, the integral I in Equation 2.15 will vanish if [31]:

$$\Gamma(\Phi'') \neq \Gamma(\Phi') \quad (2.16)$$

This has advantages in speeding up calculations because many fewer integrals need to be evaluated. Concepts from this section are frequently used in the calculation of ro-vibrational energies and wavefunctions in Chapter 6 and also in the analysis of ozone energies, including the problem of "missing" energy levels of ozone, in Chapter 5.

2.4 ExoMol methodology

The ExoMol project aims to provide line lists for molecules which are of terrestrial and astrophysical importance in the atmospheres of Earth, cool stars, brown dwarfs and of extrasolar planets [140]. The approach combines ab-initio (theoretical) calculations and semi-empirical methods to generate molecular data such as intensities and line positions which is required in modelling stellar and planetary atmospheres using radiative transfer theory and to characterise observed spectra from these regions. As part of the ExoMol project, many studies on other molecules of terrestrial interest have already been carried out, for example CO₂ [117, 162] and H₂O [118, 44].

The molecular data calculated for diatomic and polyatomic molecules includes labelled energy levels of the molecule, transition frequencies, transition probabilities (Einstein A coefficients), temperature dependent partition function and absorption cross sections. The series of steps followed in the methodology that leads to line list generation is illustrated in Figure 2.1.

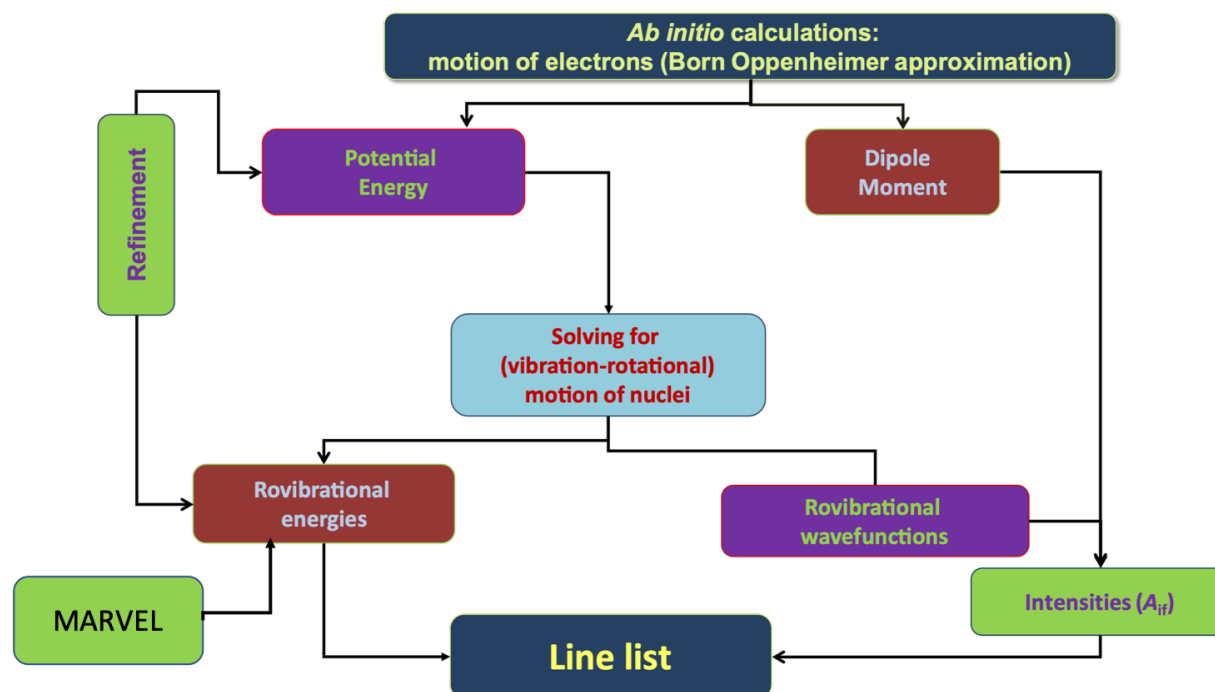


Figure 2.1: Exomol methodology

The first step involves electronic structure calculations to obtain the potential energy surface (PES) and the dipole moment surface (DMS) for the particular electronic state. The PES is used as an input into the nuclear Schrodinger equation which is solved for the rotation-vibrational energies

and wavefunctions based on principles from the matrix formulation of quantum mechanics for polyatomic molecules. The energies obtained from the calculations can be refined or replaced with experimental energies. This can be done using the MARVEL (measured active rotation-vibration experimental level) procedure [69, 68]. The rotation-vibrational wavefunctions are used with the DMS to calculate the expectation values of the transition dipole moment, which give the Einstein A coefficients and hence intensities. Line positions are differences between energy levels.

Chapter 3

Electronic Structure

This chapter outlines the theory of electronic structure methods used in calculations of the potential energy and dipole moment surfaces of ozone later in this thesis.

3.1 Hartree-Fock approximation

The electronic Hamiltonian for a molecule with n electrons and N nuclei is written as

$$\hat{H}_{elec} = -\frac{\hbar^2}{2m_e} \sum_i^n \nabla_i^2 - \sum_\alpha^N \sum_i^n \frac{Z_\alpha e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_i^n \sum_{j>i}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (3.1)$$

The last term in Equation 3.1 is the electrostatic repulsion between electrons and is often called the electron correlation term. Due to this term the electronic Hamiltonian is not separable into analytically solvable units. If however, we neglect the last term in Equation 3.1 entirely, $\hat{H}_{elec}$ is separable into a sum of n identical one-electron Hamiltonians $\hat{h}_i$ interacting with fixed N nuclei. The separable electronic Hamiltonian $\hat{H}_{elec}^{sep}$ is given as [31]

$$\begin{aligned} \hat{H}_{elec}^{sep} &= \sum_i \hat{h}_i \\ \text{where } \hat{h}_i &= -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_\alpha^N \frac{Z_\alpha e^2}{4\pi\epsilon_0 r_{i\alpha}} \end{aligned} \quad (3.2)$$

If we designate the molecule fixed coordinates of each electron to be $\mathbf{r}_i = x_i, y_i, z_i$ then the eigenfunctions $\Phi_{elec}^{sep(k)}$ of $\hat{H}_{elec}^{sep}$ can be written as a product of spatial functions $\chi_i(\mathbf{r}_i)$:

$$\Phi_{elec}^{sep(k)} = \chi_1(\mathbf{r}_1) \chi_2(\mathbf{r}_2) \dots \chi_n(\mathbf{r}_n) \quad (3.3)$$

where the spatial functions $\chi_i(\mathbf{r})$ are the solutions of the one-electron Schrodinger equation [31]

$$\hat{h} \chi_i(\mathbf{r}_i) = \varepsilon_i \chi_i(\mathbf{r}_i) \quad (3.4)$$

The dependence of $\chi_i(\mathbf{r}_i)$ on nuclear coordinates $\mathbf{r}_\alpha$ is implied. The eigenvalues $E_{sep}^{(k)}$ of $\hat{H}_{elec}^{sep}$ are given by

$$E_{sep}^{(k)} = \varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_n \quad (3.5)$$

Since an electron has spin $s = \frac{1}{2}$, $m_s = -\frac{1}{2}, \frac{1}{2}$, therefore there are two spin functions for an electron $\delta = |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle = |\alpha\rangle, |\beta\rangle$. Denoting spin coordinates by σ_i we can construct one-electron functions called spin-orbitals ϕ by combining the spatial and spin functions:

$$\phi(\mathbf{r}_i, \sigma_i) = \chi(\mathbf{r}_i) \delta(\sigma_i) \quad (3.6)$$

We can construct molecular electronic wavefunctions Φ_{elec} by taking linear combinations of spin-orbitals ϕ . Taking linear combinations of spin-orbitals is necessary in order to satisfy the so called Pauli exclusion principle which is rooted in the much more general spin statistics theorem of identical particles [31]. For example, the normalised ground electronic wavefunction of the Hydrogen molecule, for a particular configuration of electrons, can be written in the so called Slater determinant form as

$$\Phi_{elec}^{H_2} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_i(\mathbf{r}_1, \sigma_1) & \phi_j(\mathbf{r}_1, \sigma_1) \\ \phi_i(\mathbf{r}_2, \sigma_2) & \phi_j(\mathbf{r}_2, \sigma_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi(1)\alpha(1) & \chi(1)\beta(1) \\ \chi(2)\alpha(2) & \chi(2)\beta(2) \end{vmatrix} \quad (3.7)$$

where the notation $\chi(1)$ indicates the spatial part of the spin-orbital for electron labelled as number one.

In general, the electronic wavefunction for a molecule with n electrons, for a particular electronic configuration, can be written in Slater determinant form as

$$\Phi_{elec}^n = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_i(\mathbf{r}_1, \sigma_1) & \phi_j(\mathbf{r}_1, \sigma_1) & \dots & \phi_k(\mathbf{r}_1, \sigma_1) \\ \phi_i(\mathbf{r}_2, \sigma_2) & \phi_j(\mathbf{r}_2, \sigma_2) & \dots & \phi_k(\mathbf{r}_2, \sigma_2) \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \phi_i(\mathbf{r}_n, \sigma_n) & \phi_j(\mathbf{r}_n, \sigma_n) & \dots & \phi_k(\mathbf{r}_n, \sigma_n) \end{vmatrix} \quad (3.8)$$

The Slater determinant for the electronic wavefunction of the molecule in Equation 3.8 accounts for Pauli exclusion principle but entirely neglects electron correlation (electrostatic repulsion term between electrons).

Electron correlation can be approximately accounted for, in the so called Hartree-Fock approximation, by considering the potential energy of interaction of one electron with the total charge density distribution made from the sum of individual charge densities of the other $n - 1$ electrons in the molecule. This can be visualised as a single electron moving through and interacting with a cloud or smeared out charge density distribution of fixed electrons [31].

For instance, the potential energy of interaction V_{12} between two point charges (electrons) q_1 and q_2 is given by

$$V_{12} = \frac{q_1 q_2}{4\pi\epsilon_0 r_{12}} \quad (3.9)$$

If we now consider electron two q_2 to be a continuous charge distribution with charge density ρ_2 (charge per unit volume dv_2) then V_{12} becomes [89]

$$V_{12} = \frac{q_1}{4\pi\epsilon_0} \int \frac{\rho_2}{r_{12}} dv_2 = \frac{q_1}{4\pi\epsilon_0} \int \frac{q_2 |\phi_2|^2}{r_{12}} dv_2 \quad (3.10)$$

where the second equality in Equation 3.10 comes about because we can express ρ_2 in terms of its corresponding spin-orbital ϕ_2 via the relation $\rho_2 = q_2 |\phi_2|^2$. $|\phi_2|^2$ is the probability density function of the second electron. If we sum the interaction of electron one with the other $n - 1$ electrons ($V_{12}, V_{13}, V_{14} \dots$) we get the following approximate expression for the potential energy of interaction

of electron one with the other electrons [31]

$$\sum_{j=2}^n \frac{q_1}{4\pi\epsilon_0} \int \frac{q_j |\phi_j|^2}{r_{1j}} dv_j \quad (3.11)$$

The expression in Equation 3.11 contains the so called Coulomb operator $\hat{J}_j(1)$ for electron one. The effect of $\hat{J}_j(1)$ acting on an arbitrary spin orbital $\phi_i(1)$ is illustrated in Equation 3.12 below

$$\hat{J}_j(1) \phi_i(1) = \phi_i(1) \int \frac{|\phi_j(2)|^2}{r_{12}} dv_2 \quad (3.12)$$

Due to the requirement of the Pauli exclusion principle placed on the electronic wavefunction, which says that the electronic wavefunction must be anti-symmetric with respect to interchange of two electrons, a further exchange interaction is considered and defined by its effect on an arbitrary spin orbital $\phi_i(1)$ as [130]

$$\hat{K}_j(1) \phi_i(1) = \phi_j(1) \int \frac{\phi_j^*(2) \phi_i(2)}{r_{12}} dv_2 \quad (3.13)$$

where the notation $\phi_i(1)$ is used to indicate the spin-orbital for electron number one and $\hat{K}_j(1)$ is the exchange operator. Extra terms from Equations 3.11 and 3.13 can now be added to $\hat{h}_i$ in equation to construct the Hartree-Fock operator $\hat{h}_i^{HF}$ which approximately accounts for electron correlation in the manner detailed above.

$$\hat{h}_i^{HF} = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{\alpha}^N \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_{j=2}^n \frac{q_1}{4\pi\epsilon_0} \int \frac{q_j |\phi_j|^2}{r_{1j}} dv_j + \sum_{j=2}^n \phi_j(1) \int \frac{\phi_j^*(2) \phi_i^*(2)}{r_{12}} dv_2 \quad (3.14)$$

The Hartree-Fock equation for each electron is then given by

$$\hat{h}_i^{HF} \phi_i(\mathbf{r}_i, \sigma_i) = \varepsilon_i^{HF} \phi_i(\mathbf{r}_i, \sigma_i) \quad (3.15)$$

The Hartree-Fock equations can then be solved to give the spin-orbitals for each electron in the molecule [31]. However, the Hartree-Fock operator $\hat{h}_i^{HF}$ itself depends on the spin-orbitals $\phi_i(\mathbf{r}_i, \sigma_i)$, therefore an initial guess for the spin-orbitals needs to be made to determine $\hat{h}_i^{HF}$ after which the Hartree-Fock equations of (3.15) are solved for a new (and better) set of spin-orbitals. This process

is repeated until there is no appreciable change in the latest set of spin-orbitals from the previous set. The new set of spin-orbitals are used once again to construct $\hat{h}_i^{HF}$ and solve for another new set of spin-orbitals. This iterative process of using the latest spin-orbitals and using them to construct $\hat{h}_i^{HF}$ and subsequently solve for a new set of spin-orbitals is called the 'self consistent field' (SCF) method [89].

In practice, the Hartree-Fock equations are solved using linear algebra or matrix algebra methods. These calculations are known as the Hartree-Fock self consistent field (HF-SCF) method.

Linear algebra method

Representing the spin-orbitals as a linear combination of one-electron basis functions ξ_μ :

$$\phi_i(\mathbf{r}_i, \sigma_i) = \sum_{\mu=1}^d c_{i\mu} \xi_\mu \quad (3.16)$$

Inserting equation 3.16 into the Hartree-Fock equation 3.15 gives

$$\hat{h}_i^{HF} \sum_{\mu=1}^d c_{i\mu} \xi_\mu = \varepsilon_i^{HF} \sum_{\mu=1}^d c_{i\mu} \xi_\mu \quad (3.17)$$

Multiplying by ξ_ν^* and integrating on both sides gives [89]

$$\int \xi_\nu^* \hat{h}_i^{HF} \sum_{\mu=1}^d c_{i\mu} \xi_\mu d\tau = \int \xi_\nu^* \varepsilon_i^{HF} \sum_{\mu=1}^d c_{i\mu} \xi_\mu d\tau \quad (3.18)$$

$$\Rightarrow \sum_{\mu=1}^d c_{i\mu} (H_{\mu\nu}^{HF} - \varepsilon_i^{HF} S_{\mu\nu}) = 0 \quad \nu = 1, 2, 3, \dots, d \quad (3.19)$$

where $H_{\mu\nu}^{HF}$ and $S_{\mu\nu}$ are matrix elements of the Hartree-Fock and overlap matrices respectively [89].

These matrices are given by

$$H_{\mu\nu}^{HF} = \int \xi_\nu^* \hat{h}_i^{HF} \xi_\mu d\tau = \langle \xi_\nu | \hat{h}_i^{HF} | \xi_\mu \rangle \equiv \mathbf{H}_{HF} \quad (3.20)$$

$$S_{\mu\nu} = \int \xi_\nu^* \xi_\mu d\tau = \langle \xi_\nu | \xi_\mu \rangle \equiv \mathbf{S} \quad (3.21)$$

Equation 3.19 describes a set of d homogeneous linear equations where $c_{i\mu}$ are the unknown variables ($c_{i\mu}$ are the expansion coefficients of the spin-orbitals in Equation 3.16). There exists a solution if the following condition is met:

$$\det(H_{\mu\nu}^{HF} - \varepsilon_i^{HF} S_{\mu\nu}) = 0 \quad (3.22)$$

Solving the characteristic polynomial of equation (3.22) gives the spin-orbital energies ε_i^{HF} for each spin orbital. Each ε_i^{HF} can be inserted back into equations 3.19 and the set of linear equations are solved to calculate the spin-orbital expansion coefficients $c_{i\mu}$. A number of standard linear algebra methods for solving a set of linear equations are available. The set of linear equations 3.19 must still be solved iteratively because in order to determine $c_{i\mu}$ one must first calculate the matrix elements $H_{\mu\nu}^{HF}$ and $S_{\mu\nu}$ which themselves depend on the unknown variables $c_{i\mu}$ [89].

Matrix algebra method

Re-writing the set of linear Equations 3.19 we get

$$\sum_{\mu=1}^d H_{\mu\nu}^{HF} c_{i\mu} = \sum_{\mu=1}^d S_{\mu\nu} c_{i\mu} \varepsilon_i^{HF} \quad \nu = 1, 2, 3, \dots, d \quad (3.23)$$

Using the matrix multiplication notation equation, (3.23) can be written in matrix form as

$$\mathbf{H}_{HF} \mathbf{C} = \mathbf{S} \mathbf{C} \lambda \quad (3.24)$$

where $\mathbf{H}_{HF}$ and $\mathbf{S}$ matrices are defined in equations 3.20 and 3.21 respectively [89]. The matrix $\mathbf{C}$ contains the unknown coefficients $c_{i\mu}$ of the spin-orbitals and matrix λ is a diagonal matrix containing the unknown orbital energies $\varepsilon_1^{HF}, \varepsilon_2^{HF}, \dots, \varepsilon_i^{HF}$ along the diagonal. In equation 3.16 it was not assumed that the basis functions ξ_μ are orthogonal. These basis functions can be transformed into an orthogonal basis ξ'_σ by the so called Gram-Schmidt procedure [89]. Since the transformed basis functions ξ'_σ are orthogonal, the overlap matrix $\mathbf{S}'$ expressed in ξ'_σ basis is equal to an identity matrix:

$$S'_{\mu\nu} = \int \xi_\nu^* \xi'_\mu d\tau = \langle \xi'_\nu | \xi'_\mu \rangle \equiv \mathbf{S}' = \mathbf{I} = \delta_{\mu\nu} \quad (3.25)$$

Matrices expressed in the new orthogonal basis functions ξ'_σ are labelled with a ' superscript and hence equation (3.24) in the ξ'_σ basis becomes:

$$\mathbf{H}'_{HF} \mathbf{C}' = \lambda \mathbf{C}' \quad (3.26)$$

The orthogonal basis functions ξ'_σ are related to the previous basis ξ_μ by

$$\xi'_\sigma = \sum_{\mu} g_{\mu\sigma} \xi_{\mu} \quad (3.27)$$

and so [89]:

$$\mathbf{C} = \mathbf{G} \mathbf{C}' \quad \text{and} \quad \mathbf{H}'_{HF} = \mathbf{G}^\dagger \mathbf{H}_{HF} \mathbf{G} \quad (3.28)$$

where matrix $\mathbf{G}$ contains the coefficients $g_{\mu\sigma}$ from Equation 3.27. The form of Equation 3.26 is that of a matrix eigenvalue equation where matrices $\mathbf{C}'$ and λ contain the eigenvectors and eigenvalues of $\mathbf{H}'_{HF}$ to be found [89].

If we construct matrix $\mathbf{C}'$ where each column of $\mathbf{C}'$ is an eigenvector of $\mathbf{H}'_{HF}$ then the eigenvalues of $\mathbf{H}'_{HF}$ are given by

$$\lambda = \mathbf{C}'^\dagger \mathbf{H}'_{HF} \mathbf{C}' \quad (3.29)$$

where matrix λ in Equation 3.29 is a diagonal matrix containing the spin-orbital energies ϵ_i^{HF} . The process of finding matrix $\mathbf{C}'$, which diagonalises $\mathbf{H}'_{HF}$ into the diagonal form λ , is called matrix diagonalisation. Several standard methods of matrix diagonalisation are available [89].

The Hartree-Fock equations are solved for M number of spin-orbitals, greater than the n number of electrons. This creates the concept of occupied and virtual orbitals. If the electrons occupy spin-orbitals with the lowest energies, then this electronic configurations represents the ground electronic state. This leaves $M - n$ number of virtual orbitals that are unoccupied.

The electron correlation energy defined as [89]

$$E_{correlation} = E_{exact} - E_{HF} \quad (3.30)$$

is a measure of the accuracy of the Hartree-Fock method.

Although the Hartree-Fock method approximately accounts for electron correlation, the Hartree-Fock wavefunction still does not display the correct behaviour at large inter-nuclear geometries [89]. Furthermore, dissociation energies of molecules predicted under the Hartree-Fock approximation are not accurate [89, 85]. These limitations indicate that we must better account for electron correlation. Some methods that do this are: configuration interaction, CASSCF, MRCI and they will be discussed in the following sections of this chapter.

3.2 Configuration Interaction

In the Hartree-Fock approximation, the electronic wavefunction is expressed as a Slater determinant corresponding to one electronic configuration in terms of orbital occupancy. Sometimes, a linear combination of several Slater determinants is required to express an open shell electronic configuration. The concept of configuration interaction (CI) involves expressing the electronic wavefunction Φ_{elec} as a function (linear combination) of several electronic configurations. Each electronic configuration is represented by a many electron function called a configuration state function (CSF) Φ^{CSF} [31]

$$\Phi_{elec} = \sum_i a_i \Phi_i^{CSF} \quad (3.31)$$

where a CSF is a function comprising of one or more Slater determinants of spin-orbitals. Excited electronic configurations are constructed by exciting electrons from occupied orbitals into virtual orbitals [89]. The entire configuration space *i.e.* the set of M occupied and virtual orbitals are obtained from the HF-SCF calculation. If one or two electrons are excited into a virtual orbitals, the new electronic configuration and hence the new CSF is labelled as singly or doubly excited. Calculations where only singly and doubly excited CSFs are considered are called CI-SD (where S stands for singly, and D stands for doubly) [89].

CFSs belonging to the same irreducible representation as Φ_{elec} are considered in the expansion in Equation 3.31. The total number of all possible CSFs depends on the number of electrons n and the number of basis functions ξ_μ and therefore is very large. Usually a full CI calculation (where all possible CSFs are accounted for) is not computationally feasible. Triplet and quadruple

excitations can also be considered, where three or four electrons are excited into virtual orbitals, however this also increases the number of CSFs and hence make the calculation harder to perform and therefore are usually neglected. Davidson et al [88] devised an approximate formula to account for the missing triplet and quadruple excitations. This correction is called the Davidson correction and is often included in molecular electronic structure calculations [89].

The variational principle can be used to calculate the desired electronic state and its energy by using Equation 3.31 as a trial function where the coefficients a_i in Equation 3.31 are taken as variational parameters. The variational parameters a_i are varied to minimise the variational integral.

3.3 CASSCF

Since full CI is not computationally feasible for systems containing a large number of electrons, we can instead, choose a subset of CSFs to contribute to our electronic wavefunction. One such method is called the complete active space (CAS) where we divide all the spin-orbitals into active and inactive orbitals. The set of inactive spin-orbitals are always chosen to be kept doubly occupied among all CSFs that are considered. The active spin-orbitals are named such because the active electrons that occupy them are free to move and generate CSFs. Only those CSFs are chosen to contribute to the wavefunction, which are generated from distributing all active electrons among the active spin-orbitals in all possible ways. Usually, those spin-orbitals which are made from the valence atomic orbitals are chosen as active orbitals, and this choice of the active space is known as full valence complete active space [89].

Once the CSFs are defined via the choice of the CAS, we can use the variational principle where now we not only regard the a_i coefficients from equation 3.31 as variational parameters, but also we treat the coefficients $c_{i\mu}$ (expansion of spin-orbitals ϕ_i in basis functions ξ_μ) from equation (3.16) as variational parameters. This is called the CASSCF method [89].

3.4 MRCI

The multi reference configuration interaction (MRCI) method uses the set of CSFs from the CASSCF step (called reference CSFs) to generate more CSFs from each of the reference CSFs. This is done by exciting electrons to virtual orbitals from each reference CSF in turn [89].

The MRCI method helps to illustrate the difference between single reference and multiple reference electronic structure methods. In a single reference method, for example a single reference full CI, all the CSFs ($\Phi_2^{CSF}, \Phi_3^{CSF}, \dots, \Phi_k^{CSF}$) are generated from a single CSF Φ_1^{CSF} by exciting electrons to virtual orbitals. The Φ_1^{CSF} itself could be obtained by an HF-SCF calculation. In a multi reference calculation we start with the set of reference CSFs and build new CSFs from them to contribute towards the electronic wavefunction. Both coefficients a_i and $c_{i\mu}$ are still treated as variational parameters and optimised to minimise the variational integral [89]. At the MRCI level of theory, the final wavefunction can include contributions from some triplet and quadruple excitations [89].

Chapter 4

Nuclear Motion

In this chapter, the theory of nuclear motion for solving the nuclear Schrödinger equation is described. This theory forms the basis of the programs DVR3D [139] and EVEREST [108].

4.1 Ro-vibrational hamiltonian

In this section, many coordinate transformations are considered. This is necessary not only for better (more intuitive) understanding of molecular physics but also to speed up calculations of ro-vibrational energies and wavefunctions by reducing the dimensionality of the three-body triatomic nuclear motion problem [24, 31].

4.1.1 Lab-frame Cartesian coordinates

The laboratory frame and the cartesian coordinate system, with the nuclei of a triatomic molecule, are shown in Figure 4.1:

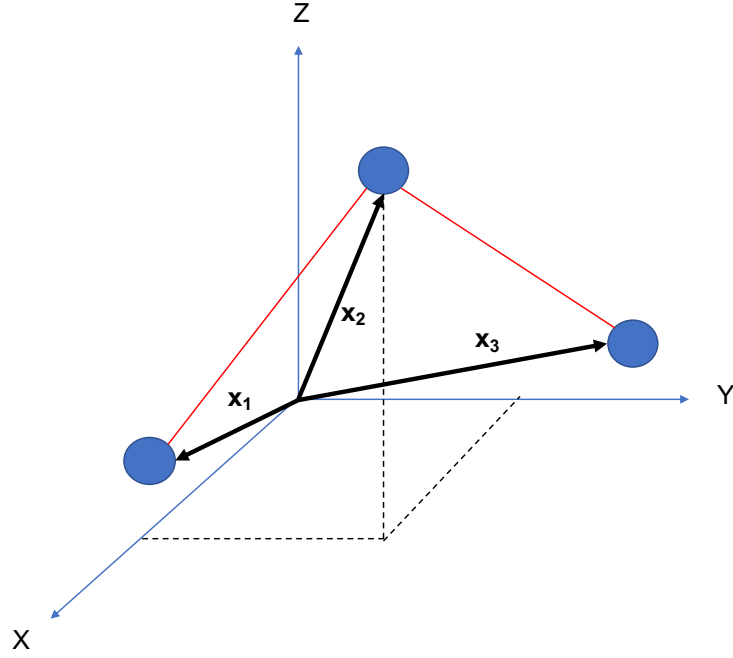


Figure 4.1: The laboratory frame and the cartesian coordinate system X,Y,Z

The Hamiltonian for the nuclei of a triatomic molecule in the laboratory frame using cartesian coordinates (in atomic units) is given by Equation 4.1.

$$\hat{H}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \hat{K} + V = -\frac{1}{2} \sum_{i=1}^3 \frac{\nabla_i^2(\mathbf{x}_i)}{m_i} + V(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \quad (4.1)$$

Where vectors $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ are the positions vectors of the nuclei as illustrated in Figure 4.1 and m_i are the nuclear masses. The Hamiltonian in the laboratory frame is a function of 3N coordinates where N is the number of nuclei [31].

4.1.2 Space-fixed coordinates

The transformation from laboratory frame ($\mathbf{x}_i$ for $i = 1, 2, 3$) to the space-fixed coordinate system ($\mathbf{t}_i$ for $i = 1, 2$) is described by Equation 4.2 and transformation matrix T. The space-fixed frame is centered at the molecular center of mass [129].

$$\mathbf{t}_1 = \sum_{j=1}^3 \mathbf{x}_j T_{ji} \quad i = 1, 2 \quad (4.2)$$

$$T = \begin{bmatrix} -g_2 & 1 \\ 1 & -g_1 \\ g_2 - 1 & g_1 - 1 \end{bmatrix} \quad (4.3)$$

The transformation matrix elements T_{ij} satisfy the conditions $\sum_{j=1}^3 T_{ji} = 0$. These conditions need to be met to ensure the translational kinetic energy of center of mass is separated from the kinetic energy of the internal motion. This transformation gives two vectors $\mathbf{t}_1$ and $\mathbf{t}_2$, as given in Equation 4.4, that describe the position of the nuclei and translate along with the molecule.

$$\begin{aligned} \mathbf{t}_1 &= (\mathbf{x}_2 - \mathbf{x}_3) + g_2(\mathbf{x}_3 - \mathbf{x}_1) \\ \mathbf{t}_2 &= (\mathbf{x}_1 - \mathbf{x}_3) + g_1(\mathbf{x}_3 - \mathbf{x}_2) \end{aligned} \quad (4.4)$$

Internal coordinates r_1 , r_2 and θ are defined by taking the lengths of $\mathbf{t}_1$ and $\mathbf{t}_2$ and the angle between them:

$$r_1 = |\mathbf{t}_1| \quad r_2 = |\mathbf{t}_2| \quad \theta = \frac{\mathbf{t}_1 \cdot \mathbf{t}_2}{|\mathbf{t}_1||\mathbf{t}_2|} \quad (4.5)$$

Jacobi (scattering) and Radau coordinates are two common space-fixed or internal coordinates and are defined by choosing parameters g_1 and g_2 as follows in Equations 4.6 and 4.7 [139]:

$$g_1 = \frac{m_2}{m_2 + m_3} \quad g_2 = 0 \quad \text{for Jacobi (scattering) coordinates} \quad (4.6)$$

and

$$\begin{aligned} g_1 &= 1 - \frac{A}{A + B - AB} \quad g_2 = 1 - \frac{A}{1 - B + AB} \\ A &= \left(\frac{m_3}{m_1 + m_2 + m_3} \right)^{1/2} \quad B = \frac{m_2}{m_1 + m_2} \quad \text{for Radau coordinates} \end{aligned} \quad (4.7)$$

The Radau and Jacobi internal coordinates are illustrated in Figure 4.2,

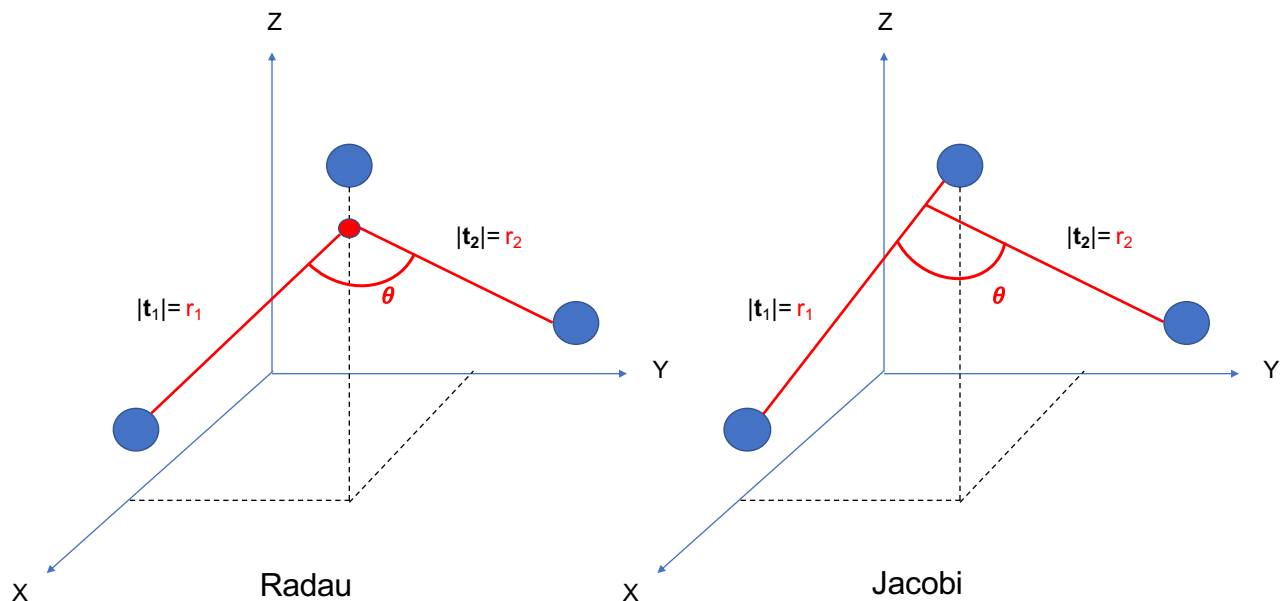


Figure 4.2: Internal coordinates r_1, r_2, θ

The r_1, r_2 and θ coordinates are contained in the plane containing the nuclei, and as the molecule rotates about a certain axis, the plane containing the nuclei and the internal coordinates, rotates along with the molecule. We can draw the vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ from the geometric point (red dot in Figure 4.2) towards the two nuclei along r_1 and r_2 .

To write the Hamiltonian in space-fixed coordinates we need to know how the partial derivatives with respect to each of the nine laboratory frame coordinates $\left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i}\right)$ for $i = 1, 2, 3$ are related to partial derivatives with respect to internal coordinates $\left(\frac{\partial}{\partial r_1}, \frac{\partial}{\partial r_2}, \frac{\partial}{\partial \theta}\right)$. The multi-variable chain rule allows us to find these relations for first and second partial derivatives as shown in Equations 4.8 - 4.9 with laboratory coordinate x_1 as an example:

$$\frac{\partial}{\partial x_1} = \frac{\partial}{\partial r_1} \frac{\partial r_1}{\partial x_1} + \frac{\partial}{\partial r_2} \frac{\partial r_2}{\partial x_1} + \frac{\partial}{\partial \theta} \frac{\partial \theta}{\partial x_1} \quad (4.8)$$

$$\frac{\partial}{\partial x_1} \left(\frac{\partial}{\partial x_1} \right) = \frac{\partial^2}{\partial x_1^2} = \frac{\partial}{\partial r_1} \frac{\partial^2 r_1}{\partial x_1^2} + \frac{\partial}{\partial r_2} \frac{\partial^2 r_2}{\partial x_1^2} + \frac{\partial}{\partial \theta} \frac{\partial^2 \theta}{\partial x_1^2} \quad (4.9)$$

Partial derivatives such as $\frac{\partial r_1}{\partial x_1}$ and $\frac{\partial^2 r_1}{\partial x_1^2}$ are derived from Equation 4.4. Once all the partial derivatives are calculated, they can be substituted into Equation 4.1 to get the space-fixed Hamiltonian.

The final result is presented in Equation 4.10 [129].

In terms of space-fixed coordinates the Hamiltonian can be written as

$$\hat{H}(\mathbf{t}_1, \mathbf{t}_2) = \hat{K} + V = -\frac{1}{2} \sum_{i,j=1}^{N-1} \mu_{ij}^{-1} \nabla_{\mathbf{t}_i} \cdot \nabla_{\mathbf{t}_j} + V(\mathbf{t}_1, \mathbf{t}_2) \quad (4.10)$$

where matrix elements $\mu_{ij}^{-1} = \sum_{k=1}^N m_k^{-1} V_{ki} V_{kj}$ and m_k are the masses of the nuclei. The $3N - 3$ space-fixed coordinates represent both vibrational and rotational degrees of freedom. The translational energy of the center of mass is completely and exactly separated in the space-fixed frame and can be neglected [31]. An advantage of using Radau internal coordinates is that they are orthogonal which means mixed derivative terms like for example $\frac{\partial^2}{\partial r_1 \partial \theta}$ do not appear in the kinetic energy operator, which makes it easier to build the Hamiltonian, when we act on the basis functions. Radau and Jacobi are examples of orthogonal internal coordinates, but not all internal coordinates are orthogonal e.g. bond-length bond-angle coordinates.

4.1.3 Molecule-fixed coordinates

We can separate the translational contribution to the total energy of the molecule, by referring the nuclei (and electrons) to the space-fixed axes (as we saw in previous section). For high accuracy calculations of ro-vibrational energies and wavefunctions it is desirable to also try to separate the rotational and vibrational degrees of freedom. This can be partially achieved by introducing a rotating x, y, z axes with origin at the nuclear center of mass - this frame is called the molecule-fixed or body-fixed axes [31]. One choice of molecule-fixed frame called bisector embedding (along with the Radau space-fixed frame) is illustrated in Figure 4.3.

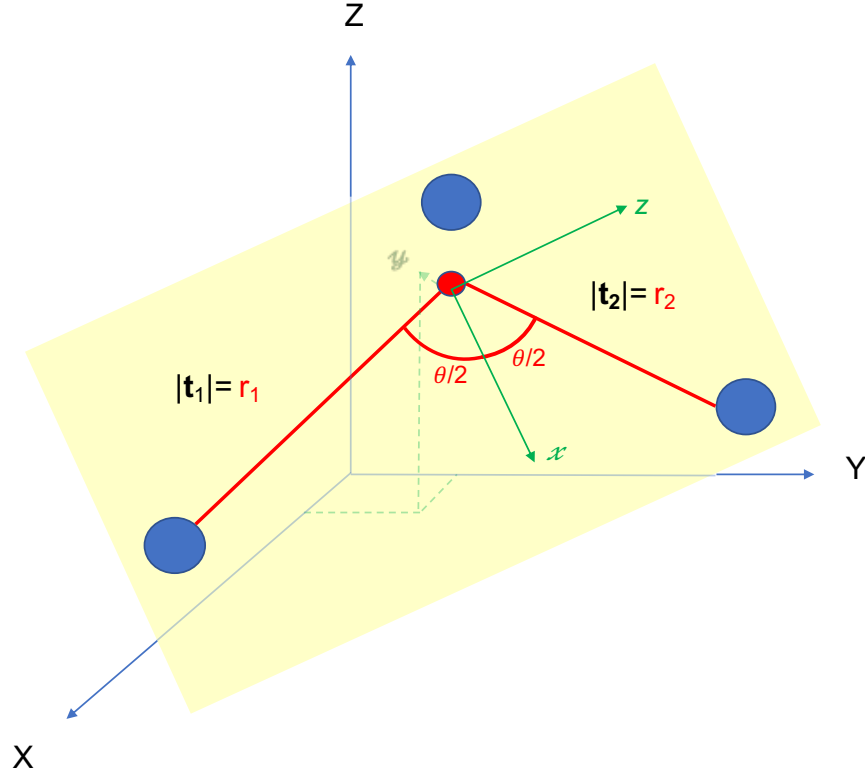


Figure 4.3: Molecule-fixed bisector embedding x, y, z with Radau internal space-fixed coordinates

The so called Euler angles α, β, γ describe the orientation of the molecule-fixed axes x, y, z with respect to the space-fixed frame. The transformation from space-fixed to molecule-fixed frame is given by the relation [128]

$$\mathbf{z} = \mathbf{C}^T \cdot \mathbf{t} \quad (4.11)$$

where $\mathbf{C}$ is the rotation matrix given by [94, 93]

$$\mathbf{C}(\alpha, \beta, \gamma) = \begin{bmatrix} \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma & \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma & -\sin \beta \cos \gamma \\ -\cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma & -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma & \sin \beta \sin \gamma \\ \cos \alpha \sin \beta & \sin \alpha \sin \beta & \cos \beta \end{bmatrix} \quad (4.12)$$

According to [129] $\mathbf{C}$ is chosen such that the two $\mathbf{z}$ vectors lie in the molecule-fixed $x - z$ plane with molecule-fixed components given by

$$\mathbf{z} = \begin{bmatrix} z_{x1} & z_{x2} \\ z_{y1} & z_{y2} \\ z_{z1} & z_{z2} \end{bmatrix} \quad (4.13)$$

The vectors $\mathbf{t}$ and $\mathbf{z}$ are illustrated in Figure 4.4 along with Radau space-fixed and molecule-fixed x, y, z frames.

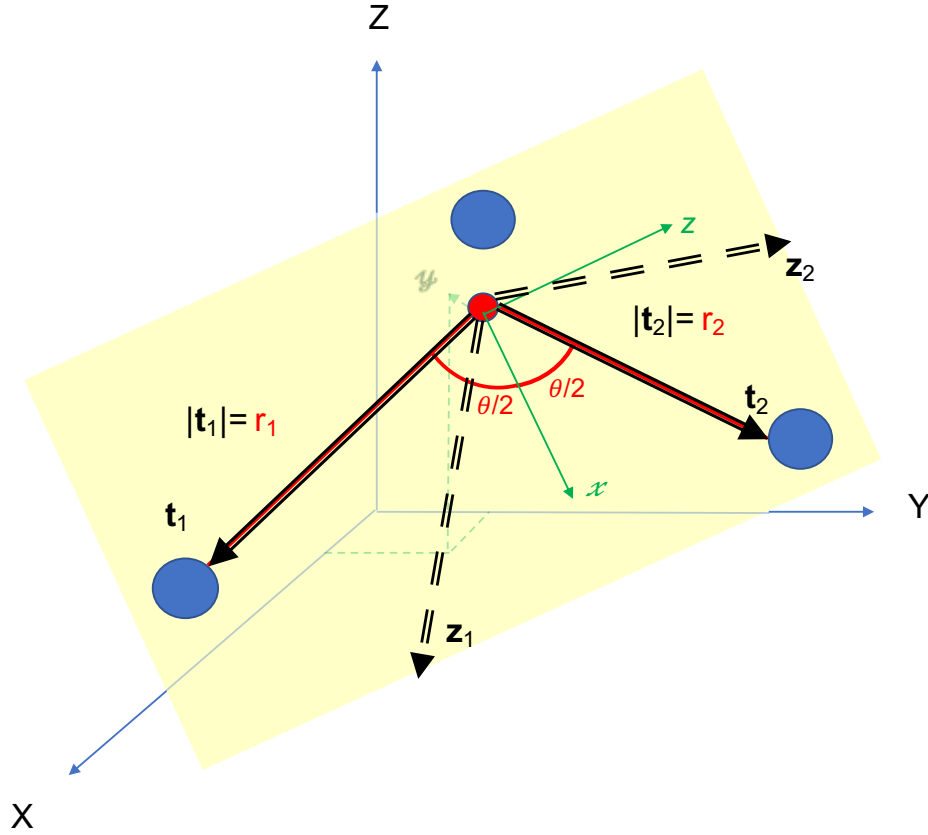


Figure 4.4: $\mathbf{t}$ and $\mathbf{z}$ vectors along with molecule-fixed bisector embedding and Radau internal space-fixed coordinates

Using the chain rule [129] the space-fixed Hamiltonian can be transformed into the molecule-fixed Hamiltonian which takes the form

$$\hat{H}(r_1, r_2, \theta, \alpha, \beta, \gamma) = \hat{K}_V^{(1)}(r_1, r_2, \theta) + \mu_{12}^{-1} \hat{K}_V^{(2)}(r_1, r_2, \theta) + \hat{K}_{VR}(r_1, r_2, \theta, \alpha, \beta, \gamma) + V(r_1, r_2, \theta) \quad (4.14)$$

where:

$$\hat{K}_V^{(1)}(r_1, r_2, \theta) = \frac{-\hbar^2}{2} \left[\frac{1}{\mu_1 r_1^2} \left(\frac{\partial}{\partial r_1} r_1 \frac{\partial}{\partial r_1} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\mu_2 r_2^2} \left(\frac{\partial}{\partial r_2} r_2 \frac{\partial}{\partial r_2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) \right] \quad (4.15)$$

$$\hat{K}_V^{(2)}(r_1, r_2, \theta) = \frac{\hbar^2}{\mu_{12}} \left[-\cos \theta \frac{\partial^2}{\partial r_1 \partial r_2} + \frac{\cos \theta}{r_1 r_2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \sin \theta \left(\frac{1}{r_1} \frac{\partial}{\partial r_2} + \frac{1}{r_2} \frac{\partial}{\partial r_1} + \frac{1}{r_1 r_2} \right) \frac{\partial}{\partial \theta} \right] \quad (4.16)$$

$$\begin{aligned} \hat{K}_{VR}(r_1, r_2, \theta, \alpha, \beta, \gamma) = & \frac{1}{2} [M_{xx} \hat{J}_x^2 + M_{yy} \hat{J}_y^2 + M_{zz} \hat{J}_z^2 + M_{xz} (\hat{J}_x \hat{J}_z + \hat{J}_z \hat{J}_x)] \\ & + \frac{\hbar}{i} \hat{J}_y \left[\left(\frac{1-a}{\mu_1 r_1^2} - \frac{a}{\mu_2 r_2^2} \right) \left(\frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right) + \frac{2a-1}{\mu_{12} r_1 r_2} \left(\cos \theta \frac{\partial}{\partial \theta} + \frac{1}{2 \sin \theta} \right) \right. \\ & \left. + \frac{\sin \theta}{\mu_{12}} \left(\frac{a}{r_2} \frac{\partial}{\partial r_1} - \frac{1-a}{r_1} \frac{\partial}{\partial r_2} \right) \right] \end{aligned} \quad (4.17)$$

The M_{ij} are elements of the moment of inertia tensor given in [129] in terms of r_1, r_2, θ internal coordinates and molecule-fixed components of vector $\mathbf{z}$ (as given in Equation 4.13). This is why $\hat{K}_{VR}$ is dependent on choice of molecule-fixed frame. Because we can choose to embed the molecule/body-fixed frame in a different way and then components of vector $\mathbf{z}$ will change, θ is the angle between r_1 and molecule-fixed z axis and $\hat{J}_i$ are the molecule-fixed total rotational angular momentum operators that can be expressed in terms of the Euler angles α, β, γ alone. Vectors $\mathbf{t}$ and $\mathbf{z}$ are projected onto the space-fixed and molecule-fixed frame respectively.

As can be seen from the term $\hat{K}_{VR}$ it is not possible to completely de-couple rotation and vibrational motion. Furthermore the exact form that $\hat{K}_{VR}$ takes depends on the molecule-fixed frame chosen (coriolis coupling is frame dependent) as we shall see later in this chapter. The Eckart frame [56] minimises the rotation-vibrational coupling. In the DVR3D program [139] a choice between four types of molecule-fixed frames are available. The Radau internal coordinates are orthogonal and due to this $\mu_{12}^{-1} = 0$ and the second term in Equation 4.14 vanishes.

4.2 Ro-vibrational basis set

Referring the triatomic ro-vibrational Hamiltonian to space-fixed and molecule-fixed frames is not only beneficial for breaking down the total energy into its rotational and vibrational contributions, it is also beneficial because it transforms the hamiltonian in terms of coordinates that correspond to coordinates of basis functions. This helps to build the Hamiltonian matrix (see section 4.3). Furthermore, symmetry adapted basis functions can be built so that all matrix elements do not need to be evaluated - this saves considerable time and computer resources.

The variational, trial, ro-vibrational wavefunction can be written in terms of basis functions in the general form as [163]

$$\left| \Phi_{rot,vib}^{(i)} \right\rangle = \sum_{u,w} \varepsilon^{(i)} \left| \Phi_{vib,u,w} \right\rangle \left| \Phi_{rot,u} \right\rangle \quad (4.18)$$

where u and w act as labels to signify sets of rotational and vibrational quantum numbers respectively. Also worth mentioning is the coupling between the rotational and vibrational basis via the commonality of u between them - this as we shall see later is important in accounting for coriolis ro-vibrational coupling.

Rotational basis functions

The symmetric top rigid rotor wavefunctions are given by

$$\left| \Phi_{rot}(\alpha, \beta, \gamma) \right\rangle = \left| J, k, M \right\rangle = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} [D_{kM}^J(\alpha, \beta, \gamma)]^* \quad (4.19)$$

where J quantum number gives eigenvalue $J(J+1)\hbar^2$ for rotational angular momentum operator $\hat{J}^2$, quantum number k gives eigenvalue $k\hbar$ for operator $\hat{J}_z$ (the projection of J onto the molecule-fixed z axis). Quantum number M gives eigenvalue $M\hbar$ for operator $\hat{J}_Z$ (the projection of J onto the space-fixed Z axis) and is usually ignored because the ro-vibrational energy levels do not depend on M . Hence rotational basis functions are written as $\left| J, k, M \right\rangle \equiv \left| J, k \right\rangle$.

$D_{kM}^J(\alpha, \beta, \gamma)$ are the so called Wigner rotation matrices [31]. Quantum number k takes on values from $k = -J, -J+1 \dots +J$ and therefore there are $2J+1$ rotational basis functions.

Vibrational basis functions

The vibrational basis functions Φ_{vib} are given as a product of one-dimensional functions in each of the internal coordinates r_1, r_2, θ [139].

$$|\Phi_{vib}\rangle = |m\rangle |n\rangle |j, k\rangle \quad (4.20)$$

The functions $|m\rangle, |n\rangle$ are so called Laguerre type polynomials corresponding to r_1 and r_2 radial coordinates (or vice versa) and they take two functional forms called Morse-oscillator and spherical-oscillator like functions. The Morse-oscillator type functions are given by Equations 4.21 [139].

$$\begin{aligned} |n\rangle &= H_n(r_1) = \beta^{1/2} N_{n\alpha} e^{\frac{y}{2}} y^{\frac{\alpha+1}{2}} L_n^\alpha(y) \\ y &= A e^{-\beta(r_1-r_e)} \\ A &= \frac{4D_e}{\omega_e} \\ \beta &= \omega_e \left(\frac{\mu}{2D_e} \right)^{1/2} \\ \alpha &= \text{integer}(A) \end{aligned} \quad (4.21)$$

The spherical-oscillator functions take the form in Equations 4.22 [139]:

$$\begin{aligned} |n\rangle &= H_n(r_2) = \sqrt{2} \beta^{1/4} N_{n(\alpha+1)} e^{\frac{-y}{2}} y^{\frac{\alpha+1}{2}} L_n^{\alpha+1/2}(y) \\ y &= \beta r_2^2 \\ \beta &= (\mu\omega_e)^{1/2} \end{aligned} \quad (4.22)$$

The vibrational basis $|j, k\rangle$ in the θ coordinate (also called the bending coordinate) is given by the so called Legendre polynomial as follows:

$$|j, k\rangle = P_j^{(|k|)} \cos \theta \quad (4.23)$$

The bending $|j, k\rangle$ basis couples the bending vibration of the molecule with the rotational motion via

the k quantum number. This accounts for the so called ro-vibrational Coriolis coupling, expressed in the $\hat{K}_{VR}$ term in the molecule-fixed ro-vibrational Hamiltonian given in equation 4.14.

At this stage, with the above basis functions so far, the full ro-vibrational Hamiltonian is labelled by the following quantum numbers: J, k, m, n, j . Hence for a given J , the full Hamiltonian has dimensions $(2J + 1)N_{r_1}N_{r_2}N_\theta$ where $N_{r_1}N_{r_2}N_\theta$ are the sizes of the $|m\rangle, |n\rangle, |j, k\rangle$ one-dimensional vibrational basis functions.

J is a good quantum number, k is an approximate quantum number and m, n, j are only labels for the vibrational basis functions.

Symmetry adapted ro-vibrational basis functions

We can construct symmetry adapted basis functions to take advantage of computational efficiencies and good quantum number labelling of energy levels that symmetry operations provide.

The parity symmetry operation E^* transforms states with quantum number k into states with quantum number $-k$. This is physically equivalent to clockwise and anti-clockwise rotation of the molecule about the molecule-fixed z axis with the energy un-affected by this transformation. We can symmetry adapt the rotational-bending basis by the following combination of Legendre polynomials and symmetric top rotational basis functions [128, 163]:

$$|J, K, j, p\rangle = \frac{1}{\sqrt{2(1 + \delta_{k0})}} |j, k\rangle [|J, k\rangle + (-1)^p |J, -k\rangle]^* \quad (4.24)$$

where the new quantum number $p = 0$ (e) or 1 (f) is the rotationless parity. $K = |k|$ with K ranging from p to J ($p = 0$ or 1). The character of E^* is given by $(-1)^{J+p}$ which gives the total parity.

The permutation symmetry operation of identical nuclei $\hat{P}_{12}$ interchanges the r_1 and r_2 coordinates and hence effectively acts on the radial vibrational basis functions. So the symmetry adapted vibrational basis can be constructed as [128, 163]:

$$|m, n, q\rangle = \frac{1}{\sqrt{2(1 + \delta_{mn})}} [|m\rangle|n\rangle + (-1)^q |n\rangle|m\rangle] \quad (4.25)$$

The character of $\hat{P}_{12}$ is given by $(-1)^q$

Hence the ro-vibrational wavefunction in the non-symmetry-adapted basis could be written as

[163]

$$|J, (i)\rangle = \sum_{k=-J}^J \sum_{m,n,j} \varepsilon_{m,n,j,k}^{(i),J} |m\rangle |n\rangle |j, k\rangle |J, k\rangle \quad (4.26)$$

where J is a good quantum number and (i) is a unique counting number label. Now, the ro-vibrational wavefunction, expanded in the symmetry adapted ro-vibrational basis set used to build and diagonalise the Hamiltonian, can be written as [163]:

$$|J, (i), p, q\rangle = \sum_{K=p}^J \sum_{m,n,j} \varepsilon_{m,n,j,K}^{(i),J,p,q} |m, n, q\rangle |J, K, j, p\rangle \quad (4.27)$$

where now J, p, q are good quantum numbers because $\hat{J}^2$, E^* and $\hat{P}_{12}$ commute with the Hamiltonian therefore all have a set of simultaneous eigenfunctions.

4.3 Building the Hamiltonian

This section illustrates how we construct the Hamiltonian given in Equation 4.14 using the non-symmetry-adapted basis functions described in section 4.2.

We use the rotational basis to integrate out the rotational coordinates, namely the Euler angles α, β, γ , to give us [163]:

$$\langle J', k' | \hat{H}(r_1, r_2, \theta, \alpha, \beta, \gamma) | J, k \rangle = \delta_{J'J} \hat{H}(r_1, r_2, \theta) = \hat{H}^J(r_1, r_2, \theta) \quad (4.28)$$

where J is a good quantum number and therefore $\hat{H}^J(r_1, r_2, \theta)$ is diagonal in J (superscript J indicates this) and block diagonal overall (non-diagonal in k in general). $\delta_{J'J}$ followed by an operator indicates that when that operator acts on basis functions with the same value of J , only then the result is non-zero. The operator is said to be diagonal in quantum number J . However, when the basis functions are also labelled by other quantum numbers such as k then the matrix representation of the operator is diagonal in J , but non-diagonal overall.

$\hat{H}^J(r_1, r_2, \theta)$ is called the effective vibrational Hamiltonian [129] and is given and takes the form [163, 129, 128]:

$$\hat{H}^J(r_1, r_2, \theta) = \delta_{k'k} \left[\hat{K}_V^{(1)'}(r_1, r_2, \theta) + V'(r_1, r_2, \theta) \right] + \hat{K}_{VR}'(r_1, r_2, \theta) \quad (4.29)$$

where k is considered a good quantum number only when coriolis ro-vibrational coupling is neglected or when the molecule is at linear geometry. Equation 4.29 shows that terms $\hat{K}_V(r_1, r_2, \theta)$ and $V(r_1, r_2, \theta)$ are diagonal in quantum numbers J and k whereas $\hat{K}_{VR}(r_1, r_2, \theta)$ is diagonal in J and partially diagonal in k (only some of its terms are diagonal in k). Hence $\hat{H}^J(r_1, r_2, \theta)$ is block-diagonal. Full forms of terms in equation 4.29 are given below [128, 129]:

$$\hat{K}_V^{(1)'}(r_1, r_2, \theta) = -\frac{\hbar^2}{2} \left[\frac{1}{\mu_1 r_1^2} \frac{\partial^2}{\partial r_1^2} + \frac{1}{\mu_2 r_2^2} \frac{\partial^2}{\partial r_2^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right) \right] \quad (4.30)$$

$$\hat{K}_{VR}'(r_1, r_2, \theta) = \delta_{k'k \pm 2} \frac{\hbar^2}{4} C_{Jk \pm 1}^\pm C_{Jk}^\pm b_- + \delta_{k'k \pm 1} \frac{\hbar^2}{2} C_{Jk}^\pm \lambda^\pm + \delta_{k'k} \frac{\hbar^2}{2} [b_+(J(J+1) - k^2) + b_0 k^2]$$

$$\begin{aligned} \lambda^\pm = \frac{1}{\mu_1 r_1^2} & \left[\mp(1-a) \left(\frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right) + \frac{z_{x2} z_{z2}}{r_2^2 \sin^2 \theta} \left(k \pm \frac{1}{2} \right) \right] \\ & + \frac{1}{\mu_2 r_1^2} \left[\mp a \left(\frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right) + \frac{z_{x1} z_{z1}}{r_2^2 \sin^2 \theta} \left(k \pm \frac{1}{2} \right) \right] \end{aligned}$$

$$C_{Jk}^\pm = [J(J+1) - k(k \pm 1)]^{1/2}$$

$$b_\pm = \frac{M_{xx} \pm M_{yy}}{2}$$

$$b_0 = M_{zz}$$

$$(4.31)$$

Terms containing $\delta_{k'k \pm 2}$ indicate that some off-diagonal matrix elements are non-zero and these non-diagonal elements contribute to the block diagonal structure of the Hamiltonian.

For certain values of the internal coordinate θ the Hamiltonian in Equation 4.29 suffers from going to infinity due to certain terms like $1/\sin \theta$. The Hamiltonian is said to contain singularities. Sutcliffe and Tennyson [137] propose that using the Legendre polynomial basis of equation 4.23 for

the bending coordinate resolves the problem of singularities. Integrating over the θ coordinate with the Legendre polynomial basis gives [128, 129]:

$$\langle j', k' | \hat{H}^J(r_1, r_2, \theta) | j, k \rangle = \hat{H}_{eff}^J(r_1, r_2) = \delta_{j'j} \delta_{k'k} \hat{K}_V^{(1)''}(r_1, r_2) + \hat{K}_{VR}''(r_1, r_2) + \delta_{k'k} V''(r_1, r_2) \quad (4.32)$$

where:

$$\begin{aligned} \hat{K}_V^{(1)''}(r_1, r_2) = & -\frac{\hbar^2}{2} \left[\frac{1}{\mu_1} \frac{\partial^2}{\partial r_1^2} + \frac{1}{\mu_2} \frac{\partial^2}{\partial r_2^2} - j(j+1) \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right) \right] \\ & - \frac{(\hbar k)^2}{2} \left[\langle j', k' | \frac{1}{\sin^2 \theta} | j, k \rangle \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right) \right] \end{aligned} \quad (4.33)$$

The exact form of term $\hat{K}_{VR}''(r_1, r_2)$ is dependent on the choice of the molecule-fixed frame because of the individual moments of inertia. For the Bisector embedding where the molecule-fixed x axis bisects the angle (as shown in section 4.1.3), $\hat{K}_{VR}''(r_1, r_2)$ takes the form [129]:

$$\begin{aligned} \hat{K}_{VR}''(r_1, r_2) = & \left[\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right] \left[\frac{\delta_{k'k}}{8} I_{j'k'jk}^{(1)} [J(J+1) - 3k^2] + \frac{\delta_{k'k} \delta_{j'j}}{16} [J(J+1) - k^2] \right] \\ & + \frac{\delta_{k'k \pm 1} C_{jk}^\pm}{4} \left[\frac{1}{\mu_2 r_2^2} - \frac{1}{\mu_1 r_1^2} \right] \left[\delta_{j'j} C_{jk}^\pm + I_{j'k'jk}^{(2)} \left(k + \frac{1}{2} \right) \right] \\ & + \frac{\delta_{k'k \pm 2} C_{jk \pm 1}^\pm C_{jk}^\pm \hbar^2}{32} \left[(2I_{j'k'jk}^{(1)} - I_{j'k'jk}^{(3)}) \right] \end{aligned} \quad (4.34)$$

where:

$$\begin{aligned} I_{j'k'jk}^{(1)} &= \langle j', k' | \frac{1}{1 - \cos \theta} | j, k \rangle & I_{j'k'jk}^{(2)} &= \langle j', k' | \frac{1 + \cos \theta}{\sin \theta} | j, k \rangle \\ I_{j'k'jk}^{(3)} &= \langle j', k' | j, k \rangle \end{aligned} \quad (4.35)$$

4.4 The DVR method

Constructing the Hamiltonian matrix, and its subsequent diagonalisation to obtain eigenvalues and eigenvectors, requires us to evaluate the matrix element integrals in the chosen basis. For example, the Hamiltonian H_{mn} matrix elements of a one-dimensional quantum mechanical system in the

basis ϕ_i are given by integrals of the following kind:

$$H_{mn} = \langle \phi_m | \hat{H}(x) | \phi_n \rangle = \int_{x=a}^b \phi_m \hat{H}(x) \phi_n dx \quad (4.36)$$

The "variational basis representation" (VBR) constitutes 'diffuse' basis set ϕ_i where the basis functions are not localised to a particular point on the coordinate axis. Another property of VBR is that the variable (e.g. x) is continuous (not discrete) and a finite number of N basis functions are used which means we get N eigenvalues and our wave-function is a linear combination (expansion) of N basis functions. Hence matrix elements in VBR can be written as:

$$H_{mn}^{VBR} = \langle \phi_m | \hat{H}(x) | \phi_n \rangle = \int_{x=a}^b \phi_m \hat{H}(x) \phi_n dx \quad m, n = 1, 2, \dots, N \quad (4.37)$$

The only approximation in VBR is the truncation of the basis set to N basis functions, which affects the accuracy of eigenvalues and eigenfunctions. Assuming the matrix element integrations are analytically performed, the accuracy of matrix elements is unaffected by basis set truncation.

Some definite integrals such as in equation 4.37 cannot be evaluated analytically, therefore a numerical integration technique can be employed. One such scheme is the so called Gaussian quadrature method to approximate definite integrals as [94, 93]:

$$\int_a^b y(x) dx \approx \sum_{\alpha=1}^n w_{\alpha} y(x_{\alpha}) \quad (4.38)$$

where there are n number of points x_{α} on the x -axis, and n number of weights w_{α} . Hence the matrix elements can be written as

$$H_{mn}^{FBR} = \sum_{\alpha=1}^N w_{\alpha} \phi_m(x_{\alpha}) \hat{H}(x_{\alpha}) \phi_n(x_{\alpha}) \approx H_{mn}^{VBR} \quad (4.39)$$

Where the label 'finite basis representation' (FBR) is used to indicate the introduction of numerical integration to compute the matrix elements, using the 'diffuse' basis functions [93].

Instead of using the diffuse basis functions, we can introduce a new set of basis functions, in a so called 'discrete variable representation' (DVR). The DVR basis functions are localised at the numerical integration points. The advantage of the DVR basis is that certain operators, like the

potential $\hat{V}(x)$, are diagonal in this basis. This reduces the number of matrix element integrals that need to be evaluated and so computational time and effort is greatly minimised [94].

The DVR basis can be constructed via the $\mathbf{T}$ matrix using the diffuse polynomial basis and the weights defined at the numerical integration points. Let the diffuse basis ϕ_i be defined as

$$\phi_i(x) = w(x)^{1/2} p_i(x) \quad (4.40)$$

where $p_i(x)$ are polynomials weighted by the function $w(x)$. $\mathbf{T}$ is then defined as [93]

$$\mathbf{T}_{i\alpha} = w(x_\alpha)^{1/2} p_i(x_\alpha) \quad (4.41)$$

The DVR basis set are given by [94]

$$f_\alpha(x) = \sum_{i=1}^N \mathbf{T}_{i\alpha} \phi_i \quad (4.42)$$

Using the matrix representation of the potential operator $\hat{V}(x)$ both representations FBR and DVR are related by [163, 93]

$$\mathbf{V}^{DVR} = \mathbf{T}^T \mathbf{V}^{FBR} \mathbf{T} \quad (4.43)$$

where $\mathbf{V}^{DVR}$ is diagonal in DVR representation. In terms of the Hamiltonian, the various representations are related by [92, 163]

$$\mathbf{H}^{VBR} \approx \mathbf{H}^{FBR} = \mathbf{T}^T \mathbf{H}^{DVR} \mathbf{T} = \mathbf{T}^T \mathbf{K}^{DVR} \mathbf{T} + \mathbf{V}^{DVR} \quad (4.44)$$

4.5 Solution procedure

Step 1: Coriolis de-coupled problem

The solution strategy and procedure of solving the molecule-fixed Hamiltonian is outlined in this section. Tennyson and Sutcliffe [139] deploy a two step procedure to solve the so called effective vibrational Hamiltonian of equation 4.32. The program DVR3DRJZ.f90 implements step 1.

In the first step, the Coriolis ro-vibrational interaction is not accounted for and K is considered a good quantum number. Hence the ro-vibrational wavefunction can be written as the following expansion [163]

$$|J, (i), p, q, K\rangle = \sum_{m,n,j} \varepsilon_{m,n,j}^{(i),J,p,q,K} |m, n, q\rangle |J, K, j, p\rangle \quad (4.45)$$

where now K is an additional quantum number label alongside J, p, q . For each J , values of K range from $K = 0, 1, 2, \dots, J$ for $p = 0$ ('e' rotation-less parity) and $K = 1, 2, \dots, J$ for $p = 1$ ('f' rotation-less parity). Since we are considering, in the first step, K (or k) to be a good quantum number and so the diagonal blocks in the matrix representation of the Hamiltonian can be labelled according to values of K along with values of J, p, q . [163]

If we choose to solve equation 4.32 for every J separately, upto some maximum value say $J_{max} = 45$, we must construct 45 different Hamiltonians. Each Hamiltonian ($\hat{H}^{J=0}, \hat{H}^{J=1}, \hat{H}^{J=2}, \dots, \hat{H}^{J=45}$) will be block diagonal and each diagonal block can be labelled with K values ranging from $K = 0, 1, 2, \dots, J$ for $p = 0$ and $K = 1, 2, \dots, J$ for $p = 1$. [163]

The pure vibrational Hamiltonian in the VBR can be written as [139]

$$\langle m, n, jk | \hat{H}^{J=0}(r_1, r_2, \theta) | m', n', j'k' \rangle \quad (4.46)$$

and rotational excitations, i.e. ro-vibrational wavefunctions with $J > 0$ in the coriolis de-coupled first step, are given by

$$\begin{aligned} \langle m, n, jk, Jk | \hat{H}_{step1}^{J \geq 0}(r_1, r_2, \theta) | m', n', jk', Jk' \rangle &= \langle m, n, jk | \hat{H}^{J=0}(r_1, r_2, \theta) | m', n', jk' \rangle \\ &+ \langle m, n | \hat{K}_{VR}^{Coriolis\ decoupled}(r_1, r_2) | m', n' \rangle \end{aligned} \quad (4.47)$$

where only terms from $\hat{K}_{VR}''$ (equation 4.34) that are diagonal in k (or K) are retained in $\hat{K}_{VR}^{Coriolis\ decoupled}$.

For a given J , a set of Hamiltonians for $K = p, p + 1, \dots, J$ is considered for $p = 0, 1$.

The VBR Hamiltonian in equation 4.47 is transformed into DVR by the following transformation

[77]

$$H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'}^{J \geq 0 (step1)} = \sum_{m,n,jk,Jk} \sum_{m',n',jk',Jk'} (T_{m,n,j}^{\alpha,\beta,\gamma})^T \langle m, n, jk, Jk | \hat{H}_{step1}^{J \geq 0}(r_1, r_2, \theta) | m', n', jk', Jk' \rangle T_{m',n',j'}^{\alpha',\beta',\gamma'} \quad (4.48)$$

where the 3D transformation $T_{m,n,j}^{\alpha,\beta,\gamma}$ is given as a product of 1D transformations in each internal coordinate r_1, r_2, θ :

$$T_{m,n,j}^{\alpha,\beta,\gamma} = T_{r_1}^{\alpha} T_{r_2}^{\beta} T_{\theta}^{\gamma} \quad (4.49)$$

where $T_i^{\eta} = (w_{\eta})^{1/2} |i(\eta)\rangle \quad i = m, n, jk; \eta = \alpha, \beta, \gamma$

The symbols α, β, γ indicate the grid points of internal coordinates r_1, r_2, θ respectively. $i = m, n, jk$ indicates the polynomials in the respective internal coordinates r_1, r_2, θ .

The DVR coriolis de-coupled Hamiltonian can now be diagonalised in a series of steps involving the construction and diagonalisation of 1D, 2D and 3D matrices in the grid points. Details of this procedure can be found in the DVR3D manual [139].

The eigenfunctions $|J, k, h\rangle_{\alpha,\beta,\gamma} = \psi_{\alpha,\beta,\gamma}^{J,k,h}$ from the first step are labelled with J, k and h quantum numbers on a grid of points α, β, γ .

Step 2: Coriolis coupled problem

The second step involves including terms from $\hat{K}_{VR}''(r_1, r_2)$ that were neglected in the first step. This is called solving the so called Coriolis coupled problem and it involves mixing states with different values of K . The ro-vibrational wavefunctions $|J, (i), p, q\rangle$ are given as an expansion of states with different K values as indicated by the second summation sign in K in equation 4.50 [163].

$$|J, (i), p, q\rangle = \sum_{m,n,j} \sum_{K=p}^J \varepsilon_{m,n,j,K}^{(i),J,p,q} |m, n, q\rangle |J, K, j, p\rangle \quad (4.50)$$

Solutions from the first step are taken as the basis for the second step. Eigenfunctions from the first step are symmetry adapted in the form $|k, h, p, q\rangle$ and then used to construct the coriolis coupled in bisector embedding Hamiltonian as follows [139]:

$$\begin{aligned}
\langle k, h, p, q | \hat{H}_{step2} | k', h', p', q' \rangle &= \delta_{kk'} \langle m, n, jk | \hat{H}_{step1}^{J \geq 0} | m', n', jk' \rangle \\
&- (1 + \delta_{k,0} + \delta_{k',0})^{-1/2} \delta_{k',k \pm 1} C_{J,k}^{\pm} \sum_{\alpha, \beta, \gamma, \gamma'} \psi_{\alpha, \beta, \gamma}^{J, k, h} \psi_{\alpha, \beta, \gamma'}^{J, k', h'} \\
&\quad \times \left(M_{\alpha, \alpha, \beta, \beta}^{(1)} - M_{\alpha, \alpha, \beta, \beta}^{(2)} \right) J_{k \pm 1, k, \gamma, \gamma'}^{(1)} \\
&- (1 + \delta_{k,0} + \delta_{k',0})^{-1/2} \delta_{k',k \pm 1} C_{J,k \pm 1}^{\pm} C_{J,k}^{\pm} \sum_{\alpha, \beta, \gamma} \psi_{\alpha, \beta, j}^{J, k, h} \psi_{\alpha, \beta, \gamma}^{J, k', h'} \\
&\quad \times \left(\frac{1 + \gamma}{1 - \gamma} \right) \left(M_{\alpha, \alpha, \beta, \beta}^{(1)} - M_{\alpha, \alpha, \beta, \beta}^{(2)} \right) J_{k \pm 2, k, \gamma, \gamma'}^{(1)} \\
&\quad k = p, p + 1, \dots, J \quad ; \quad p = 0, 1
\end{aligned} \tag{4.51}$$

where $\langle m, n, jk | \hat{H}_{step1}^{J \geq 0} | m', n', jk' \rangle$ in equation 4.51 are the energy eigenvalues from the Coriolis decoupled step 1 and also the diagonal terms of the matrix representation of $\hat{H}_{step2}$ in Coriolis coupled problem in step 2.

Computational details of nuclear motion calculations of $^{16}\text{O}_3$ using the DVR3D programs are given in Chapter 6 of this thesis.

Chapter 5

MARVEL analysis of high-resolution spectra of ozone ($^{16}\text{O}_3$)

5.1 Introduction

There have been many high-resolution spectroscopic studies of the pure rotational and rotation-vibration (ro-vibrational) spectrum of $^{16}\text{O}_3$ in the ground electronic $\tilde{X}^1A_1$ state [124, 42, 9, 75, 10, 47, 33, 54, 145, 115, 132, 90, 19, 50, 110, 18, 86, 37, 113, 112, 16, 23, 17, 15, 21, 106, 49, 22, 59, 51, 121, 123, 35, 36, 52, 111, 120, 4, 28, 60, 26, 29, 20, 27, 13, 58, 5, 38, 14, 7, 6, 11, 105, 48, 127, 78]. Experimental determination of $^{16}\text{O}_3$ energy levels has been performed in several works [32, 8, 83, 154, 10, 47, 33, 34], some of which also give empirical uncertainties for these energies. On the theoretical side, *ab-initio* variational models have been able to predict transition intensities accurately [150, 119, 147] particularly for many high intensity ro-vibrational bands of $^{16}\text{O}_3$. However, it is still very challenging for variationally calculated energy levels and line positions to reach experimental accuracy using *ab-initio* methods alone as illustrated in a study on $^{16}\text{O}_3$ by Tyuterev et al [151] where sub 1 cm^{-1} root mean squared (RMS) deviation between predicted and experimental ro-vibrational band centers was achieved. *Ab-initio* variational calculations are often supplemented with refinement of the potential energy surface (PES) where accuracy can be improved significantly by fitting to MARVEL (Measured Active Rotation Vibration Energy Levels [69, 68]) or empirical energies. The semi empirical approach of PES refinement has been applied to

numerous studies including H_2^{16}O [109, 43], NH_3 [40], C_2H_4 [98], TiO [99] and $^{16}\text{O}_3$ [119] among others. Polyansky et al [119] fitted a refined PES for $^{16}\text{O}_3$ which reproduces a set of 371 energies with a standard deviation of 0.027 cm^{-1} . A refined PES can generate accurate ro-vibrational wavefunctions which could subsequently be used to calculate line intensities with greater accuracy [109]. A particular advantage of variational calculations is that they are complete so that in principle all energy levels and transitions can be calculated and used as a validating dataset.

Effective Hamiltonian (EH) models are able to predict line positions and energies more accurately than *ab-initio* variational methods [22]. Jacquemart et al [80] created a hybrid line-list for $^{16}\text{O}_3$ containing *ab-initio* variational intensities and EH transition frequencies to remedy this limitation of *ab-initio* and semi empirical variational calculations. There are some exceptions to the usual high accuracy of EH models as explored in a study on $^{16}\text{O}_3$ by Barbe et al [22] who describe the challenges involved in accounting for ro-vibrational resonance interactions especially at high energies. In such situations, EH transition frequencies have been replaced with experimentally measured line positions in the latest editions of the S&MPO [3] and HITRAN [72] databases for transitions of $^{16}\text{O}_3$ where EH models do not meet the target accuracy of 10^{-3} cm^{-1} [22]. The MARVEL approach is model-free and therefore does not have to be adjusted to allow for resonances.

Numerous MARVEL studies have been performed on molecules of astrophysical and terrestrial importance as part of the ExoMol [141] project including for H_2^{16}O and its isotopologues [135, 66, 65, 64]; NH_3 [67]; SO_2 [143]; H_2S [39] among many others. For several line lists in the ExoMol database (such as H_2CO [1, 71], AlO [30] and NH_3 [41]) the computed energy levels are substituted with MARVEL ones. This substitution is used to generate MARVEL based line positions with spectroscopic accuracy as was done in a study on H_2CO by Al-Derzi et al [1]. The inclusion of MARVEL levels in the variational line list of H_2CO yields an extra 351 183 transitions with experimental accuracy of line positions from only 16 596 non-redundant transitions [1]. Additionally MARVEL energies can be used to calculate accurate temperature dependent partition functions which could aid better predictions of ro-vibrational line intensities [155, 70]. Several MARVEL based line positions and energy levels have already been incorporated into the HITRAN database with many also being considered for future updates [72].

In this study we present a MARVEL analysis of ro-vibrational line positions of $^{16}\text{O}_3$, the results

of which we hope will improve the accuracy of ozone spectroscopic data.

5.2 Theory

This section focuses on the theory behind the MARVEL program and also on the quantum mechanical description of the energy levels and transitions of ozone.

5.2.1 Marvel theory

In the theory of spectroscopic networks, energy levels and transitions between them are represented by nodes and edges respectively [45]. MARVEL (Measured Active Rotation Vibration Energy Levels) is a program based on the theory of spectroscopic networks (developed by Furtenbacher et al [69, 68]) that determines the energy levels of molecules. An input file of measured line positions, uncertainties and quantum number labels for each transition is created from scientific literature.

Once the data is collected, it is prepared into an input file which gets processed by the MARVEL program. The line positions are inverted into energy levels. Marvel does this by solving the matrix equation

$$\mathbf{a} \mathbf{X} = \mathbf{Y} \quad (5.1)$$

where vector $\mathbf{Y}$ contains N_t number of measured transitions (σ_{ij}), vector $\mathbf{X}$ contains E_j number of energy levels and matrix $\mathbf{a}$ has elements +1, -1 or 0 [68]. The matrix Equation 5.1 can be solved by method of weighted least-squares [69, 68]

$$\mathbf{A} \mathbf{X} = \mathbf{B} \quad (5.2)$$

where

$$\mathbf{A} = \mathbf{a}^T \mathbf{w} \mathbf{a} \quad \text{and} \quad \mathbf{B} = \mathbf{a}^T \mathbf{w} \mathbf{Y} \quad (5.3)$$

where we have introduced the weight matrix $w_{ij} = \delta_{ij}^{-2}$ where δ_{ij} is the uncertainty associated with the measured transition σ_{ij} . [69, 68]

In this work we use the recently implemented MARVEL4 version of the procedure which allows

the uncertainties in the final energy levels to be determined as before or by using a bootstrap procedure [136] which corrects for inconsistencies between different experimental uncertainties. The bootstrap method works by randomly varying the uncertainties of line positions over a chosen number of iterations and representing the uncertainty of each MARVEL energy level by a statistical measure over these iterations. We note that use of the bootstrap method usually results in slightly increased uncertainties [136, 161].

5.2.2 Ozone energy levels and transitions

The ozone adiabatic ground electronic $\tilde{X}^1A_1$ state has four minima due to the complex nature of its electronic structure with interacting electronic states and the Jahn-Teller effect [2, 84]. One so-called “ring” minimum corresponds to the equilateral triangle configuration. The other three identical minima, which are spectroscopically relevant and the focus of this study, reside approximately 1.34 eV lower than the “ring” minimum and correspond to “open” geometric configurations and can be characterised by the C_{2v} point group at equilibrium [84]. The three identical “open” minima are related to permutations of oxygen nuclei and could interact with each other via tunneling, however the tunneling time scales are so long that each minimum can be considered independently [133].

In the ground electronic state ozone is an asymmetric top molecule [61]. Vibrational normal mode labels of ozone are v_1, v_2, v_3 where v_1 and v_3 correspond to symmetric and anti-symmetric stretching modes of vibrations while v_2 corresponds to the bending mode. Rotational states are labelled by J, K_a and K_c where J is the rotational angular momentum quantum number while K_a and K_c give projections of J onto molecule fixed z axis (or equivalently projections onto principal axes a and c respectively) for prolate and oblate symmetric top molecules respectively. The set of quantum numbers used to uniquely label a ro-vibrational energy level of ozone are: $(v_1, v_2, v_3, J, K_a, K_c)$.

Total parity (corresponding to inversion operator E^*), p (e/f rotation-less parity), q (interchange symmetry of radial basis functions corresponding to nuclear permutation operator (12)) and J are called rigorous quantum labels because their corresponding operators commute with the molecular Hamiltonian while labels v_1, v_2, v_3, K_a, K_c are approximate. Operators E^* and (12) belong to the complete nuclear permutation inversion (CNPI) $C_{2v}(M)$ group. Irreducible representations Γ

(called irrep or symmetry) of vibrational, rotational and ro-vibrational wavefunctions of $^{16}\text{O}_3$ can be deduced from Table 5.1 [61, 31, 152].

Table 5.1: Character table of C_{2v} point group and CNPI $\text{C}_{2v}(\text{M})$ group for $^{16}\text{O}_3$ with symmetry classification of its vibrational, rotational and ro-vibrational wavefunctions from their approximate and rigorous quantum labels. Labels e and o/f denote even and odd values respectively. The operators given in square brackets belong to CNPI group $\text{C}_{2v}(\text{M})$, equivalent to their C_{2v} point group counterparts adjacent to them.

Γ	$\hat{E} [E]$	$\hat{C}_2 [(12)]$	$\hat{\sigma}_{xz} [(12)^*]$	$\hat{\sigma}_{yz} [E^*]$	Normal coordinate	J_{even} J_{odd}		(p, q)	(p, q)
						K_a	K_c		
A_1	1	1	1	1	Q_1, Q_2	e	e	(e, e)	(f, e)
A_2	1	1	-1	-1		o	o	(f, o)	(e, o)
B_1	1	-1	1	-1	Q_3	o	e	(f, e)	(e, e)
B_2	1	-1	-1	1		e	o	(e, o)	(f, o)

The nuclei of $^{16}\text{O}_3$ are bosons, and therefore due to so called Bose-Einstein spin statistics, the complete total internal wavefunction $\Phi_{^{16}\text{O}_3}$ obeys

$$(12) \Phi_{^{16}\text{O}_3} = + \Phi_{^{16}\text{O}_3} \quad (5.4)$$

implying that $\Phi_{^{16}\text{O}_3}$ remains unchanged upon interchange of two identical ^{16}O nuclei. Operator (12) is the “interchange of two identical nuclei” operator belonging to the complete nuclear permutation inversion (CNPI) $\text{C}_{2v}(\text{M})$ group. Since operator (12) is equivalent to operator C_2 in C_{2v} point group, upon inspecting the character table in Table 5.1, we can see that irreps Γ_{total} (to which all $\Phi_{^{16}\text{O}_3}$ belong) are restricted to A_1 and A_2 [31].

The irrep of the complete total internal wavefunction is given by

$$\Gamma_{\text{total}} = \Gamma_{\text{electronic}} \otimes \Gamma_{\text{vibration}} \otimes \Gamma_{\text{rotation}} \otimes \Gamma_{\text{nuclearspin}} \quad (5.5)$$

The ground electronic state of $^{16}\text{O}_3$ belongs to A_1 irrep ($\Gamma_{\text{electronic}} = A_1$). The symmetry of the vibrational normal coordinates for $^{16}\text{O}_3$ in terms of irreps is [142]

$$\Gamma_Q = 2A_1 \oplus B_1 \quad (5.6)$$

Thus the symmetry of the vibrational wavefunctions is given by

$$\Gamma_{vibration} = (A_1)^{v_1} \otimes (A_1)^{v_2} \otimes (B_1)^{v_3} \quad (5.7)$$

The symmetry of rotational wavefunctions $\Gamma_{rotation}$ is determined according to the values of rotational quantum numbers K_a and K_c as given in Table 5.1. For ^{16}O the nuclear spin angular momentum quantum number $I = 0$ and therefore its projection onto the space-fixed Z axis $\sigma = 0$. Hence the individual nuclear spin function for ^{16}O nucleus is $\delta_{16\text{O}} = |0, 0\rangle$. This results in only one nuclear spin function $\Phi_{nuclearspin} = \delta_{16\text{O}} \delta_{16\text{O}} \delta_{16\text{O}}$ with symmetry A_1 [31].

Rovibronic states with symmetry A_1 and A_2 can be combined with the single nuclear spin wavefunction to produce allowed complete total internal wavefunction with symmetry $\Gamma_{total} = A_1, A_2$. This results in "missing" states of ozone in the sense that half the ro-vibronic (rve) energy levels obtained do not physically exist as is illustrated in table 6.2.

Table 5.2: "Missing" energy levels of ozone $^{16}\text{O}_3$

Γ_{rve}	$\Gamma_{nuclearspin}$	Γ_{total}	g_{ns}
A_1	A_1	A_1	1
A_2	A_1	A_2	1
B_1	-	-	0
B_2	-	-	0

In terms of approximate quantum numbers, the symmetry of allowed ro-vibrational energy levels in the ground electronic $\tilde{X}^1A_1$ state (with respect to the symmetry of allowed wavefunctions $\Phi_{16\text{O}_3}$) can be determined by the quantum numbers v_3, K_a, K_c as follows: If v_3 is even, select rotational levels with $K_a + K_c$ even. If v_3 is odd, select rotational levels with $K_a + K_c$ odd. The dipole allowed transitions of $^{16}\text{O}_3$ follow the strict selection rules [61]: $A_1 \leftrightarrow A_2, \Delta J = 0, \pm 1$.

If we define rotation-less parities e as $p = 0$ and f as $p = 1$, then rotation-less parity in

terms of rigorous quantum labels is given by the expression $(-1)^p$ with total parity (+/-) given by $(-1)^{J+p}$. We can also calculate rotation-less parity from approximate quantum numbers as follows: if $K_a + K_c = \text{even}$, then the state has e rotation-less parity; if $K_a + K_c = \text{odd}$, then the state has f rotation-less parity.

5.3 Experimental sources

We searched the literature for experimentally measured ro-vibrational line positions with assigned quantum numbers ($v_1, v_2, v_3, J, K_a, K_c$) for upper and lower states and found many articles that contain data either in tables within the paper or as part of the supplementary information. A detailed summary of data sources used in MARVEL analysis is given in Table 5.3. Data from most sources was scanned, digitised (using the *FineReader OCR Pro* application) and cleaned in order to be used as input into the MARVEL program. The digitization process often led to errors in the scanned data (such as mislabelling of line positions and quantum numbers) which we corrected manually and by using the technique of combination differences implemented within the MARVEL program.

This MARVEL project on ozone was run as part of the ORBYTS outreach project [126], which provides opportunities to school students to be involved in scientific research in collaboration with PhD students. I worked as an ORBYTS tutor, teaching students spectroscopy and supervising the ORBYTS-MARVEL project. During the project, the students learnt about spectroscopy and quantum physics, searched for research papers that contain experimental line positions of ozone, digitised the data and prepared MARVEL input files. The students also performed MARVEL analysis to obtain MARVEL energy levels of ozone.

Table 5.3: Summary and statistics of all sources of transition frequencies used in the MARVEL input.

Source	Reference	Wavenumber range	A/V	δ_{AOU}	δ_{AMR}	Ratio
01SmDeBeRi	[124]	991.61402 – 1128.75165	376/376	1.827e-05	1.207e-05	0.661

Continued on next page

Source	Reference	Wavenumber range	A/V	δ_{AOU}	δ_{AMR}	Ratio
01WeDeFl	[156]	6503.66932 – 6593.61037	397/396	1.401e-03	9.077e-04	0.648
05CoBaDeMa	[42]	5.78685 – 21.97570	252/248	2.226e-06	5.506e-07	0.247
07BaDeTyKa	[9]	6225.12000 – 6395.37869	2451/2451	2.000e-03	1.815e-05	0.009
10GuMoJaCa	[75]	1132.59923 – 1134.50971	15/15	4.233e-05	1.236e-05	0.292
11BaDeTyKa	[10]	6392.75549 – 7292.60504	1320/1320	1.000e-03	1.097e-05	0.011
12DeBaStTy	[47]	7346.27000 – 7584.05051	1212/1212	1.000e-03	7.674e-06	0.008
15CaKaMoBa	[33]	7629.46367 – 7864.68990	782/782	1.500e-03	4.520e-06	0.003
17DrCrYu	[54]	23.09493 – 24.00969	7/7	1.243e-07	1.909e-09	0.015
22JaBoElJe	[79]	997.55214 – 2132.34946	816/816	3.000e-05	1.798e-05	0.599
53TrGhBuGo	[145]	1.42874 – 3.94821	4/4	7.425e-06	2.931e-06	0.395
69PoStFl	[115]	0.36934 – 0.36934	1/1	3.300e-06	4.411e-06	1.337
70TaMo	[132]	0.30278 – 2.20853	39/39	3.300e-06	9.243e-07	0.280
71LiGaCl	[90]	1.73372 – 10.53644	69/69	2.300e-05	7.645e-06	0.332
77BaSeJoMo	[19]	0.32254 – 1071.52850	1023/1020	9.629e-04	1.740e-03	1.808
77DeDuBe	[50]	0.49439 – 12.61810	111/110	3.300e-06	1.375e-06	0.417
78MoDeBeBa	[110]	0.66880 – 1046.94800	1084/1075	4.091e-02	1.070e-02	0.262
81BaSeJoGo	[18]	1006.27900 – 1218.87800	1912/1902	1.335e-02	3.069e-03	0.230
81KoHiFa	[86]	1039.32761 – 1053.91977	18/18	2.667e-04	2.292e-04	0.859
84CaDiFuTr	[37]	7.91030 – 147.43060	967/966	2.675e-04	3.092e-04	1.156
85PiCoMa	[113]	0.49439 – 1218.05960	3089/3047	6.965e-04	3.752e-04	0.539
88PiCoBrRi	[112]	0.89794 – 859.41300	3248/3237	6.078e-04	3.103e-04	0.510
92BaPlBoFl	[16]	2080.12827 – 2083.58555	10/10	7.000e-05	1.090e-04	1.557
92BeDeDiFu	[23]	50.20949 – 135.01084	63/63	2.888e-06	5.565e-07	0.193
94BaPlBoSu	[17]	1961.66095 – 2253.32424	637/637	1.000e-05	6.422e-06	0.642
96BaPL	[15]	4144.21860 – 4150.48330	55/55	7.000e-04	6.700e-04	0.957
96BaSuPlTy	[21]	4220.04140 – 4225.73790	34/34	7.000e-04	6.970e-04	0.996

Continued on next page

Source	Reference	Wavenumber range	A/V	δ_{AOU}	δ_{AMR}	Ratio
96MiBaTyRe	[106]	4642.00760 – 4643.61830	30/30	6.000e-04	1.210e-03	2.016
97DeLoInNo	[49]	52.07695 – 122.81379	28/26	1.577e-06	3.376e-08	0.021
MagentaSMPO	[22, 72]	16.50080 – 5569.00410	30226/29960	5.500e-04	1.496e-04	0.272

Source: Unique label for each data source.

Wavenumber range of transitions given in cm^{-1} .

A/V: total number of available lines in the input/ total number of lines validated.

δ_{AOU} : average original (experimental) uncertainty of source transitions given in cm^{-1} .

δ_{AMR} : average MARVEL reproduction of source transitions given in cm^{-1} .

Ratio = $\delta_{AMR}/\delta_{AOU}$

A number of transitions were not validated (and hence excluded from analysis) as indicated by the A/V column in Table 5.3 because these lines are considered by the MARVEL program as inconsistent with the other transitions in the network. The excluded lines are retained in the MARVEL input with a negative value for the transition frequency.

There are many sources (particularly in the energy level range $3000 - 6000 \text{ cm}^{-1}$) which we considered but could not use for MARVEL analysis because the actual measured line positions were not available. All such data sources along with their respective reasons for us being unable to include them in this work are listed in Table 5.4. The unavailable measurement data contributes to the incompleteness of the MARVEL dataset of ozone energies (as illustrated in Figure 5.4). In these circumstances, we extract what appear to be measured line positions from the HITRAN database [72]. Extracted transitions from the HITRAN database are contained in a source labelled as MagentaSMPO, further details of which are given in the following section.

Table 5.4: List of data sources considered but not included for MARVEL analysis.

Source	Reference	Wavenumber region (cm^{-1})	Reason
87FlCaDeRib	[59]	1000	Measured data not available
87DeFlCa	[51]	900 – 2000	Measured data not available
88RiSmFlCa	[121]	2100	Measured data not available
90SmRiDeFl	[123]	2700 – 3000	Measured data not available
90CaFlRiSm	[35]	3330	Measured data not available
90CaFlSmRi	[36]	5200	Measured data not available
90DePeFlCa	[52]	3600 – 3900	Measured data not available
91PeVaFlCa	[111]	4000	Measured data not available
90RiSmDeFl	[120]	2400	Measured data not available
93BaBoPlJa	[4]	4325	Measured data not available
93BoBaPlFl	[28]	3050	Measured data not available
93FlCaPeDe	[60]	3333	Measured data not available
94BoBaMiPl	[26]	3450	Measured data not available
95BoMiBaRe	[29]	3700	Measured data not available
95BaSuPlHa	[20]	2300 – 2600	Measured data not available
95BoBaPl	[27]	3700	Measured data not available
95BaMiTyHa	[13]	3850	Measured data not available
96FlBaCaPl	[58]	4900	Measured data not available
98BaCh	[5]	5700	Measured data not available
98ChBaTyPl	[38]	5780	Measured data not available
98BaPlTyMi	[14]	5080	Measured data not available
98BaChTyTab	[7]	5500 – 5570	Measured data not available
98BaChTyTaa	[6]	1300 – 1500	Measured data not available
98BaMiPlTy	[11]	2300 – 2600, 3050 – 3110	Measured data not available
02MiBaTy	[105]	2900 – 3400	Measured data not available

Continued on next page

Source	Reference	Wavenumber region	Reason
04DeBaTy	[48]	4100	Measured data not available
06SuBaDeTy	[127]	4300	Measured data not available
77DeDuBe	[50]	0.40 – 12.70	Data taken from original sources
53Hughes	[78]	–	Poor accuracy
24TyBaMaGr	[146]	0 – 300	Only calculated data given
24TaBaMiSt	[134]	0.3 – 7999.0	Measured data not available
06CaKaRoBa	[34]	6225 – 6830	Measured data not available

An extract from the MARVEL input file is given in Table 5.5. We note that the MARVEL input format has two uncertainty columns, where the first column refers to the original experimental uncertainty. The MARVEL program can change the original uncertainty of the transition, and the new uncertainty value is given in the second column; this option was not used here. The complete MARVEL input file is provided as part of the supplementary material of this article. The MARVEL program also requires a file containing a list of all sources and their units for line positions as input (this file is also provided in the supplementary section of this paper).

5.3.1 Notes on experimental sources

Although line-by-line experimental uncertainties are preferred, they are not provided in some sources such as **11BaDeTyKa** [10] and **12DeBaStTy** [47]. In this situation, we used the generic experimental uncertainty of 0.001 cm^{-1} (as provided in the articles) for all bands in these sources. Where line-by-line uncertainties are not available, we use an overall uncertainty for all measured line positions in the experiment, where we assume the uncertainties to be generic (since the assignment of spectra is done after the measurements are collected). Consequently, for cases where we have used generic uncertainty, the input uncertainties for some transitions are likely to be underestimated.

77BaSeJoMo [19]: This data source contains many so-called “blended” lines. These are transitions that each have a unique set of quantum numbers but have the same value of the transition

Table 5.5: Extract from the MARVEL input file for $^{16}\text{O}_3$.

$\tilde{\nu}$	δ	δ	v'_1	v'_2	v'_3	J'	K'_a	K'_c	v''_1	v''_2	v''_3	J''	K''_a	K''_c	Source
128.1211	0.0004	0.0004	0	1	0	32	17	15	0	1	0	31	16	16	88PiCoBr.Ri.354
128.9547	0.0004	0.0004	0	1	0	33	17	17	0	1	0	32	16	16	88PiCoBr.Ri.356
0.3571047	0.0000033	0.0000033	0	0	1	17	2	15	0	0	1	16	3	14	70TaMo.5
$\tilde{\nu}$: line position in cm^{-1} .															
δ : uncertainty of line position in cm^{-1} .															
$'$ and $''$ denote upper and lower states respectively.															

frequency (probably due to low resolution of the measuring apparatus). For example, the two transitions 77BaSeJoMo.874 and 77BaSeJoMo.875 are blended with the same value of line position, so the uncertainty of one of the pair (along with all such cases in this source) is increased from 0.001 cm^{-1} to 0.003 cm^{-1} .

78Lovas [95]: This source is a useful compilation of spectroscopic measurements; however we took measured line positions directly from the original sources cited in this source.

81BaSeJoGo [18]: This source only provides J and K_{-1} quantum numbers. K_{-1} is assumed to be K_a based on the notation of 77BaSeJoMo [19]. K_c can then be uniquely determined by:

$$\begin{aligned} K_c &= J - K_a \text{ if } \nu_3 \text{ is even} \\ K_c &= J - K_a + 1 \text{ if } \nu_3 \text{ is odd} \end{aligned} \tag{5.8}$$

The values of K_c for this source were calculated from Eqs (5.8) and subsequently used in the MARVEL input.

78MoDeBeBa [110] and **88PiCoBrRi** [112]: We encountered issues with a very large number of inconsistent lines between these sources described by the MARVEL program as “very bad” lines. The MARVEL program recommends an optimal uncertainty for every input transition and very bad lines are defined as those having the ratio of optimal and original (experimentally estimated) uncertainty between 10 and 100. We analyze common transitions between 78MoDeBeBa and 88PiCoBrRi and plot the distribution of line position differences as shown in Figure 5.1(a). Assuming a normal distribution of line position differences, the standard deviation of the distribution is 0.016 cm^{-1} with the mean equal to $-0.002189 \text{ cm}^{-1}$. We add the mean of the distribution ($-0.002189 \text{ cm}^{-1}$) as a recalibration shift to all line positions of 78MoDeBeBa for the 010-000 band.

81BaSeJoGo [18]: A similar problem to that of 78MoDeBeBa [110] occurred for this source with the MARVEL program highlighting that the original experimental uncertainties of line positions were too small for the 001-000 and 100-000 bands. Both bands have much more recent sources of line position data so we compare 81BaSeJoGo with all the other sources in the MARVEL input for matching transitions. The distribution of line position differences is shown in Figure 5.1(b) along with the combined mean of both bands. Line positions of both bands 100-000 and 001-000 for

81BaSeJoGo are recalibrated by $-0.001918 \text{ cm}^{-1}$.

Recalibrating the transitions of 78MoDeBeBa and 81BaSeJoGo resulted in a significant reduction of very bad lines from 4086 to 2761 in the early stages of our analysis. Furthermore, by identifying and correcting errors in the scanned data, the final number of very bad lines are reduced to zero. We note that the use of the bootstrap method ensures that any issues with the underlying transitions is reflected in the uncertainty associated with the resulting energy level provided the number of transitions reaching that level (N_t) is greater than one.

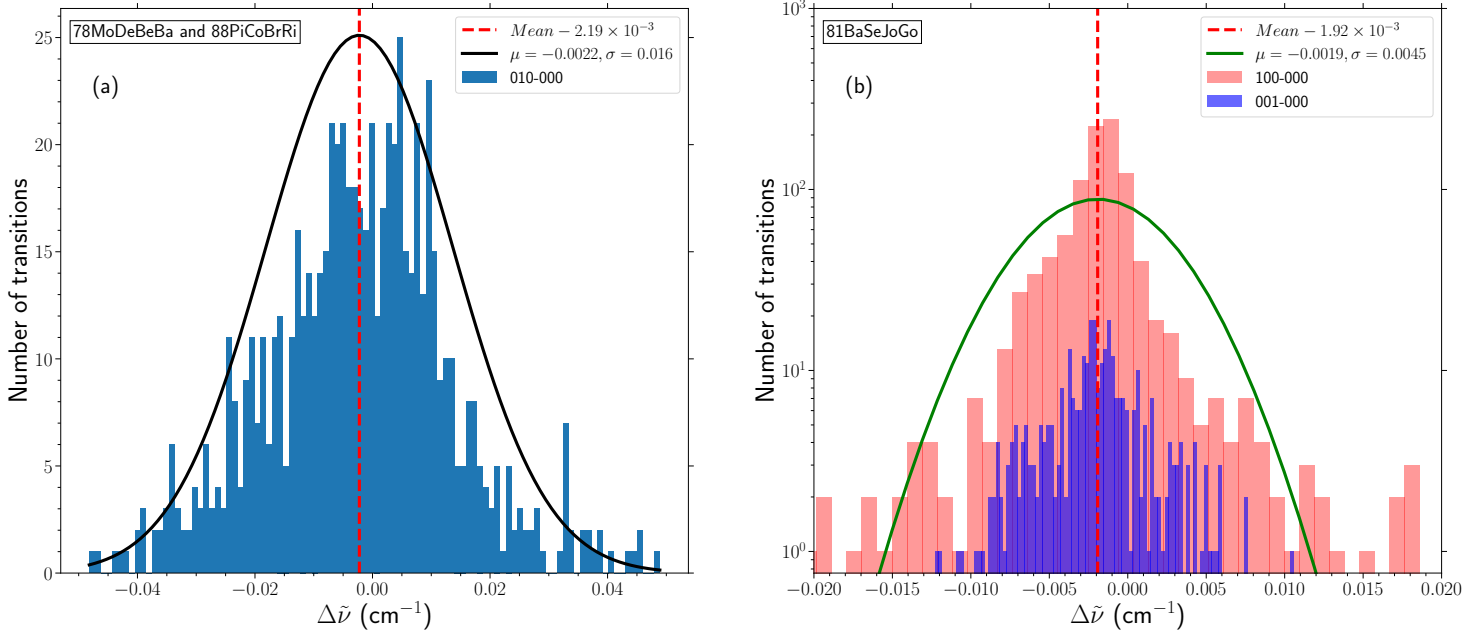


Figure 5.1: Recalibration of line positions. Distribution of line position differences ($\Delta\tilde{\nu}$) of 78MoDeBeBa with 88PiCoBrRi for the 010-000 band is shown in panel (a). The distribution of line position differences of 81BaSeJoGo with all other sources in the MARVEL input for the 100-000 and 001-000 bands is shown in panel (b). The line positions are shifted (recalibrated) by an amount equal to the mean of each distribution. μ and σ in this figure are parameters of the Gaussian curves fitted to the distributions.

MagentaSMPO [22, 72]: This source is constructed because of lack of availability of measured line positions data. Empirical line position corrections from the S&MPO database [3] (line list SMPO_20d [22]) have been incorporated into the HITRAN 2020 line list for $^{16}\text{O}_3$ [72]. However, to the best of our knowledge, there does not appear to be a line-by-line labelling of empirically corrected lines in SMPO_20d and HITRAN, so we try to extract them by matching and comparing individual transitions of HITRAN 2020 line list [72] with HITRAN 2016 line list [73] for $^{16}\text{O}_3$. We try to filter out calculated lines based on the criteria that the absolute change in transition frequency

(from HITRAN 2016 to HITRAN 2020) is greater than 0.0003 cm^{-1} [72]. A further comparison is performed with what appears to be a purely EH line list (SMPO_2019 [3, 22]) generated from EH parameters to filter out the calculated line positions. If the transition frequency value exactly matches one in the SMPO_2019 line list, it is removed. However, it is not possible to completely filter out all calculated lines from the MagentaSMPO source because EH parameters have been updated since the release of the SMPO_2019 line list [3, 22]. Therefore MagentaSMPO contains a mixture of transitions with calculated and observed line positions. Furthermore, we are unable to identify which individual lines in MagentaSMPO are observed or calculated. It will be the responsibility of future MARVEL studies on $^{16}\text{O}_3$ to ensure the identification and replacement of as many calculated lines as possible with observed ones in this source. Several lines from this source are deleted because they are inconsistent with other lines in the MARVEL input.

5.4 Results of MARVEL analysis

Due to the uncertainty regarding the number of lines with calculated line positions in the MagentaSMPO source, there are a number of levels within the MARVEL dataset with partial or complete contributions from calculated lines. To this end, we provide the CheckTransitions.txt file in the supplementary section that provides details of individual lines that contribute to each MARVEL energy level.

5.4.1 The $^{16}\text{O}_3$ MARVEL network

The principal component of the MARVEL spectroscopic network of $^{16}\text{O}_3$ comprises 13664 energy levels connected by 49794 transitions. The MARVEL4.1 program is used to perform the calculations with Cholesky decomposition chosen as the solution method. The bootstrap method of calculating MARVEL uncertainties (along with the conventional method) is implemented with 100 iterations. Both types of MARVEL energy level uncertainties are provided in the supporting information to this paper. The mean uncertainty of all MARVEL energies using the conventional method is $8.57 \times 10^{-4} \text{ cm}^{-1}$ while the mean uncertainty using the bootstrap method is $1.42 \times 10^{-3} \text{ cm}^{-1}$. An extract of the MARVEL energy level output file is shown in Table 5.6. The complete output files

are provided as part of the supplementary material of this article [153].

Table 5.6: Extract from the MARVEL energy level output file for $^{16}\text{O}_3$.

v_1	v_2	v_3	J	K_a	K_c	E_{MARVEL}	ε	N_t
0	0	0	0	0	0	0.0000000000	0.000e+00	21
0	0	0	2	0	2	2.519473468	5.203e−06	53
0	0	0	1	1	1	3.948214755	3.300e−06	51
0	0	0	2	1	1	5.729320884	8.902e−06	73

E_{MARVEL} : MARVEL energy in cm^{-1} .
 ε : MARVEL uncertainty of the energy level (bootstrap enabled) in cm^{-1} .
 N_t : Number of transitions involving the energy level.

Table 5.7 shows statistics of the MARVEL dataset for ozone organized by vibrational band origins.

Table 5.7: Statistics of the MARVEL energy level dataset of $^{16}\text{O}_3$.

$v_1v_2v_3$	J	N_{rot}	E	Mean ε	N_t	Data sources
range						
000	0-67	1257	0.00-3175.39	3.02×10^{-3}	34072	94BaPlBoSu,88PiCoBrRi, 05CoBaDeMa,10GuMoJaCa, 96BaSuPlTy,81BaSeJoGo, 01SmDeBeRi,12DeBaStTy, 15CaKaMoBa,01WeDeFl, 81KoHiFa,96MiBaTyRe, 92BeDeDiFu,96BaPL, 92BaPlBoFl,77DeDuBe, 97DeLoInLo,85PiCoMa, 53TrGhBuGo,69PoStFl,

Continued on next page

Table 5.7: Statistics of the MARVEL energy level dataset of $^{16}\text{O}_3$.

$v_1v_2v_3$	J	N_{rot}	E	Mean ε	N_t	Data sources
range						
						07BaDeTyKa,MagentaSMPO, 11BaDeTyKa,71LiGaCl, 17DrCrYu,22JaBoElJe, 84CaDiFuTr,77BaSeJoMo, 78MoDeBeBa
001	1-64	1083	1042.91-3442.55	2.56×10^{-3}	9581	85PiCoMa,MagentaSMPO,81KoHiFa, 70TaMo,22JaBoElJe,81BaSeJoGo, 77BaSeJoMo,01SmDeBeRi
002	8-43	94	2096.54-3577.47	2.08×10^{-4}	106	94BaPlBoSu,22JaBoElJe, MagentaSMPO
003	5-62	86	3061.68-4803.52	2.39×10^{-3}	523	MagentaSMPO
004	0-53	298	4001.31-5260.42	7.49×10^{-4}	1027	MagentaSMPO
005	1-48	236	4920.00-5890.84	5.96×10^{-4}	1329	MagentaSMPO
007	5-36	35	6579.91-7072.18	1.45×10^{-3}	65	01WeDeFl
010	0-62	896	700.93-3091.06	1.33×10^{-3}	11197	97DeLoInLo,MagentaSMPO,70TaMo, 22JaBoElJe,81BaSeJoGo,88PiCoBrRi, 78MoDeBeBa
011	2-47	253	1731.47-2613.91	1.71×10^{-3}	401	78MoDeBeBa,22JaBoElJe, MagentaSMPO
012	2-61	65	2728.55-4233.58	7.31×10^{-4}	703	MagentaSMPO
013	1-55	261	3699.10-4919.29	6.79×10^{-4}	1460	MagentaSMPO
014	5-50	247	4653.47-5756.93	5.68×10^{-4}	1585	96MiBaTyRe,MagentaSMPO
020	0-54	537	1399.27-2934.11	1.08×10^{-3}	1695	88PiCoBrRi,78MoDeBeBa,70TaMo, MagentaSMPO
Continued on next page						

Table 5.7: Statistics of the MARVEL energy level dataset of $^{16}\text{O}_3$.

$v_1v_2v_3$	J	N_{rot}	E	Mean ε	N_t	Data sources
range						
022	6-52	50	3407.92-4452.58	6.12×10^{-4}	413	MagentaSMPO
023	1-47	176	4347.53-5299.77	5.84×10^{-4}	814	MagentaSMPO
025	1-40	367	6305.83-7084.36	2.01×10^{-3}	913	07BaDeTyKa
030	15-26	20	2194.20-2377.15	9.93×10^{-4}	29	MagentaSMPO
031	5-39	31	3150.45-3782.14	6.59×10^{-4}	128	MagentaSMPO
044	11-49	147	6559.12-7416.59	1.01×10^{-3}	427	11BaDeTyKa
045	2-23	53	7456.95-7673.29	1.00×10^{-3}	146	12DeBaStTy
100	0-64	993	1103.14-3638.68	2.79×10^{-3}	7611	85PiCoMa,MagentaSMPO,81KoHiFa, 22JaBoElJe,81BaSeJoGo, 77BaSeJoMo,10GuMoJaCa, 01SmDeBeRi
101	1-53	357	2111.61-3378.23	2.06×10^{-4}	858	94BaPIBoSu,92BaPIBoFl, MagentaSMPO, 22JaBoElJe
102	4-63	127	3104.06-4679.96	9.75×10^{-4}	782	MagentaSMPO
103	1-60	251	4022.66-5496.54	1.13×10^{-3}	980	MagentaSMPO
104	2-34	118	4924.99-5678.23	5.73×10^{-4}	646	MagentaSMPO
110	2-46	272	1798.77-2661.98	1.05×10^{-3}	644	MagentaSMPO,81BaSeJoGo
111	2-61	156	2800.27-4434.20	8.17×10^{-4}	878	MagentaSMPO
112	2-59	213	3747.24-5146.93	6.64×10^{-4}	1623	MagentaSMPO
113	1-51	416	4659.75-5808.21	6.17×10^{-4}	2662	96MiBaTyRe,MagentaSMPO
114	8-40	24	5569.35-6164.11	5.53×10^{-4}	100	MagentaSMPO
121	3-50	84	3464.08-4655.10	6.25×10^{-4}	542	MagentaSMPO
122	10-47	106	4434.53-5257.81	5.73×10^{-4}	504	MagentaSMPO
123	1-35	112	5295.12-5926.20	6.28×10^{-4}	441	MagentaSMPO
Continued on next page						

Table 5.7: Statistics of the MARVEL energy level dataset of $^{16}\text{O}_3$.

$v_1v_2v_3$	J	N_{rot}	E	Mean ε	N_t	Data sources
range						
124	14-42	31	6439.37-7021.99	2.00×10^{-3}	61	07BaDeTyKa
125	1-33	173	7131.55-7588.41	1.00×10^{-3}	443	11BaDeTyKa
130	8-37	8	3256.60-3733.06	6.31×10^{-4}	25	MagentaSMPO
131	3-39	133	4148.81-4796.44	6.43×10^{-4}	851	MagentaSMPO
132	19-32	7	5275.03-5527.85	5.53×10^{-4}	14	MagentaSMPO
153	1-25	155	7290.73-7672.57	1.00×10^{-3}	447	11BaDeTyKa
200	4-54	243	2209.52-3393.23	3.34×10^{-4}	508	94BaPlBoSu,MagentaSMPO
201	3-52	92	3219.02-4399.17	1.07×10^{-3}	507	MagentaSMPO
202	6-58	197	4170.39-5499.02	6.37×10^{-4}	669	96BaPL,MagentaSMPO
203	1-43	157	5077.88-5870.95	5.82×10^{-4}	349	MagentaSMPO
205	1-37	157	6587.77-7120.85	1.47×10^{-3}	331	01WeDeFl
210	12-55	57	2979.91-4187.40	6.63×10^{-4}	632	MagentaSMPO
211	1-47	292	3850.73-4873.83	6.24×10^{-4}	1638	MagentaSMPO
212	8-51	101	4821.46-5836.04	5.96×10^{-4}	382	MagentaSMPO
213	1-35	143	5519.60-6188.38	5.68×10^{-4}	517	MagentaSMPO
220	16-46	8	3679.25-4427.45	6.02×10^{-4}	21	MagentaSMPO
221	1-39	259	4512.15-5320.35	5.78×10^{-4}	1419	MagentaSMPO
223	1-37	284	6387.78-7100.76	2.00×10^{-3}	717	07BaDeTyKa
230	32-32	1	4688.22-4688.22	5.55×10^{-4}	2	MagentaSMPO
243	2-30	116	7691.38-8097.25	1.50×10^{-3}	271	15CaKaMoBa
271	3-26	83	7744.16-7996.29	1.50×10^{-3}	213	15CaKaMoBa
301	2-49	202	4255.11-5206.59	6.30×10^{-4}	508	96BaSuPlTy,MagentaSMPO
310	8-50	201	4023.08-5105.27	5.93×10^{-4}	438	MagentaSMPO
311	2-42	152	4911.99-5650.03	5.68×10^{-4}	1166	MagentaSMPO
						Continued on next page

Table 5.7: Statistics of the MARVEL energy level dataset of $^{16}\text{O}_3$.

$v_1v_2v_3$	J	N_{rot}	E	Mean ε	N_t	Data sources
range						
320	8-39	32	4702.10-5314.54	5.55×10^{-4}	152	96MiBaTyRe,MagentaSMPO
321	19-19	2	5719.00-5741.30	5.52×10^{-4}	6	MagentaSMPO
330	25-25	1	5630.80-5630.80	5.53×10^{-4}	4	MagentaSMPO
351	2-25	127	7461.26-7770.35	1.00×10^{-3}	369	12DeBaStTy
400	17-17	1	4547.51-4547.51	5.52×10^{-4}	6	MagentaSMPO
401	2-34	124	5312.64-5900.68	5.63×10^{-4}	279	MagentaSMPO
405	1-26	120	7863.94-8167.33	1.50×10^{-3}	298	15CaKaMoBa
430	11-35	36	6449.13-6880.48	2.00×10^{-3}	75	07BaDeTyKa
501	1-35	271	6356.53-6976.90	2.00×10^{-3}	685	07BaDeTyKa
521	1-30	122	7579.60-7966.30	1.00×10^{-3}	310	12DeBaStTy
530	15-15	1	7545.27-7545.27	1.00×10^{-3}	4	12DeBaStTy
601	1-31	153	7395.60-7891.81	1.00×10^{-3}	383	12DeBaStTy
610	13-13	1	7275.63-7275.63	1.00×10^{-3}	3	11BaDeTyKa

$v_1v_2v_3$: vibrational normal mode quantum numbers defining the vibrational state.

E : energy range of vibrational state in cm^{-1} .

Mean ε : mean of the (bootstrap enabled) MARVEL uncertainties in cm^{-1} .

N_{rot} : number of rotational levels in the vibrational state.

N_t : number of transitions involving the vibrational state.

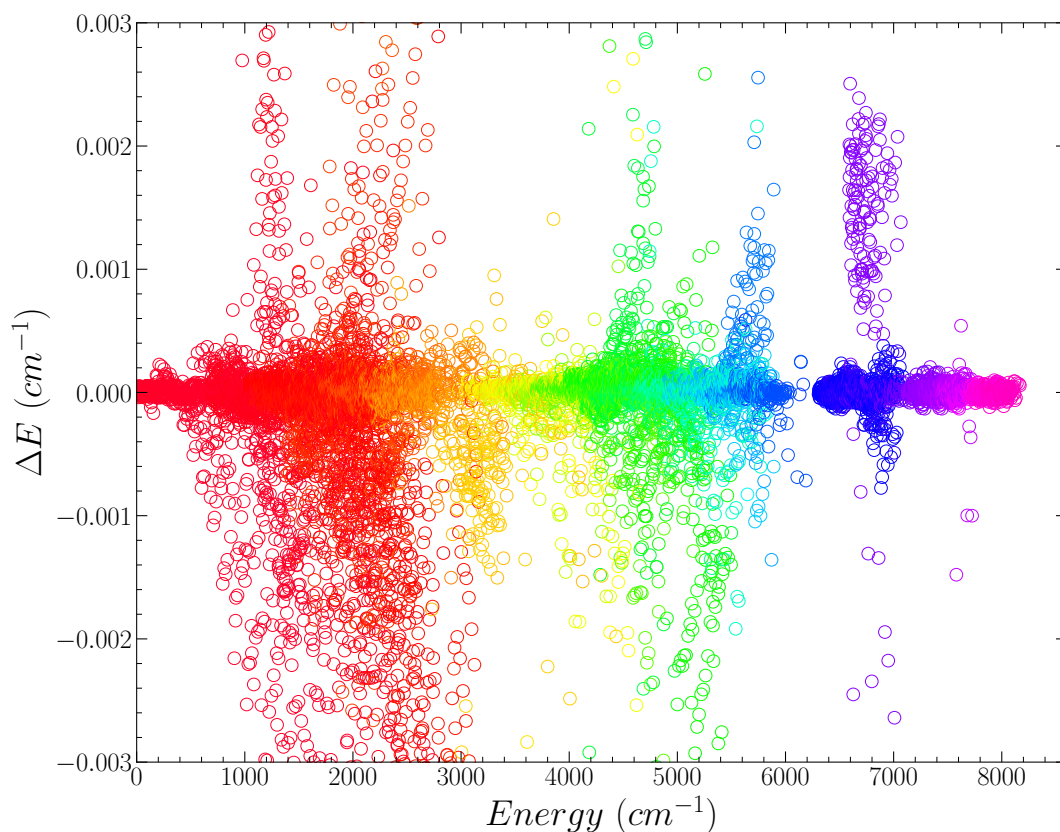
The MARVEL energy range extends to 8167.33 cm^{-1} with 70 vibrational states and the maximum value of the rotational angular momentum quantum number $J = 67$. Only five vibrational states with a $J = 0$ level exist in the MARVEL dataset because not many measured transitions involve levels with $J = 0$ in the MARVEL input and, of course, states with odd quanta in ν_3 do not possess a $J = 0$ level. Out of a total of 29 experimental data sources considered for analysis, 19 have all their transitions validated. The $^{16}\text{O}_3$ MARVEL network is rather fragmented due to missing

input data with a number of components comprising of single transitions. Transitions belonging to non principal components of the $^{16}\text{O}_3$ MARVEL network are not considered as validated.

MARVEL energy levels determined by single transitions (predominantly in the high-energy region) do not have their uncertainties adjusted by the bootstrap procedure, which means MARVEL uncertainties for these levels are likely to be underestimated; in particular, most of these transitions in the high-energy range have generic experimental uncertainties which are likely to be underestimates in some cases.

5.4.2 Comparison with SMPO_20d line list

MARVEL energy levels of $^{16}\text{O}_3$ are compared with energies from the SMPO_20d line list obtained from the S&MPO [3] database as shown in Figure 5.2 where the energy levels are matched on quantum numbers $(v_1, v_2, v_3, J, K_a, K_c)$. In terms of line positions and energy levels, the SMPO_20d line list is based largely on EH models with empirical corrections [22]. A total of 13476 energy levels are matched between MARVEL and SMPO_20d datasets with mean energy difference $\Delta E_{mean} = -9.52 \times 10^{-4} \text{ cm}^{-1}$ and standard deviation $4.40 \times 10^{-3} \text{ cm}^{-1}$. While the overall agreement between the two datasets is good, cases of discrepancies are highlighted and discussed in this section. 11116 SMPO_20d energy levels fall within the (bootstrap enabled) MARVEL uncertainty range which equates to 92.6% of all energy levels matched between the two datasets. There are 188 MARVEL energy levels that did not match on approximate quantum numbers and J with the energies from SMPO_20d.



$v_1 v_2 v_3$											
• 000	• 110	• 111	• 130	• 211	• 301	• 113	• 104	• 213	• 501	• 205	• 351
• 010	• 002	• 210	• 022	• 004	• 023	• 230	• 203	• 114	• 223	• 125	• 530
• 001	• 101	• 003	• 121	• 103	• 122	• 320	• 132	• 330	• 124	• 153	• 243
• 100	• 030	• 102	• 220	• 310	• 221	• 212	• 123	• 321	• 430	• 601	• 271
• 020	• 200	• 031	• 013	• 131	• 400	• 311	• 401	• 025	• 044	• 045	• 405
• 011	• 012	• 201	• 112	• 202	• 014	• 005					

Figure 5.2: Comparison of matched energy levels between MARVEL and SMPO_20d line list. ΔE is the energy difference. *Energy* on the horizontal axis gives the energy value of a ro-vibrational level. The energy levels are classified according to their vibrational band origins with legend $v_1 v_2 v_3$ giving the vibrational normal mode labels.

EH models are often excellent at representing energy levels within particular ro-vibrational band(s) that they are fitted to, but can struggle with extrapolating to energies beyond that region. This has led to significant differences between MARVEL and EH treatments in previous studies [63]. EH models can also have difficulty completely accounting for ro-vibrational resonances arising from interactions between different states; for ozone these interactions are common at higher energies close to the relatively low-lying dissociation threshold of around 8500 cm^{-1} [22]. MARVEL energy levels have an advantage over EH models in that shifts due to resonances are automatically captured

from measurements by the MARVEL procedure. There are many known resonance regions for $^{16}\text{O}_3$ where it is difficult to predict energy levels and line positions to experimental accuracy [22]. One such example is the 2000 - 3000 cm^{-1} region where vibrational states 101 and 030 interact. In particular, the (1,0,1,19,2,17) level is known to resonate with level (0,3,0,19,3,17) [22].

In the MARVEL dataset the (1,0,1,19,2,17) level is determined by sources MagentaSMPO and 22JaBoElJe whereas the (0,3,0,19,3,17) level is determined by lines only from MagentaSMPO (see the CheckTransitions.txt file available in supplementary material to this article for details of individual lines that contribute to these resonating levels). The energy difference between MARVEL and SMPO_20d for the (1,0,1,19,2,17) level in particular is substantially larger than other levels in both these vibrational states as illustrated in Figure 5.3 and its inset.

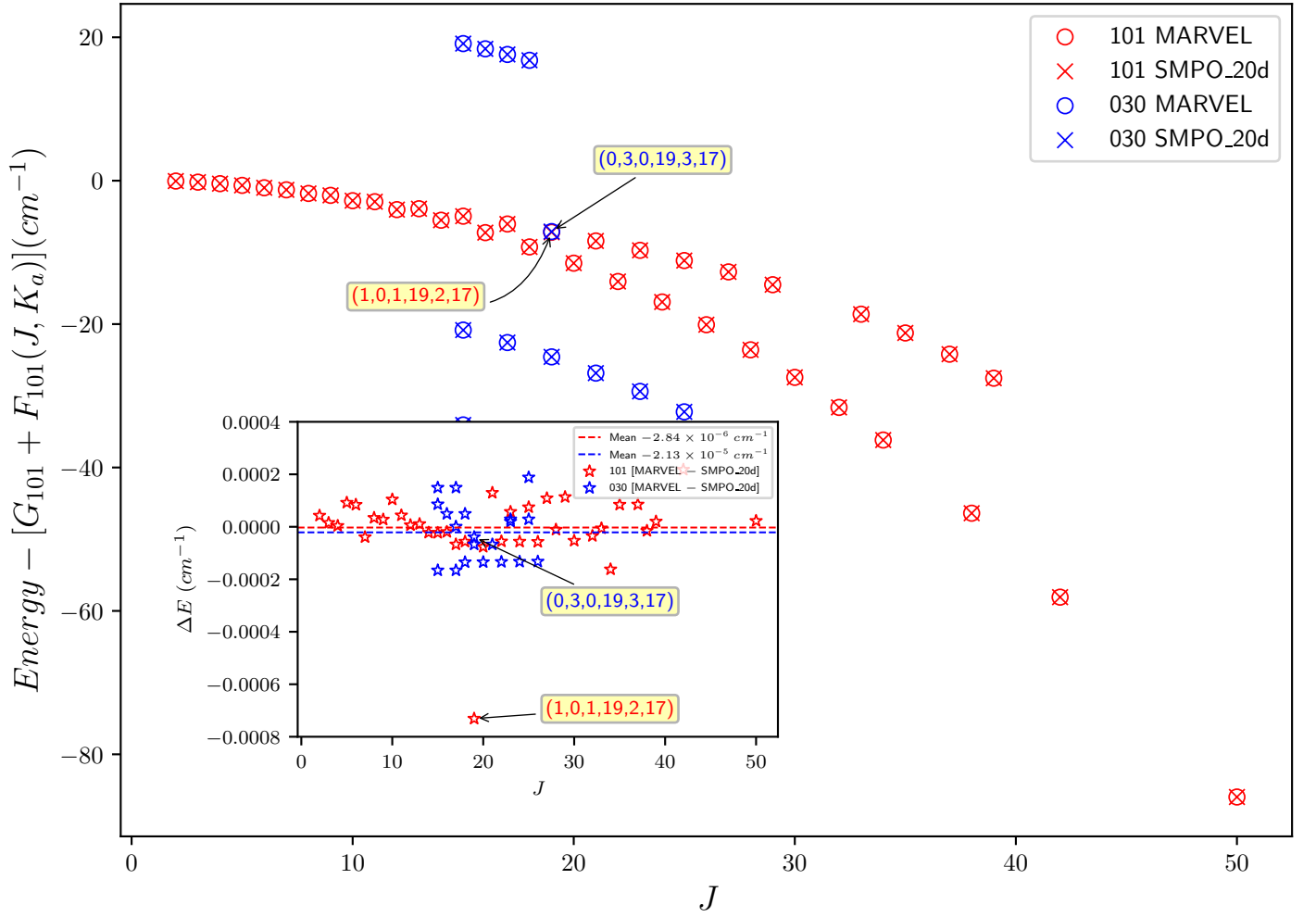


Figure 5.3: MARVEL and SMPO.20d energies of two interacting vibrational states (101 and 030) are plotted against rotational angular momentum quantum number J . The resonant energy levels with quantum numbers $(v_1, v_2, v_3, J, K_a, K_c)$ are $(1,0,1,19,2,17)$ and $(0,3,0,19,3,17)$. The energies of MARVEL and SMPO.20d levels are shifted by prolate symmetric top energies with vibrational band origin of the 001 state $G_{101} = 2110.78 cm^{-1}$. The inset shows the difference between SMPO.20d and MARVEL energies (ΔE) for interacting vibrational states with resonant energy levels labelled with their respective quantum numbers.

Figure 5.3 shows and compares the energies of interacting vibrational states for MARVEL and SMPO.20d line list with the resonant ro-vibrational levels highlighted. This resonance interaction was chosen as an illustration not because the shifts are particularly large but because of the good empirical coverage of the energy levels belonging to both vibrational states. In order to better visualize the energies of both interacting vibrational states, all MARVEL and SMPO.20d energies in Figure 5.3 are shifted by prolate symmetric top ro-vibrational energies $[G_{101} + F_{101}(J, K_a)]$ of the 101 vibrational state, with rotational energies given by Eq. (5.10). Parameter κ_v , see Eq. (5.9), [31]

for a particular vibrational state indicates the extent to which the energy levels of an asymmetric top molecule are correlated to prolate or oblate symmetric top energies. For vibrational states 101 and 030 of $^{16}\text{O}_3$, $\kappa_{101} = -0.97$ and $\kappa_{030} = -0.98$. Therefore all MARVEL and SMPO_20d energies in Figure 5.3 are shifted by prolate symmetric top energies. The values of spectroscopic constants $A_v, B_v, C_v, \Delta_J, \Delta_{JK}$ and Δ_K are obtained from Barbe et al. [22].

$$\kappa_v = \frac{2B_v - A_v - C_v}{A_v - C_v} \quad (5.9)$$

$$F_{101}(J, K_a) = B_v J(J+1) + (A_v - B_v)K_a^2 - \Delta_J J^2(J+1)^2 - \Delta_{JK} J(J+1)K_a^2 - \Delta_K K_a^4 \quad (5.10)$$

The inset within Figure 5.3 shows the difference between MARVEL and SMPO_20d energies indicating that the two datasets disagree more for one of the pair of resonating levels. As illustrated in the inset of Figure 5.3, $\Delta E = -7.31 \times 10^{-4} \text{ cm}^{-1}$ between MARVEL and SMPO_20d for the resonant level (1,0,1,19,2,17) is significantly larger in absolute terms than $\Delta E_{mean} = -2.84 \times 10^{-6} \text{ cm}^{-1}$ for the 101 vibrational state. If transitions contributing to (1,0,1,19,2,17) from MagentaSMPO have measured line positions, and if the corresponding energy from SMPO_20d is from an EH model, then Figure 5.3 and its inset could be an illustration of the MARVEL algorithm being able to capture resonance shifts automatically by analyzing transitions with measured line positions, although further analysis for many more resonating levels is required which is beyond the scope of this study.

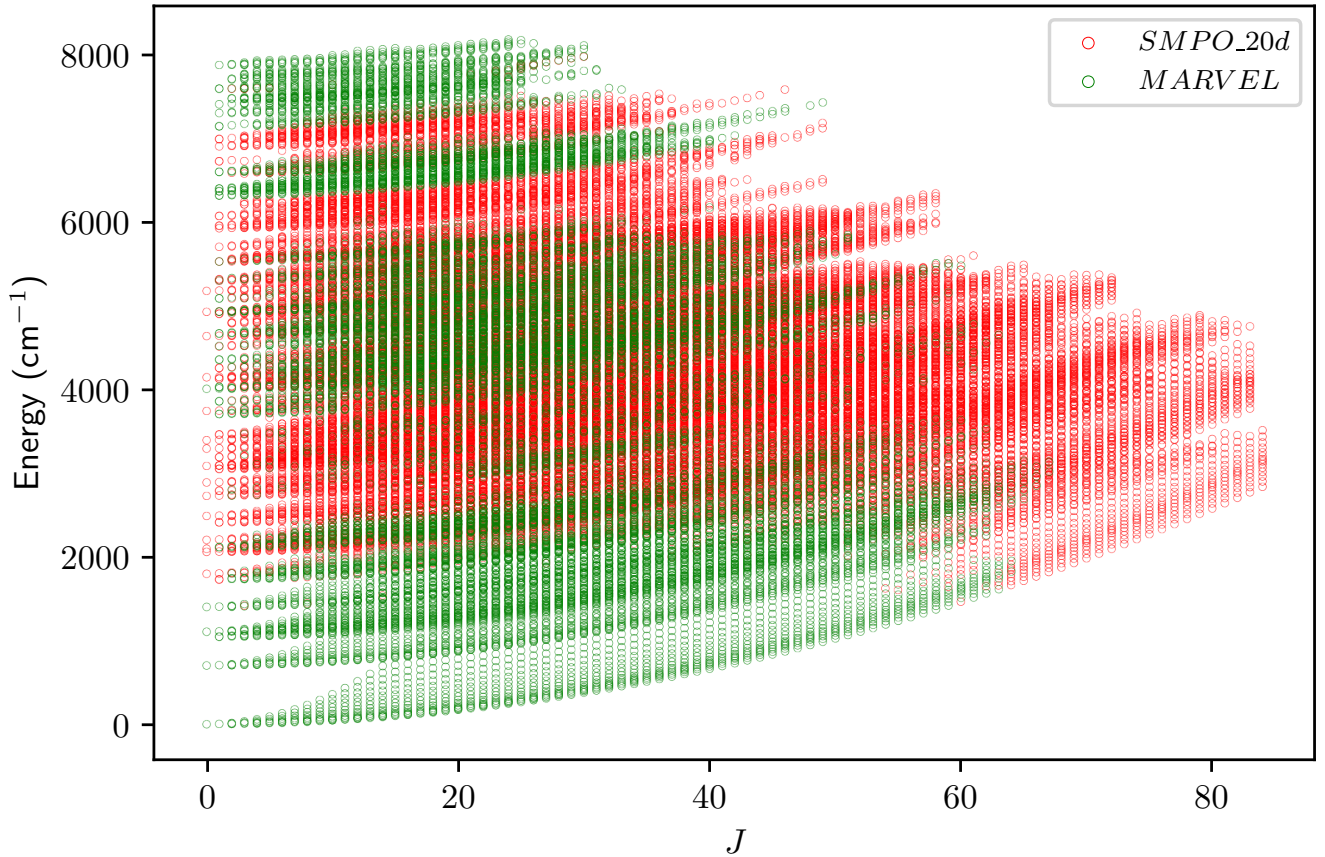


Figure 5.4: Overview of all MARVEL energy levels of $^{16}\text{O}_3$. Energies obtained from the SMPO_20d linelist [3, 22] are used to indicate regions where there are missing MARVEL levels.

Despite extracting data from the HITRAN database to build the MagentaSMPO source, lack of availability of experimental line position data in certain spectral regions contributes to missing energy levels in the ozone MARVEL dataset. All MARVEL energy levels of ozone from this work are shown in Figure 5.4.

5.4.3 Comparison with variational calculations

As mentioned, comparing MARVEL energy levels with variationally calculated energies is a test of completeness of the MARVEL dataset since every energy level that exists can be calculated in principle.

We initially run variational nuclear motion calculations for the ro-vibrational energy levels of $^{16}\text{O}_3$ in its ground electronic state using the DVR3D program. However, for $60 \leq J \leq 70$ we encountered the following error printed in the DVR3D output file relating to the DGEMM fortran

routine for matrix multiplication: “Intel MKL ERROR: Parameter 8 was incorrect on entry to DGEMM .”. This error means that there is larger (than normal) uncertainty in the calculated energies for the range $60 \leq J \leq 70$. The energies for $0 \leq J \leq 60$ are expected to be more reliable since no such error occurs for this range of J values. Curiously, the error does not occur outside the range $60 \leq J \leq 70$. We are currently investigating the source of this error. It could be that there is some issue with the input files, input parameters or the input wavefunctions from the previous step of the calculations. It should be noted that this error has not occurred (to the best of our knowledge) for energy level calculations for other molecules. Due to time restrictions on the submission of this thesis we decided that further time spent tracing the source of this error is not feasible. Therefore we decided to also use another nuclear motion program called EVEREST to calculate the ro-vibrational energies, especially since the largest J value in the MARVEL dataset is $J = 67$. EVEREST is very much similar to DVR3D in the approach it takes to solve the nuclear motion problem and so the theory and approach described in chapter 4 applies to EVEREST as well as DVR3D. One of the major differences between EVEREST and DVR3D is that EVEREST uses the Sinc-DVR functions as basis to construct the Hamiltonian.

EVEREST [108] is a computational program that solves the time-independent nuclear motion Schrödinger equation variationally for triatomic molecules using an exact kinetic energy operator in a generalised coordinate system. This program is used to calculate ro-vibrational energy levels of $^{16}\text{O}_3$ in its ground electronic $\tilde{X}^1A_1$ state in order to verify our MARVEL analysis. The calculations are performed in Radau internal coordinates (r_1, r_2, θ) with bisector molecule fixed embedding [122]. We use 60 associated Legendre polynomials as basis functions for the angular coordinate θ with range $[0, 180]$ and 40 Sinc-DVR (discrete variable representation) functions as basis for the r_1 and r_2 radial coordinates with range $[1.0, 4.0]$ Å. An atomic mass of ^{16}O equal to 15.994915 Da is used in calculations which accounts very approximately for non-adiabatic effects. The dimension of the Hamiltonian in the first step of the calculation is 5000. Number of eigenvectors from the first step taken as basis functions in the second step of the calculation is equal to 4000. The resulting variational energies span up to the dissociation threshold of $^{16}\text{O}_3$ of around 8500 cm^{-1} and $J = 80$. The number of basis functions, grid size and dimensions of the Hamiltonian are varied to ensure convergence of calculated energies. The fitted potential energy surface (PES1) from Polyansky et

al [119] is used as input to EVEREST calculations in this work.

In EVEREST the symmetries of ro-vibrational levels $\Gamma_{rot-vib}$ are determined by the CNPI $C_{2v}(M)$ operators E^* and (12) (equivalent to operators $\hat{\sigma}_{yz}$ and $\hat{C}_2$ respectively in C_{2v} point group) [31]. EVEREST transforms the ro-vibrational wavefunctions under operators E^* and (12) and assigns their characters to each ro-vibrational energy level. Table 5.1 illustrates how we can determine $\Gamma_{rot-vib}$ of each energy level from the characters and then subsequently filter half the energy levels to retain allowed physical energies with symmetry $\Gamma_{rot-vib} = A_1, A_2$ that satisfy Eq. 5.4 as per the spin statistics theorem. MARVEL energy levels should automatically belong to total symmetry A_1 or A_2 if they are determined exclusively from observed line positions, however due to an unknown number of calculated lines present in MagentaSMPO, we checked the symmetries of all MARVEL levels from their approximate quantum numbers v_3 , K_a and K_c using Table 5.1, and indeed there are no non-physical MARVEL levels with symmetry B_1 or B_2 .

EVEREST energies are filtered for symmetries $\Gamma_{rot-vib} = A_1, A_2$ and subsequently matched uniquely to MARVEL energies on J , symmetry and nearest energy. The results of this comparison is shown in Figure 5.5.

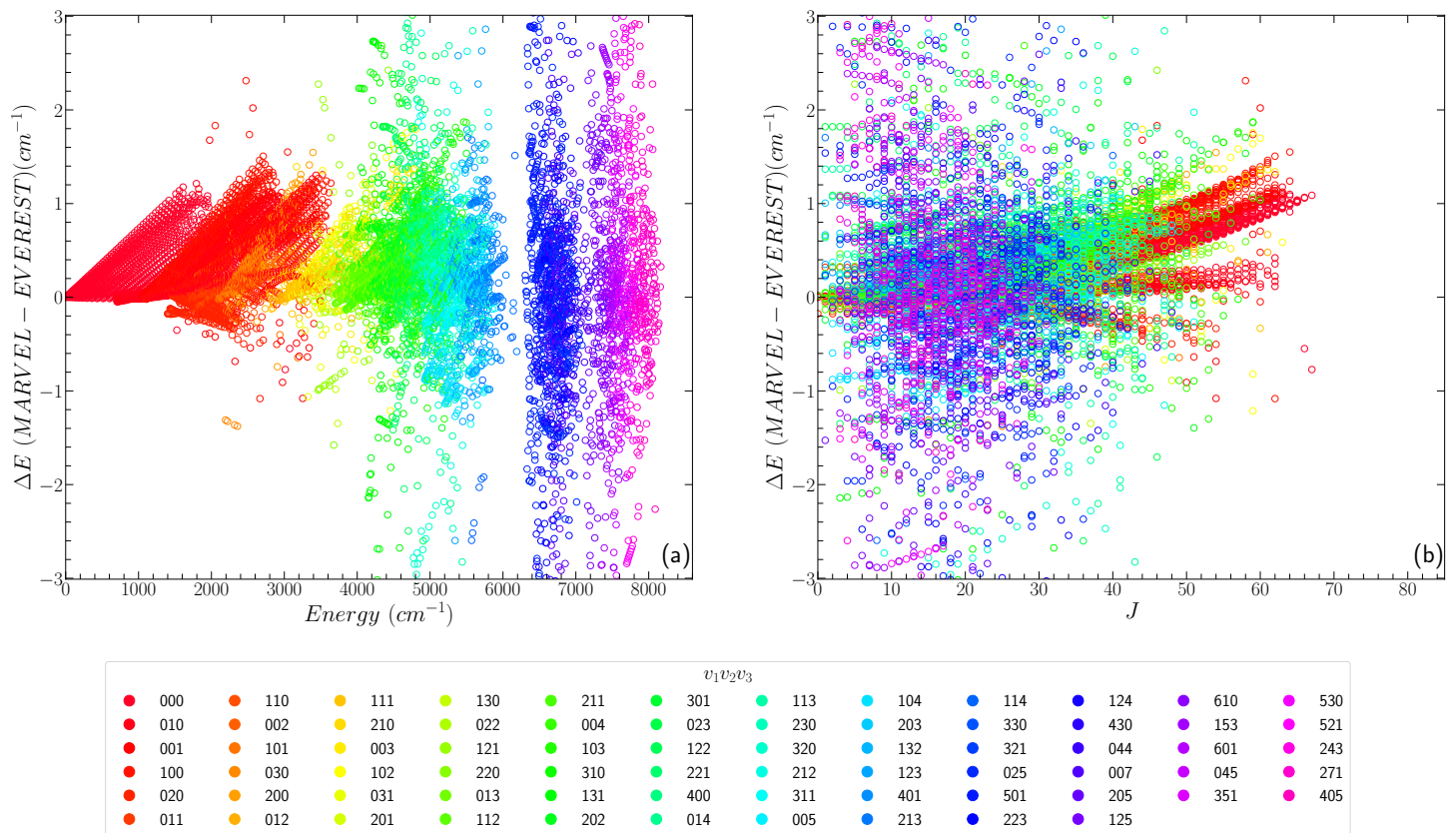


Figure 5.5: Comparison of MARVEL and EVEREST energy levels. Energy levels are uniquely matched on J , symmetry and nearest energy. The energies are classified according to their vibrational band origins. The difference in energy (ΔE) is plotted as a function of energy and J in panels (a) and (b) respectively.

All MARVEL levels are uniquely matched and validated against EVEREST variational energies with $\Delta E_{\text{mean}} = 0.25 \text{ cm}^{-1}$ and standard deviation 1.09 cm^{-1} . The potential energy surface PES1 from Polyansky et al [119] performs less well at high J 's as illustrated in Figure 5.5(b) because it is fitted to 371 energy levels up to $J = 5$ and 6000 cm^{-1} . We note the *ab-initio* potential of Tyuterev et al [151] has the correct shape and dissociation asymptote at large internuclear distances and therefore we expect it to be more accurate than PES1 above 6000 cm^{-1} . Systematic structures in ΔE at lower energies in Figure 5.5(a) also indicate scope for improvement in the fitted PES1 potential energy surface from Polyansky et al [119].

5.5 Summary

A total of 13664 MARVEL ro-vibrational energy levels of the main isotopologue of ozone ($^{16}\text{O}_3$) in its ground electronic $\tilde{X}^1A_1$ state up to 8167.33 cm^{-1} are derived along with their uncertainties, by analyzing 50276 transitions from 30 data sources. 49926 transitions are validated. Line positions of 78MoDeBeBa (band 010-000) and 81BaSeJoGo (bands 100-000 and 001-000) are recalibrated.

Unusually we were unable to obtain a substantial proportion of the measured line positions as listed in Table 5.4; with access to these data our results would have been even more comprehensive. However, we tried to extract as many measured line positions as possible from the HITRAN database (as empirically corrected line positions from SMPO_20d line list were incorporated into the latest version of HITRAN) by constructing the MagentaSMPO source. Extracting the empirically corrected measured lines became a complex task because (to the best of our knowledge) there does not appear to be line-by-line labelling to distinguish observed lines from calculated ones in HITRAN and SMPO_20d. Therefore MagentaSMPO source also contains an unknown number of calculated lines because we are unable to identify them and completely filter them out. As a result the MARVEL dataset suffers from a number of its levels having partial or complete contributions from calculated lines. The CheckTransitions.txt file provided as part of the supplementary material shows the contribution of individual lines for every MARVEL energy level. We hope that subsequent MARVEL studies on $^{16}\text{O}_3$ will be able to identify and replace calculated lines in MagentaSMPO by transitions with measured line positions as data availability improves in the future. At present the unavailability of experimental data makes it difficult to prove the consistency of the available data compilations.

MARVEL energies are extensively compared with SMPO_20d line list energies obtained from the S&MPO database [3] with $\Delta E_{mean} = -9.52 \times 10^{-4}\text{ cm}^{-1}$ and standard deviation $4.40 \times 10^{-3}\text{ cm}^{-1}$ for all 13476 energy levels matched between them on approximate quantum numbers and J as shown in Figure 5.2. The inset within Figure 5.3 shows that MARVEL and SMPO_20d energies disagree more for the (1,0,1,19,2,17) resonant level which (providing that the MARVEL levels are determined exclusively by measured lines) perhaps illustrates the ability of the MARVEL algorithm to automatically capture resonance shifts.

The nuclear Schrödinger equation is solved variationally for $^{16}\text{O}_3$ up to the dissociation threshold and $J = 80$ using the EVEREST program [108]. All MARVEL energies are uniquely matched and validated against variationally calculated ro-vibrational energies with $\Delta E_{\text{mean}} = 0.25 \text{ cm}^{-1}$ and standard deviation 1.09 cm^{-1} as shown in Figure 5.5.

A small section of the spectroscopic network of $^{16}\text{O}_3$ is shown in Figure 5.6. Nodes and edges represent energy levels and spectroscopic transitions respectively. The vibrational states are represented by nodes of different colours. Each node is labelled by the unique set of quantum numbers $[v_1, v_2, v_3, J, K_a, K_c]$. The size of a node is defined as being directly proportional to the number of transitions connected to it. The largest node is the ground vibrational state involved in most transitions.

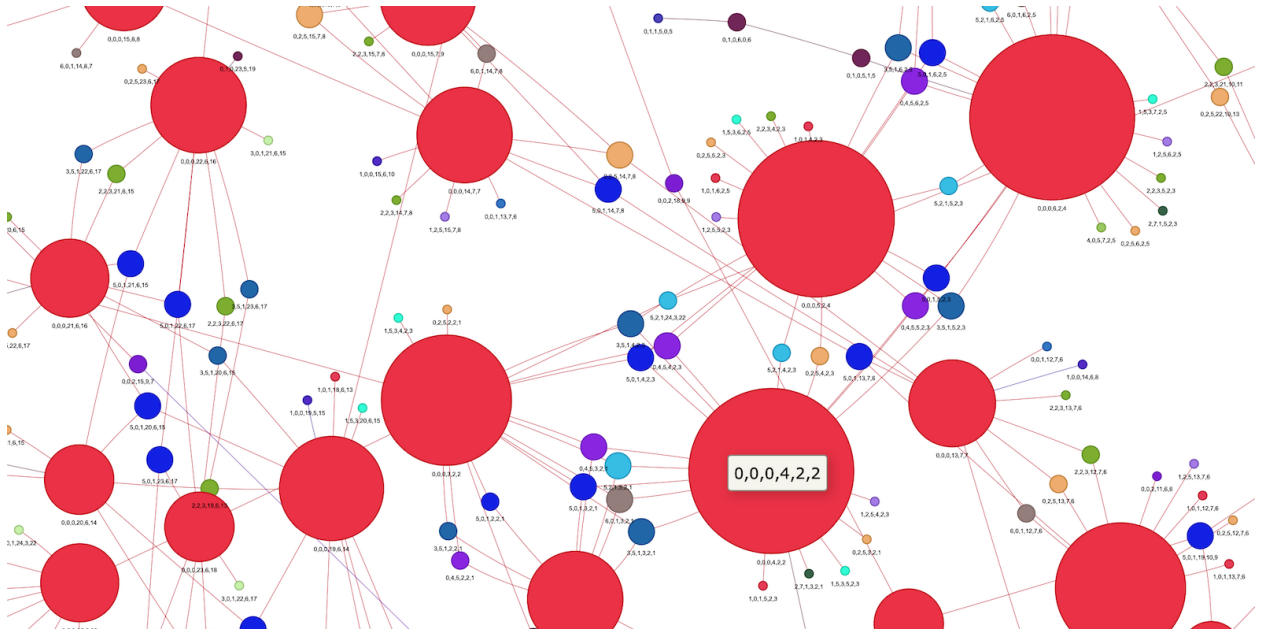


Figure 5.6: Spectroscopic network graph of $^{16}\text{O}_3$

The results of this study will be used to improve the accuracy of variational line list calculations for ozone as part of the ExoMol [141] project (paper currently in preparation). A significant contribution to this study was made by the students of Parmiter's School as part of the ORBYTS project [126].

After submission of this study for publication, Tashkun et al. [134] provide a rather similar analysis giving energy levels of ozone. Their analysis is based on a more complete set of measured transitions data which, to the best of our knowledge, is not made available either in their article

[134] or elsewhere. The results from this chapter are published in our paper [153].

Chapter 6

Variational line list calculations of $^{16}\text{O}_3$ and $^{18}\text{O}_3$ isotopologues

In this chapter, spectroscopic properties of ozone are calculated and compared to high accuracy measurements [79] and calculations in scientific literature. A new empirically refined potential energy surface (PES) for $^{16}\text{O}_3$ is calculated. A new PES for $^{18}\text{O}_3$ is constructed using diagonal Born Oppenheimer correction (DBOC) surfaces. Two new dipole moment surfaces (DMSs) for the ground $\tilde{X}^1A_1$ ($\tilde{X}^1A'$) electronic state of ozone are calculated. All the new surfaces calculated in this work, along with calculations published in literature, are tested for their accuracy by performing nuclear motion calculations using the DVR3D program and then comparing the predictions with measured data in literature.

6.1 Rotation vibration spectrum of $^{16}\text{O}_3$

Ab-initio electronic structure calculations of the ground electronic $\tilde{X}^1A_1$ state of ozone are performed to obtain the discrete potential energy and dipole moment values on a grid of geometries. The potential energy values are fitted and refined to empirical energy levels to give a new refined PES of ozone. The new empirically refined PES is extensively tested by using it as input for nuclear motion calculations and comparing its predictions with measured properties (energy levels, line positions and intensities). Similarly, two new DMSs are constructed by fitting to a functional

form and tested against measured transition intensities. Comparisons with spectroscopic databases and other notable studies in scientific literature are also highlighted.

6.1.1 Potential energy surface - ab initio calculations and refinement

Ozone in its ground electronic state is a closed shell singlet [107]. Since no electronic orbital angular momentum operator commutes with the polyatomic molecular electronic Hamiltonian, we must rely on irreducible representations of point groups to label the electronic states (instead of angular momentum labels). If we use the C_{2v} point group the ground electronic state is labelled as X^1A_1 . If we use the C_s point group the ground electronic state is labelled as X^1A' .

Electronic structure calculations of ozone in its ground X^1A' electronic state are carried out. The MOLPRO program is used to perform these calculations [157]. CASSCF and MRCI level of electronic structure theory is used to calculate the ab initio points. The active space of (18,12) was used which means 18 active electrons distributed among 12 active orbitals to generate the CSFs. In MOLPRO notation and using the C_s point group, we define the active space as:

CASSCF; OCC ; 12,3 ; CLOSED ; 3,0 ; FROZEN; 0,0 ; WF

The OCC directive gives us the total number of orbitals in each irreducible representation (called irrep). In this case we have 12 orbitals in A' irrep and 3 orbitals in A'' irrep. The CLOSED directive allows us to control the number of orbitals that are to be kept doubly occupied in all CSFs (i.e. these orbitals can be described as in-active orbitals). Both OCC and CLOSED directives together define the active space where the number of active orbitals in each irrep is given by subtracting OCC and CLOSED for each irrep. The FROZEN directive tells us if the orbitals that are always kept doubly occupied are optimised or not. In this case the all the in-active orbitals are optimised meaning the $c_{i\mu}$ coefficients are treated as variational parameters to give the optimal functional forms of the orbitals. This large active space is chosen to ensure contributions to the wavefunction from 8029 configuration state functions (24202 Slater determinants).

We use contracted Gaussian type functions (CGTF basis) aug-cc-pV5Z and aug-cc-pwCV5Z for our calculations in MOLPRO. The '5Z' in the basis set indicates that there are five CGTFs for each spin orbital, each with its own unique orbital exponent (called zeta)[89]. The 'V' in our

basis indicates splitting of the valence shells and the inner (core) shells with more than one CGTFs allocated to valence shell and only one CGTF allocated to inner (core) shell. Due to centers of charge shifting as the molecule vibrates, additional functions called polarisation functions are added and this is labelled with a 'p' in the basis [89]. 'C' stands for accounting for core-valence electron interaction. 'aug' stands for the addition of diffuse functions, primitive functions and polarization functions. 'w' adds extra variational parameters to the basis. 'cc' stands for correlation consistent functions and refers to specialised basis functions designed by Dunning et al [55] for CI calculations.

The effect of the size of the basis set is investigated on the dipole moments of ozone later in this chapter (see Figure 6.3). Valence electron correlation is accounted for along with Davidson correction and relativistic effects.

The ab-initio points were calculated on a grid of 5091 geometries. The internal coordinates r_1, r_2, θ used to define these geometries. The range of the internal coordinates considered for the electronic structure calculations are as follows

$$\begin{aligned} 2.0938 &\leq r_1 \leq 3.2654 \\ 2.1014 &\leq r_2 \leq 3.2730 \\ 96.8800 &\leq \theta \leq 136.8800 \end{aligned} \tag{6.1}$$

where r_1 and r_2 are in atomic units (a.u.) and θ is in degree. The UCL Myriad parallel computing facility is used to calculate the ab-initio points. We used shared memory parallelism (OpenMP) where a calculation for each geometry is split into 5 jobs. Each job is distributed among 4 threads. Each thread is shared among 4 different cores. Each job typically took 1.5 – 2 days.

The results of our calculations of the ground electronic state of ozone are shown in Figure 6.1 where the red scatter points are the ab-initio points of the potential energy surface of the X^1A' state. Although calculations for 5091 geometries were performed, the potential values were obtained for 3960 geometries as MOLPRO did not return a potential energy value for the other geometries.

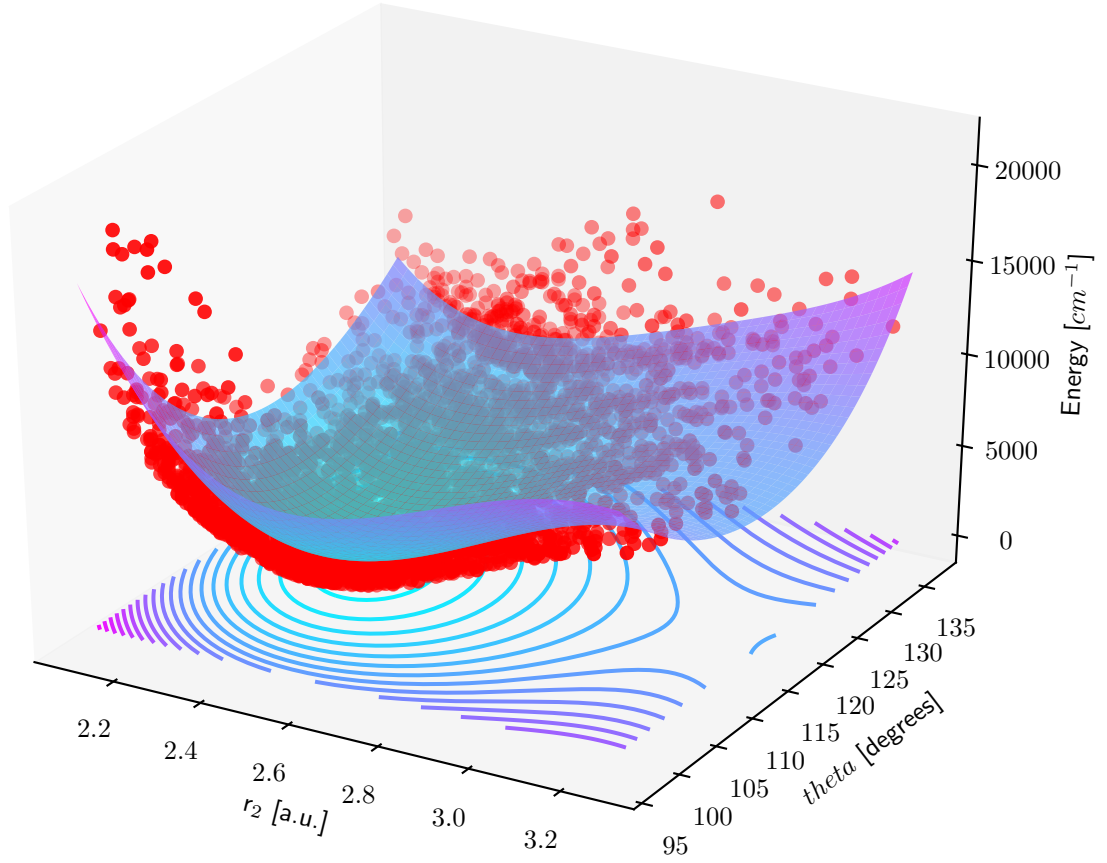


Figure 6.1: Two-dimensional slice of the PES of the X^1A' ground electronic state of $^{16}O_3$. The scatter points in red are the calculated discrete *ab-initio* values.

The discrete *ab-initio* potential values are fitted to the following functional form to create a potential energy surface:

$$\begin{aligned}
 V(r_1, r_2, \theta) = \sum_{ijk} d_{ijk} P_1^i P_2^j P_3^k e^{-n_1[\Delta r_1^2 + \Delta r_2^2]} + V_1[e^{-2\tau\Delta r_1} - 2e^{-\tau\Delta r_1}] \\
 + V_1[e^{-2\tau\Delta r_2} - 2e^{-\tau\Delta r_2}] + e^{-n_2(\theta - \theta_e)}
 \end{aligned} \tag{6.2}$$

where

$$\begin{aligned}
P_1 &= \frac{r_1 + r_2}{2} - r_e \quad ; \quad P_2 = \frac{r_1 - r_2}{2} \quad ; \quad P_3 = \cos \theta_e - \cos \theta \\
\Delta r_1 &= r_1 - r_e \quad ; \quad \Delta r_2 = r_2 - r_e \quad ; \quad V_1 = 11500 \quad ; \quad \tau = 3.31 \\
n_1 &= 2.15 \quad ; \quad n_2 = 10 \\
\theta_e &= 116.88 \quad ; \quad r_e = 1.282
\end{aligned} \tag{6.3}$$

Parameters V_1 , θ_e , and r_e are in units cm^{-1} , degrees, and $\text{\AA}$, respectively. The parameters d_{ijk} are varied and fitted to the ab-initio points of the potential energy. These parameters are further iteratively refined by fitting to 371 empirical ro-vibrational energy levels with $J = 0, 2, 5$ and upto 6000 cm^{-1} in energy. The root mean square (RMS) deviation of the fit is $0.62 \times 10^{-3} \text{ cm}^{-1}$.

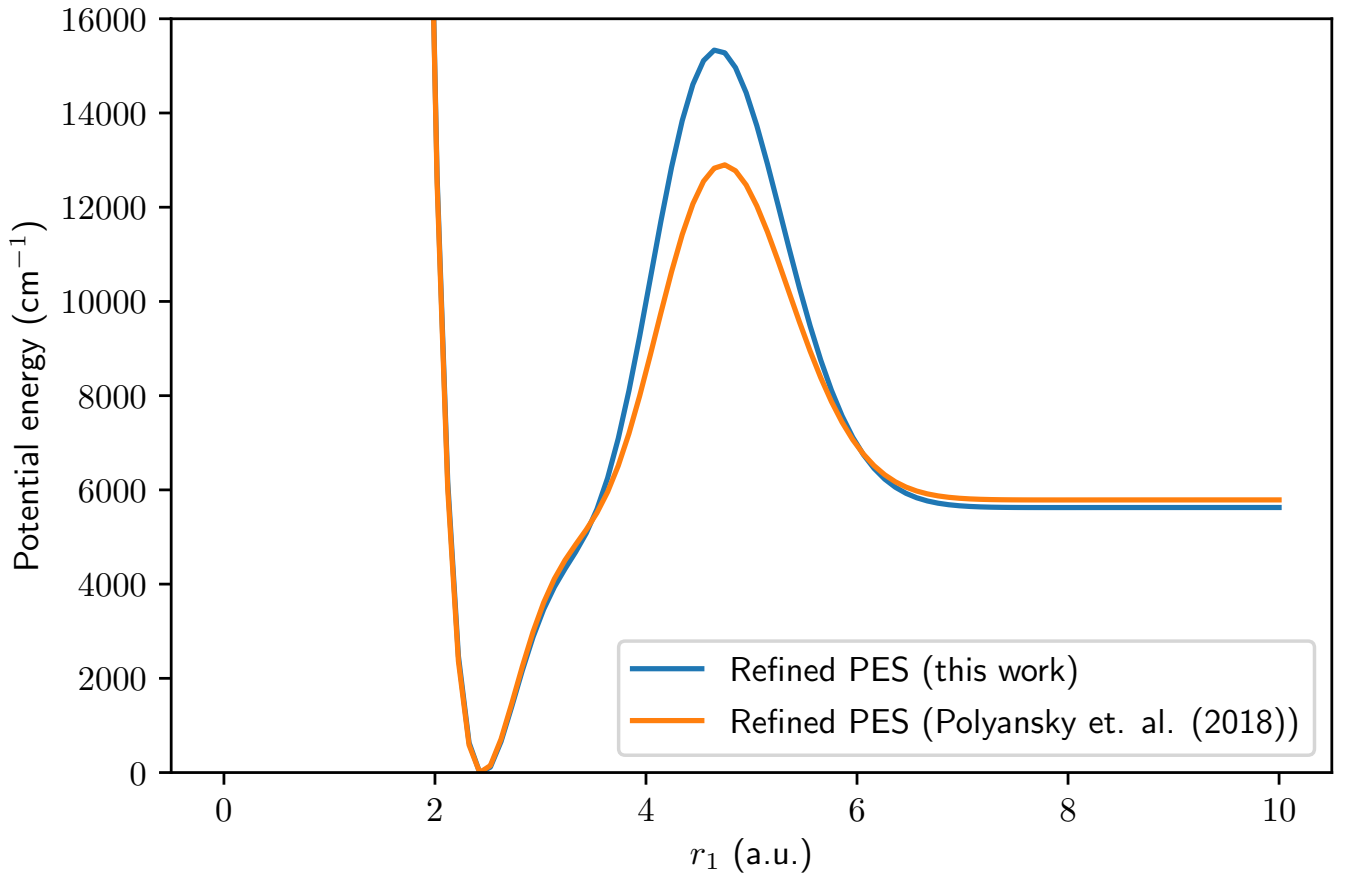


Figure 6.2: One-dimensional slice of the PES of the X^1A' ground electronic state of $^{16}\text{O}_3$

Figure 6.2 shows the new refined PES (this work) and the refined PES of Polyansky et al

[119]. Both fitted potential functions do not display the correct behaviour close to the dissociation threshold, however this is not likely to impact the calculation of ro-vibrational energies when using these potential energy functions as input because they are fitted to empirical energy levels upto 6000 cm^{-1} , well below the dissociation threshold. The fitting parameters d_{ijk} (Equation 6.2) of the new refined PES of this work are provided in Appendix A of this thesis.

6.1.2 Dipole moment surface

The dipole moment vector μ of a collection of charges is given by

$$\begin{aligned}\mu &= \mu_x \hat{\mathbf{i}} + \mu_y \hat{\mathbf{j}} + \mu_z \hat{\mathbf{k}} \\ &= \sum_i q_i x_i \hat{\mathbf{i}} + \sum_i q_i y_i \hat{\mathbf{j}} + \sum_i q_i z_i \hat{\mathbf{k}}\end{aligned}\tag{6.4}$$

and it describes the degree of polarisation or separation of opposite charges within a system such as a molecule. Integrals of the kind:

$$\langle \Phi' | \mu | \Phi'' \rangle\tag{6.5}$$

are called transition dipole moments as they are often a factor in quantities such as transition intensities as illustrated by Equations 6.12 and 6.15 along with quantities such as so called Einstein-A coefficients. The dipole moment vector μ (and its components μ_x and μ_y) can be expressed as a function of internal coordinates r_1, r_2, θ and therefore can be thought of as scalar functions of multiple variables.

The electronic structure of ozone has been studied extensively with many previous and recent theoretical studies [151] [150] [147]. We calculate the dipole moment surface of ozone in its ground X^1A' electronic state using the MOLPRO program [157]. Two new DMSs are calculated in this work and they are labelled or named as DMS D and DMS F respectively. CASSCF and MRCI level of electronic structure theory was used to calculate the ab initio points. The active space of (18,12) was used which corresponds to 18 active electrons distributed among 12 active orbitals. This large active space is chosen to ensure contributions from 8029 configuration state functions (24202 Slater determinants). We use a large aug-cc-pV5Z and aug-cc-pwCV5Z basis sets. Valence

electron correlation is accounted for along with Davidson correction and relativistic effects. The ab-initio points were calculated on a grid of 5091 geometries.

DMS D uses the aug-cc-pV5Z basis with the `CORE 3,0` directive in MRCI stage which means we do not account for core-valence electron correlation in DMS D. DMS F uses the aug-cc-pwCV5Z basis with the `CORE 3,0` directive in MRCI stage which means that we are still not accounting for core-valence electron correlation in DMS F but there are extra variational parameters in the basis used to calculate DMS F.

We use the finite field method where the components of the dipole moment vector are expressed as derivatives of energy with respect to an externally applied electric field $\lambda = 3.0 \times 10^{-4}$ au. The electric field is applied in the negative and positive directions of corresponding component of the dipole moment. For example $E_x^{(-)}$ indicates the energy of ozone at a particular geometry when the electric field of strength $\lambda = 3.0 \times 10^{-4}$ au is applied in the negative x direction. The subscript x in $E_x^{(-)}$ is only there to indicate the μ_x component of the dipole moment. Equation 6.6 gives the expressions used to compute the components of the dipole moment.

$$\mu_x = \frac{E_x^{(+)} - E_x^{(-)}}{2\lambda} \quad \mu_y = \frac{E_y^{(+)} - E_y^{(-)}}{2\lambda} \quad (6.6)$$

The advantage of using the finite field method is that corrections such as relativistic effects and Davidson corrections can be added as perturbations, whereas if the expectation value method is used for dipole moment calculations these effects would have to be incorporated into the wavefunction and so it would be harder to investigate their individual effects on the dipole moment.

Varying the size of the basis set and its effect on the components on the dipole moment is investigated as illustrated in Figure 6.3. The number of contracted Gaussian type functions (CGTF) are varied in the basis set as denoted by an 'X' in aug-cc-pwCVXZ, plotted against the value of the x-component of the dipole moment in Figure 6.3. The MOLPRO calculations were performed for three values of $X = 3, 4, 5$.

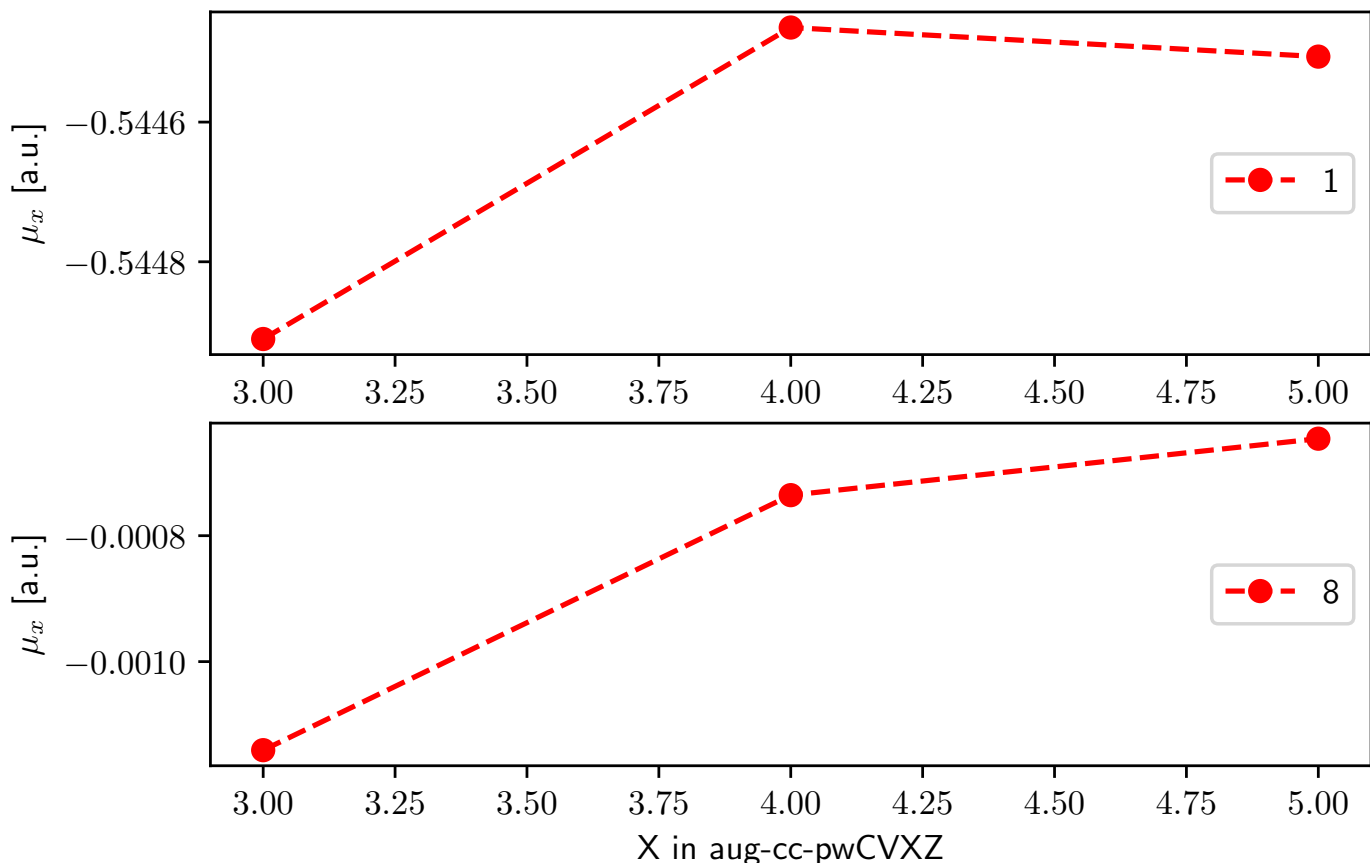


Figure 6.3: Effect of varying the basis on the x-component of dipole moment values of ozone for two different geometries (DMS F).

The two subplots in Figure 6.3 correspond to two separate geometries. The values of the dipole moment appear to be converging to a particular value in Figure 6.3. This asymptotic behaviour indicates that we are using a large enough basis set to perform our calculations because convergence gives us re-assurance that we are close to the true value of the instantaneous dipole moment.

We also investigate the effect of including relativistic corrections on the dipole moment values of ozone as illustrated in Figure 6.4. Although we restrict ourselves to non-relativistic quantum mechanical calculations in this thesis, the motivation for including relativistic corrections is that due to a large value of the nuclear charge in ozone we anticipate that the innermost electrons in the lowest occupied orbitals (1A', 2A' and 3A') are travelling with very high velocities (i.e. a large fraction of the speed of light) and therefore we anticipate that including relativistic correction would benefit the accuracy of our calculations.

The Hamiltonian that accounts for relativity and some other effects such as electron spin-orbit

interaction is the so called Pauli Hamiltonian given by:

$$\hat{H}_{Pauli} = \hat{H}_0 + \hat{H}_{S.O.} + \hat{H}_{MV} + \hat{H}_{Darwin} \quad (6.7)$$

where $\hat{H}_0$ is the non-relativistic Hamiltonian given in Equation 2.1. The terms accounting for relativistic effects are $\hat{H}_{MV}$ which stands for the mass-velocity term and $\hat{H}_{Darwin}$ which is the so called Darwin term. Both the mass-velocity and Darwin terms can be accounted for in MOLPRO by the directives `MASSV` and `DARWIN`. The directive `EREL` calculates both the relativistic terms and takes the sum of them.

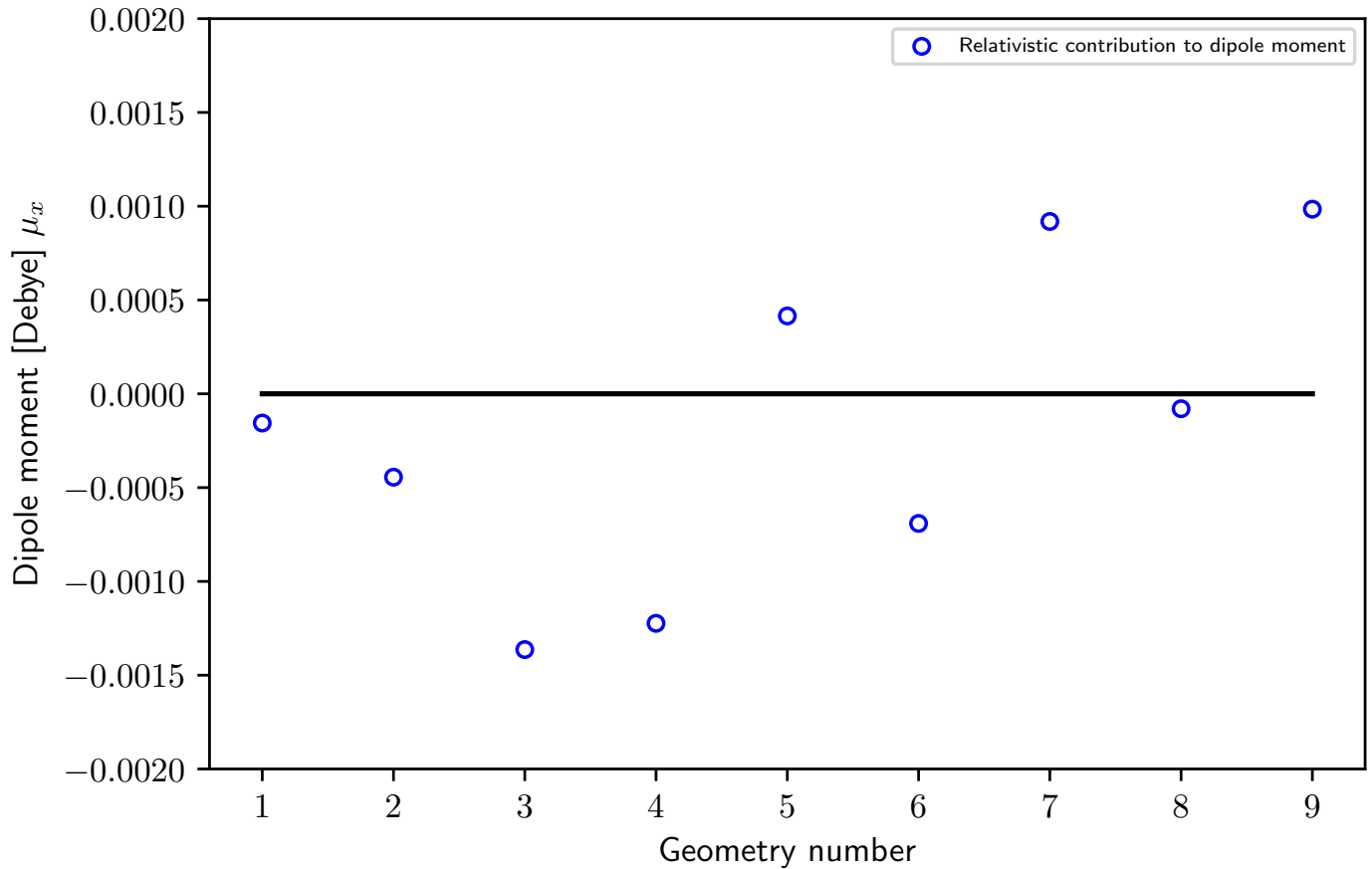


Figure 6.4: Effect of relativistic corrections on the x-component of dipole moment for ten geometries of DMS D (this work). The solid horizontal guideline indicates zero relativistic contribution to the x-component of dipole moment.

The results of relativistic corrections on the dipole moments of ozone are shown in Figure 6.4 for nine different geometries. The dipole moment calculations are run with and without relativistic

corrections and the difference is taken between them to obtain the values of the relativistic contribution to the dipole moment. As Figure 6.4 shows, the relativistic contributions are small but appreciable and therefore we have included relativistic corrections to our DMS calculations in this work for all geometries.

The UCL Myriad parallel computing facility was used to calculate the ab-initio points. We used shared memory parallelism (OpenMP) where a calculation for each geometry is split into 5 jobs. Each job is distributed among 4 threads. Each thread is shared among 4 different cores. Each job typically took 1.5 – 2 days totally roughly 3.5 months. Running the ab-initio electronic structure calculations in MOLPRO would probably not be feasible if the calculations were run serially

The ab-initio dipole moment points of two new DMSs calculated in this work (DMS D and DMS F) are fitted to functional form of Equations 6.8 and 6.9.

$$\mu_x(r_1, r_2, \theta) = \sum_{ijk} c_{ijk}^x B_1^i B_2^j B_3^k \quad (6.8)$$

$$\mu_y(r_1, r_2, \theta) = \sum_{ijk} c_{ijk}^y B_1^i B_2^j B_3^k \quad (6.9)$$

$$where \ B_1 = \frac{r_1 + r_2}{2} - r_e \ ; \ B_2 = \frac{r_1 - r_2}{2} \ ; \ B_3 = \theta_e - \theta \quad (6.10)$$

The hyper-parameters r_e and θ_e are chosen to have values 2.40 au and 116.88 degrees respectively. Hyper-parameters are those parameters that are not optimised in a fitting procedure with respect to the ab-initio points but are chosen arbitrarly. For the μ_x component of DMS D, 49 non-zero c_{ijk}^x parameters are fitted with a standard deviation of 0.12061×10^{-03} au. And for the μ_y component of DMS D, 49 non-zero c_{ijk}^y parameters are fitted with a standard deviation of 0.38256×10^{-04} au.

$$(6.11)$$

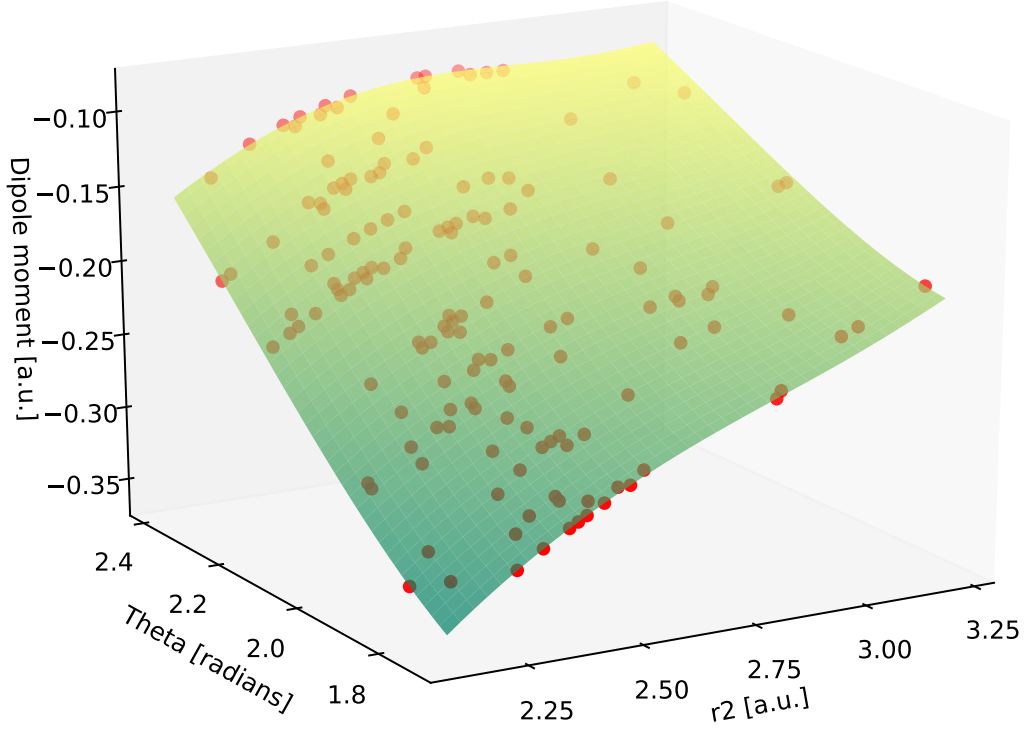


Figure 6.5: Two-dimensional slice of the functional fit of DMS_D

Two-dimensional slice of DMS D (μ_x component) along coordinate $r_1 = 2.3584$ au is shown in Figure 6.5. Red scatter points are the ab initio dipole moment points. The smoothness of the fit of our DMS is evident from Figure 6.5 and it serves an important purpose for intensities of overtone transitions. This is so because the the transition intensities of overtone bands are related to the derivative of the DMS with respect to the internal coordinates by the following approximate expression [138] for the transition dipole moment:

$$\mu_{0 \rightarrow m} \approx \sum_i \left\langle 0 \left| \frac{d^m \mu(Q_i)}{dQ_i^m} \right| m \right\rangle \quad (6.12)$$

where Q_i represent the different normal modes of vibration while $|0\rangle$ and $|m\rangle$ represent the ground vibrational and higher vibrational states respectively. Since the transition dipole moment depends on higher order derivatives of the DMS with respect to the Q_i we require the DMS function to be smooth and hence its important for the underlying ab-initio electronic structure calculations to be

accurate.

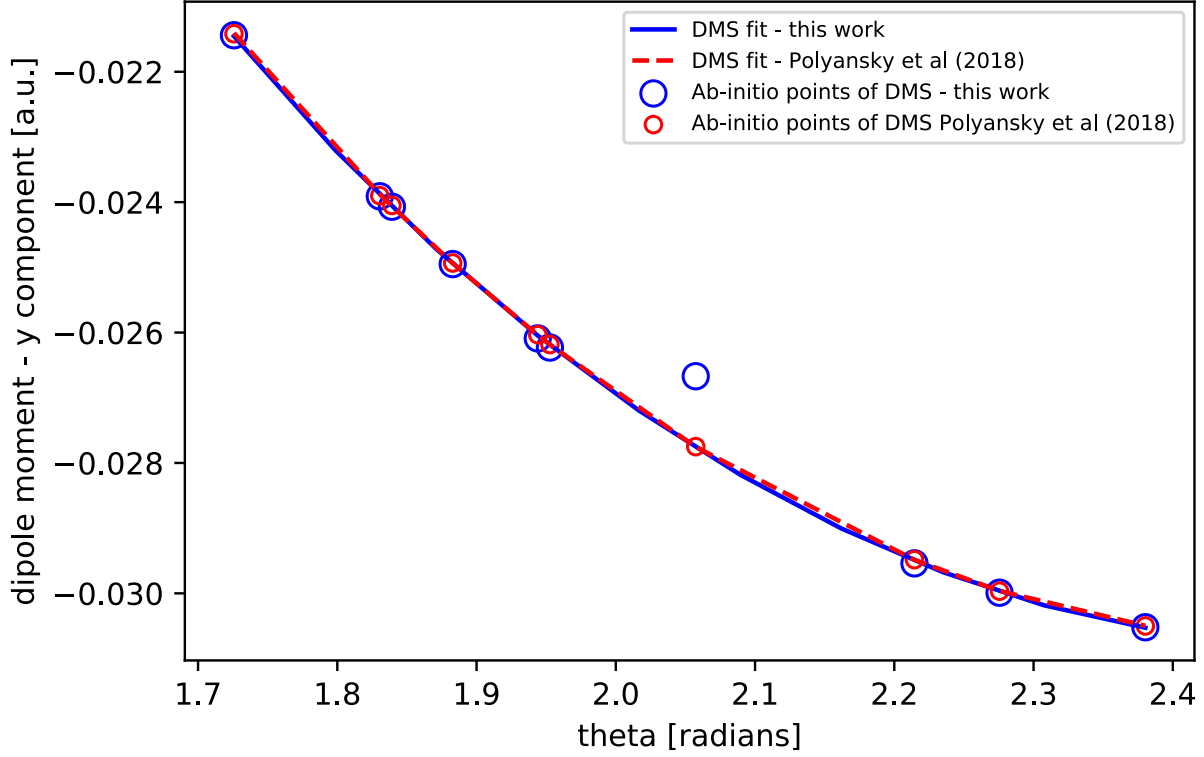


Figure 6.6: One-dimensional slice of the functional fit of DMS-D

Figure 6.6 compares the ab-initio DMS points of this work with that of Polyansky et al [119] along $r_1 = 2.43$ au and $r_2 = 2.38$ au. As can be seen in Figure 6.6, even though one of the dipole moment points seems like an anomaly, the functional fit of the DMS however does not deviate much to account for it. The fitting parameters c_{ijk}^x and c_{ijk}^y of both DMS D and DMS F are provided in Appendix B of this thesis.

6.1.3 Computing and comparing spectra of $^{16}\text{O}_3$

In this section we present the computational details of the nuclear motion calculations of ozone ($^{16}\text{O}_3$). The DVR3D suite of programs [139] are used, with the PES and DMS as inputs, to calculate the rotation-vibrational spectrum of ozone.

The number of DVR grid points in the internal coordinates r_1 , r_2 and θ are given by the directives NPNT2 and NALF respectively in DVR3DRJZ.f90 input. NEVAL allows us to control the number of eigenvalues and eigenvectors calculated by the program in the Coriolis de-coupled step of

the calculation. **MAX3D** defines the final size of Hamiltonian in the first step. The parameters D_e , ω_e and r_e in the Morse-oscillator basis functions (Equations 4.21) are required to be optimised (with respect to the $J = 0$ vibrational band origins) in order to calculate the most accurate eigenvalues and eigenvectors. Usually a choice between nuclear or atomic masses of the nuclei need to be made. Choosing atomic masses approximately accounts for the breakdown of the Born-Oppenheimer approximation. Nuclear masses of ^{16}O were chosen as 15.990526 au because they best replicate results of Polyansky et al [119].

In the second step of the Coriolis-coupled stage of the calculation performed by ROTLEV3B.f90, the parameter **NVIB** determines the number of eigenvectors read in from the first step, to be used as the basis for the complete problem.

Table 6.1: Parameters of DVR3D calculations for ozone ($^{16}\text{O}_3$).

Parameter	Value	Description
ω_e	0.0024	Morse parameter for r_1 and r_2
D_e	0.10	Morse parameter for r_1 and r_2
r_e	2.8	Morse parameter for r_1 and r_2
NPNT2	20	Number of DVR points in r_1 and r_2
NALF	70	Number of DVR points in θ
NEVAL	500	Number of eigenvalues and eigenvectors to be calculated in first step
MAX3D	1500	Dimension of final Hamiltonian matrix
NVIB	$\leq \text{NEVAL}$	Number of eigenvectors to be taken as basis in second step

The values of some of the main parameters used in DVR3D calculations, along with their descriptions, are listed in Table 6.1. As a test of the accuracy of our DVR3D calculations, vibrational band origins of ozone are compared in Table 6.2. Vibrational band origins calculated using DVR3D in this work show good agreement between observed and calculated data in literature as illustrated in Table 6.2.

Table 6.2: Comparison of calculated and observed vibrational band origins of ozone ($^{16}\text{O}_3$) for all vibrational states belonging to the A_1 irrep of $C_{2v}(\text{M})$ CNPI group upto 6766 cm^{-1} . PES1 from Polyansky et al [119] is used as input to DVR3D to compute $E_{cal}(\text{this work})$.

Γ_{vib}	$v_1v_2v_3$ [151]	$E_{obs}[151]$	$v_1v_2v_3[119]$	$E_{obs}[119]$	$E_{cal}(\text{this work})$	$E_{cal}([151])$
A_1	0 1 0	700.931	0 1 0	700.9310	700.9484	700.68
A_1	1 0 0	1103.137	1 0 0	1103.1370	1103.1529	1103.12
A_1	0 2 0	1399.273	0 2 0	1399.2730	1399.2638	1398.76
A_1	1 1 0	1796.262	1 1 0	1796.2620	1796.2790	1796.05
A_1	0 0 2	2057.891	0 0 2	2057.8910	2057.9575	2056.88
A_1	0 3 0	2094.992	0 3 0	2094.9920	2094.9357	2094.23
A_1	2 0 0	2201.155	2 0 0	2201.1550	2201.1446	2200.92
A_1	1 2 0	2486.576	1 2 0	2486.5760	2486.5260	2486.17
A_1	0 1 2	2726.107	0 1 2	2726.1070	2726.1649	2724.77
A_1	-	-	0 4 0	2787.9000	2788.3553	2787.02
A_1	2 1 0	2886.178	2 1 0	2886.1780	2886.1552	2885.80
A_1	1 0 2	3083.703	1 0 2	3083.7030	3083.7066	3083.60
A_1	1 3 0	3173.929	1 3 0	3173.9290	3174.3949	3173.35
A_1	3 0 0	3289.930	3 0 0	3289.9300	3289.9372	3289.51
A_1	0 2 2	3390.918	0 2 2	3390.9180	3390.9525	3389.26
A_1	-	-	0 5 0	3478.4000	3478.0029	3477.09
A_1	2 2 0	3568.070	2 2 0	3568.0700	3568.2500	3567.56
A_1	1 1 2	3739.427	1 1 2	3739.4270	3739.4133	3739.15
A_1	-	-	1 4 0	3858.6000	3856.4159	3857.36
A_1	3 1 0	3966.686	3 1 0	3966.7000	3966.7020	3966.16
A_1	0 0 4	4001.314	0 0 4	4001.3140	4001.3294	4000.53
A_1	-	-	-	-	4052.2261	4050.29
A_1	2 0 2	4141.418	2 0 2	4141.4180	4141.4450	4140.25
A_1	-	-	-	-	4168.2760	4164.36
A_1	-	-	2 3 0	4246.7000	4245.0504	4245.71

A ₁	-	-	4 0 0	4730.3000	4369.9481	4369.24
A ₁	1 2 2	4390.463	1 2 2	4390.5000	4390.3073	4390.02
A ₁	-	-	-	-	4544.6554	4537.85
A ₁	0 1 4	4632.888	0 1 4	4632.8880	4632.7418	4632.17
A ₁	-	-	3 2 0	4643.8000	4643.5973	4642.93
A ₁	-	-	-	-	4711.1791	4707.84
A ₁	2 1 2	4783.461	2 1 2	4783.4610	4783.4149	4782.14
A ₁	-	-	-	-	4848.8607	4848.75
A ₁	1 0 4	4922.572	1 0 4	4922.5720	4923.4104	4919.24
A ₁	-	-	-	-	4924.6799	4923.55
A ₁	-	-	-	-	5036.6625	5035.63
A ₁	-	-	4 1 0	5038.5000	5039.3539	5038.14
A ₁	3 0 2	5172.004	3 0 2	5172.0000	5171.9346	5171.31
A ₁	-	-	-	-	5200.5451	5214.19
A ₁	-	-	0 2 4	5266.9000	5266.0840	5264.50
A ₁	-	-	3 3 0	5310.5000	5310.3863	5309.39
A ₁	-	-	-	-	5362.3920	5361.99
A ₁	-	-	-	-	5418.5872	5417.15
A ₁	-	-	5 0 0	5443.0000	5440.7358	5439.73
A ₁	-	-	-	-	5534.9134	5530.16
A ₁	1 1 4	5540.896	1 1 4	5540.8980	5542.6431	5541.79
A ₁	-	-	-	-	5569.7030	5585.72
A ₁	-	-	-	-	5671.6230	5678.01
A ₁	-	-	4 2 0	5701.6000	5701.0568	5700.92
A ₁	2 0 4	5766.322	2 0 4	5766.3200	5769.0293	5767.71
A ₁	-	-	3 1 2	5812.6000	5814.0879	5813.00
A ₁	-	-	-	-	5889.4587	5885.25
A ₁	-	-	-	-	5900.6490	5889.07

A ₁	-	-	-	-	5960.9751	5970.11
A ₁	-	-	0 0 6	5997.0000	5995.1877	5992.19
A ₁	-	-	-	-	6022.3137	6013.14
A ₁	0 3 4	6046.076	-	-	6044.6956	6044.71
A ₁	5 1 0	6100.216	5 1 0	6100.2100	6099.8934	6099.29
A ₁	1 2 4.1	6154.702	-	-	6155.2569	6155.53
A ₁	-	-	-	-	6205.0842	6204.11
A ₁	-	-	-	-	6212.0518	6208.45
A ₁	-	-	-	-	6254.2238	6239.03
A ₁	1 2 4.2	6343.983	-	-	6344.2465	6319.50
A ₁	-	-	-	-	6349.3311	6343.95
A ₁	4 3 0	6365.264	-	-	6365.9083	6365.96
A ₁	-	-	-	-	6442.2300	6443.32
A ₁	-	-	-	-	6501.8800	6500.75
A ₁	0 4 4	6506.129	-	-	6509.7958	6505.56
A ₁	-	-	-	-	6533.5385	6548.86
A ₁	-	-	-	-	6573.3317	6566.97
A ₁	-	-	-	-	6617.9541	6613.26
A ₁	-	-	-	-	6633.6281	6627.10
A ₁	-	-	-	-	6657.1034	6662.26
A ₁	-	-	-	-	6679.0620	6668.86
A ₁	-	-	-	-	6748.4515	6749.63
A ₁	2 4 2	6764.789	-	-	6766.4177	6765.49

The last column of Table 6.2 shows calculated vibrational band origins from the study of Tyuterev et al [151] which uses a purely ab-initio PES (i.e. not fitted to empirical energy levels). It appears that PES1 from Polyansky et al [119] is in better agreement with observed band origins calculated vibrational band origins from the study of Tyuterev et al [151] because the mean

vibrational energy difference between DVR3D calculations using PES1 (this work) and observed vibrational energies from Tyuterev et al [151] is -0.34 cm^{-1} as compared to 0.50 cm^{-1} for calculations from Tyuterev et al [151].

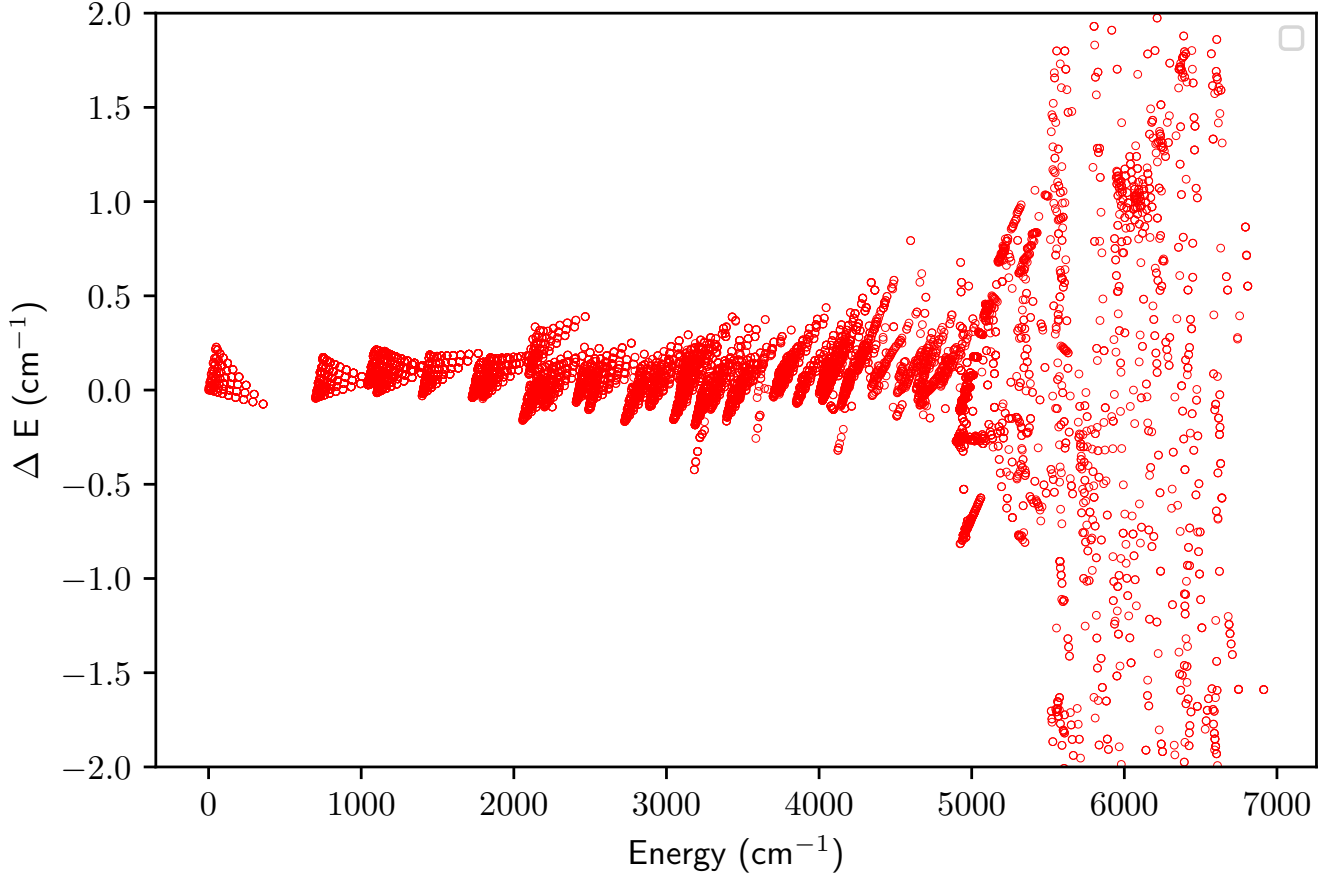


Figure 6.7: Comparison of energy levels of $^{16}\text{O}_3$ computed with DVR3D using the new refined PES (this work) with energy levels taken from the HITRAN database.

Figure 6.7 compares energy levels of $^{16}\text{O}_3$ obtained from DVR3D calculations using the new refined PES (this work) and energy levels from the HITRAN database. Figure 6.7 shows a total of 13344 energy levels being compared with a mean energy difference $\Delta E_{\text{mean}} = -0.00944 \text{ cm}^{-1}$ with standard deviation 0.850 cm^{-1} demonstrating good agreement between both datasets.

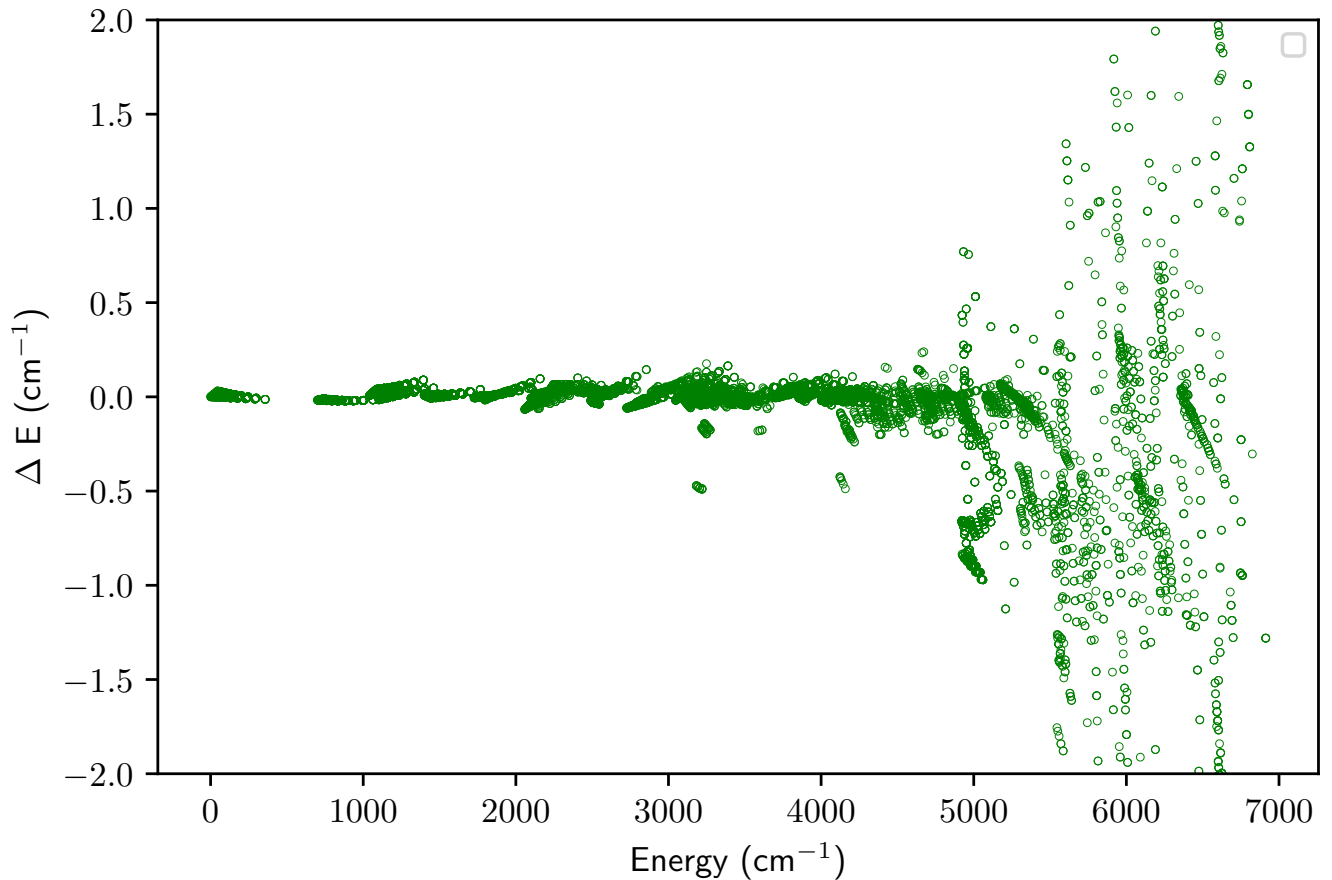


Figure 6.8: Comparison of energy levels of $^{16}\text{O}_3$ computed with DVR3D using the PES of Polyansky et al [119] with energy levels taken from the HITRAN database.

Figure 6.8 compares energy levels of $^{16}\text{O}_3$ obtained from DVR3D calculations using the PES of Polyansky et al [119] and energy levels from the HITRAN database [72]. Figure 6.8 shows a total of 13330 energy levels being compared with a mean energy difference $\Delta E_{mean} = -0.119 \text{ cm}^{-1}$ with standard deviation 0.670 cm^{-1} . The ΔE_{mean} for PES of Polyansky et al [119] is larger than the new refined PES (this work - see Figure 6.7) indicating that the new refined PES could be more accurate. However the standard deviation for the PES of Polyansky et al [119] is smaller than the new refined PES (this work) indicating that the ΔE_{mean} is more narrowly defined in Figure 6.8.

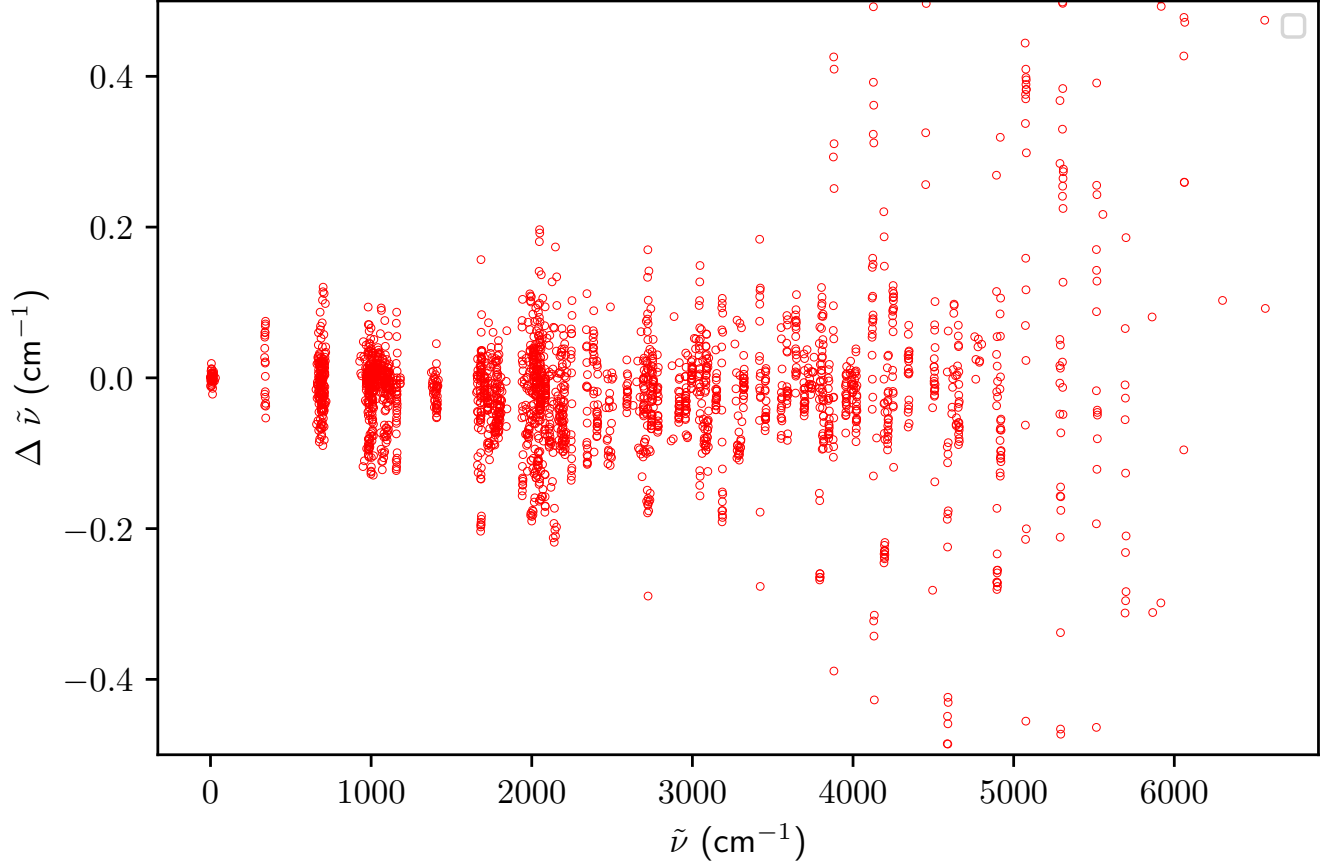


Figure 6.9: Comparison of transition frequencies of $^{16}\text{O}_3$ computed with DVR3D using the new refined PES (this work) with line positions taken from the HITRAN database.

Figure 6.9 compares line positions of $^{16}\text{O}_3$ obtained from DVR3D calculations using the new refined PES (this work) and line position data from the HITRAN database. Figure 6.9 shows a total of 2496 line positions being compared with a mean difference of $\Delta\tilde{\nu}_{mean} = -0.00455 \text{ cm}^{-1}$ with standard deviation 0.285 cm^{-1} .

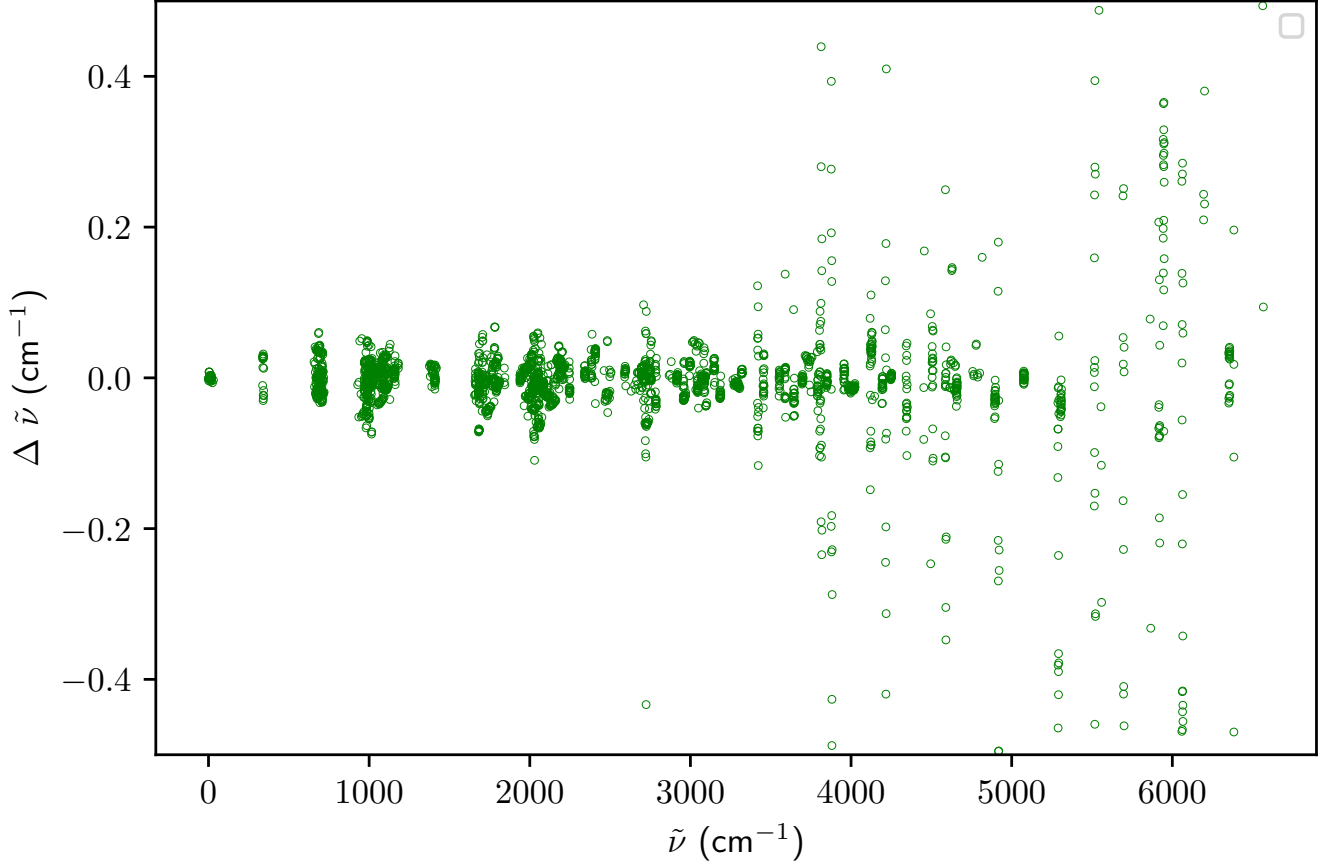


Figure 6.10: Comparison of transition frequencies of $^{16}\text{O}_3$ computed with DVR3D using the PES of Polyansky et al [119] with line positions taken from the HITRAN database.

Figure 6.10 compares line positions of $^{16}\text{O}_3$ obtained from DVR3D calculations using the PES of Polyansky et al [119] and line positions from the HITRAN database. Figure 6.10 shows a total of 2531 line positions being compared with a mean difference of $\Delta\tilde{\nu}_{mean} = -0.0355 \text{ cm}^{-1}$ with standard deviation 0.305 cm^{-1} .

The intensity I (also known as the integrated absorption coefficient) of a ro-vibrational transition in units of $\text{cm}/\text{molecule}$, as expressed in the DVR3D program, is given by the following expression [139]:

$$I(\omega_{if}) = 4.162034 \times 10^{-19} \omega_{if} g_i \frac{e^{\frac{E''}{kT}} - e^{\frac{E'}{kT}}}{Q(T)} S(f - i) \quad (6.13)$$

where ω_{if} is the transition frequency between the initial (i) and final (f) energy levels, g_i is the nuclear spin degeneracy factor, E'' and E' are the energy values of the lower and upper energy levels respectively, k is the so called Boltzmann constant, T is the temperature, $Q(T)$ is the partition

function and $S(f - i)$ is the line strength. If complete knowledge of the energy levels of a system is there, as is often the case with variational nuclear motion calculations where all energy levels of the system can be calculated, then the partition function can be calculated by directly summing over all the energy levels. The formula for the partition function is given by [139]

$$Q(T) = \sum_j \sum_i (2J + 1) g_i e^{\frac{E_j}{kT}} \quad (6.14)$$

The line strength $S(f - i)$ is a function of the transition dipole moment (see Equation 6.15) which itself is dependent on the DMS $\mu(r_1, r_2, \theta)$ and the upper and lower ro-vibrational wavefunctions. The line strength is often given in a condensed form as [24]:

$$S(f - i) = \sum |\langle \Phi'_{ro-vib} | \mu(r_1, r_2, \theta) | \Phi''_{ro-vib} \rangle|^2 \quad (6.15)$$

In the DVR3D program the line strength is given by equation number fifty-five [139] in the DVR3D manual involving the DMS $\mu(r_1, r_2, \theta)_{\alpha\beta\gamma}$ and the wavefunctions $\Phi_{ro-vib}^{\alpha'\beta'\gamma'}$, $\Phi_{ro-vib}^{\alpha''\beta''\gamma''}$ at the grid points α, β, γ .

Transition intensities of $^{16}\text{O}_3$ are computed using the DVR3D program, and compared with values from the HITRAN database. The results of the intensity comparisons are shown in Figures 6.11 and 6.12.

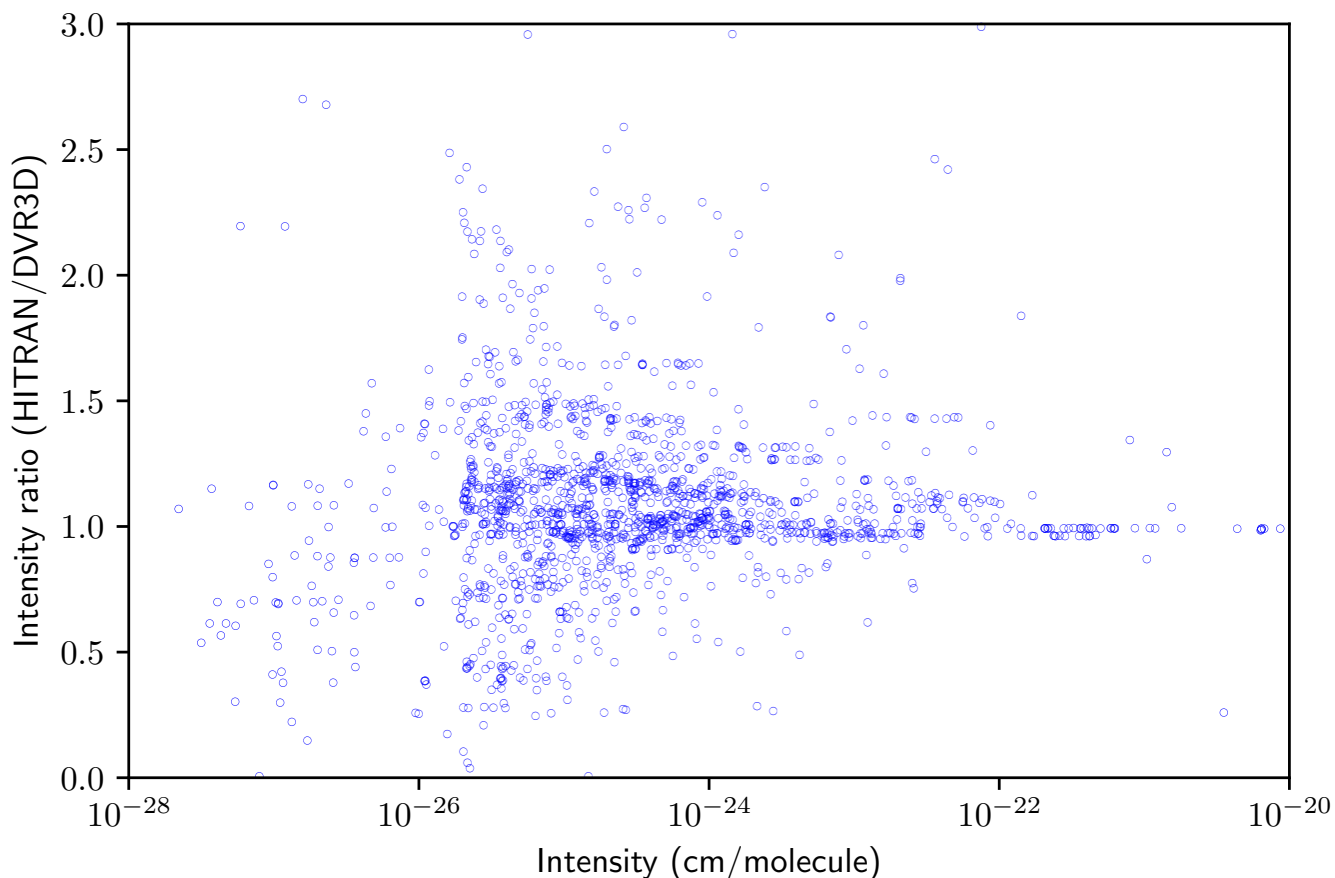


Figure 6.11: Comparison of transition intensities of $^{16}\text{O}_3$ computed with DVR3D using the new refined PES (this work) with intensities taken from the HITRAN database.

Figure 6.11 shows better agreement between DVR3D and HITRAN for strong bands (i.e. transitions with a larger intensity value) as demonstrated by larger deviation of points from intensity ratio = 1.0 for intensity values in the region of 10^{-26} cm/molecule. This highlights the large uncertainty associated with weak transitions (transitions with smaller intensity value). A similar result is obtained in Figure 6.12 for the comparison of intensities using the PES of Polyansky et al [119]. In both Figures 6.11 and 6.12 the same DMS is used (DMS F from this work) to calculate the intensities.

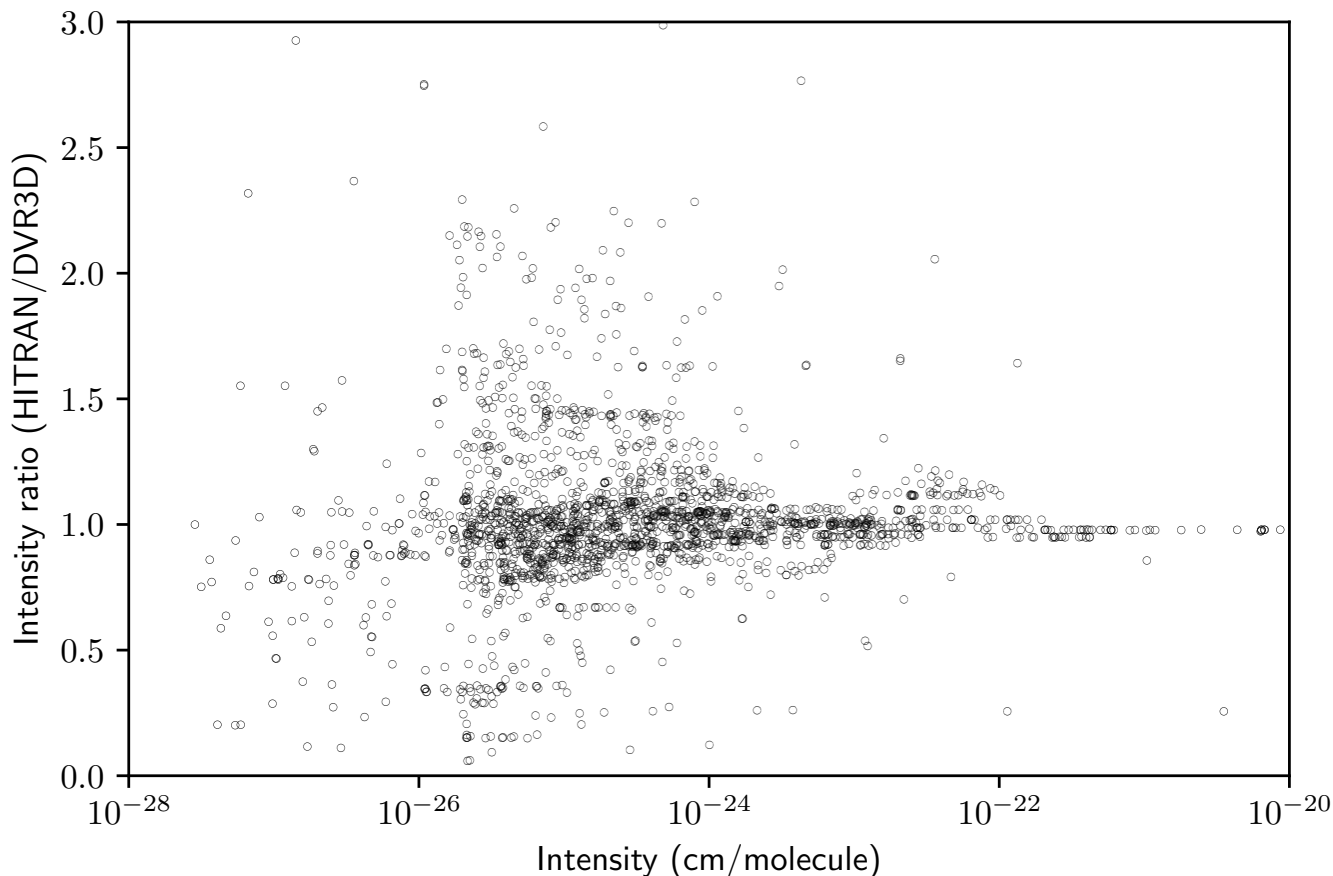


Figure 6.12: Comparison of transition intensities of $^{16}\text{O}_3$ computed with DVR3D using the PES of Polyansky et al with intensities taken from the HITRAN database.

6.1.4 Comparing dipole moment surfaces

Several important studies regarding ro-vibrational transition intensities of $^{16}\text{O}_3$ have been published in recent years [150, 147, 119, 80]. In this section, we compare DMSs published in these studies with those calculated in this work. All DMSs are tested for their accuracy by comparing to high accuracy intensity measurements [79].

Before comparing DMSs for their accuracy, it is important to ensure we have an accurate and reliable nuclear motion model. Towards this end, we have successfully replicated the results of Polyansky et al [119] which are also published in Jacquemart et al [80] as illustrated in Figure 6.13.

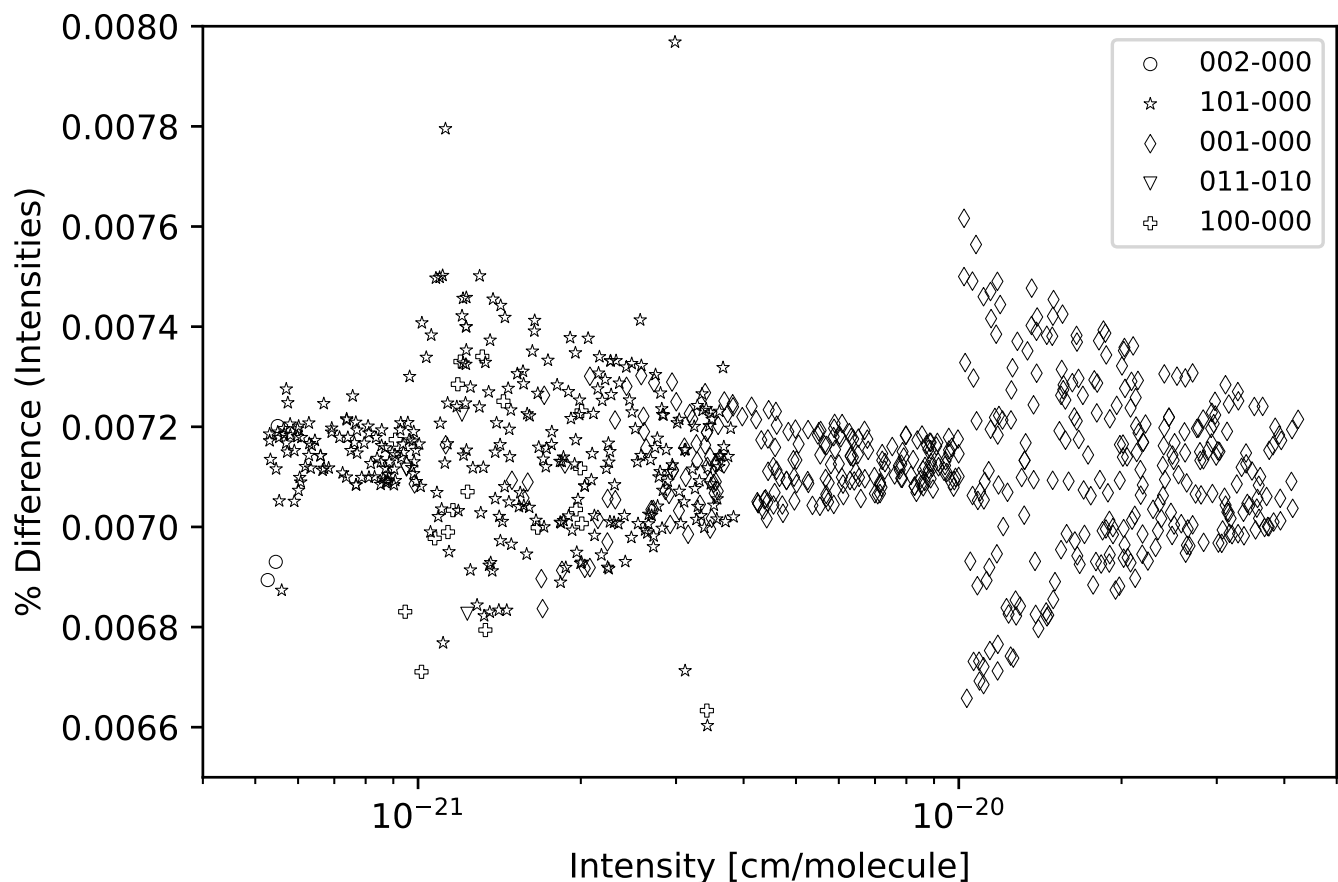


Figure 6.13: Comparison of calculated intensities of $^{16}\text{O}_3$ (this work) with intensities published in literature. The intensities are calculated using the DVR3D program, potential PES1 from Polyansky et al [119], and DMS F2 from Tyuterev et al [150]. The intensities from literature are taken from the published work of Jacquemart et al [80] which also use PES1 and DMS F2 (column of intensities labelled S0). Different shaped markers indicate different vibrational bands. Percentage difference of intensities are calculated using the formula: $\% \text{ Difference} = [(I_{\text{calc}} - I_{S0})/I_{\text{calc}}] \times 100$

Figure 6.13 shows intensity comparisons of our calculations with intensity calculations from Jacquemart et al [80]. The mean % difference of intensities is $7.14 \times 10^{-3} \%$ with a standard deviation of $2.78 \times 10^{-4} \%$. These statistics indicate that our DVR3D calculations are reliable because they reproduce existing intensity calculations in literature [119, 80] with good agreement. A particularly challenging aspect of reproducing existing calculations in literature was the fact that there were discrepancies between values of hyper-parameters of the functional form of some DMSs published, and the values of hyper-parameters actually used in the published calculations.

Having reproduced the existing results in literature with good agreement and therefore having established a reliable nuclear motion model, we now proceed to comparing our DMS D and DMS

F (this work) to intensity measurements and other DMS calculations in literature. The results of these comparisons for $^{16}\text{O}_3$ are shown in Figures 6.14, 6.15, 6.16, 6.17 and Table 6.3. For many DMSs considered from literature, a separate line-list calculation is performed for each (in this work) using the DVR3D program. Table 6.3 provides a summary of all comparisons and details whether a dataset was calculated in this work or taken from literature.

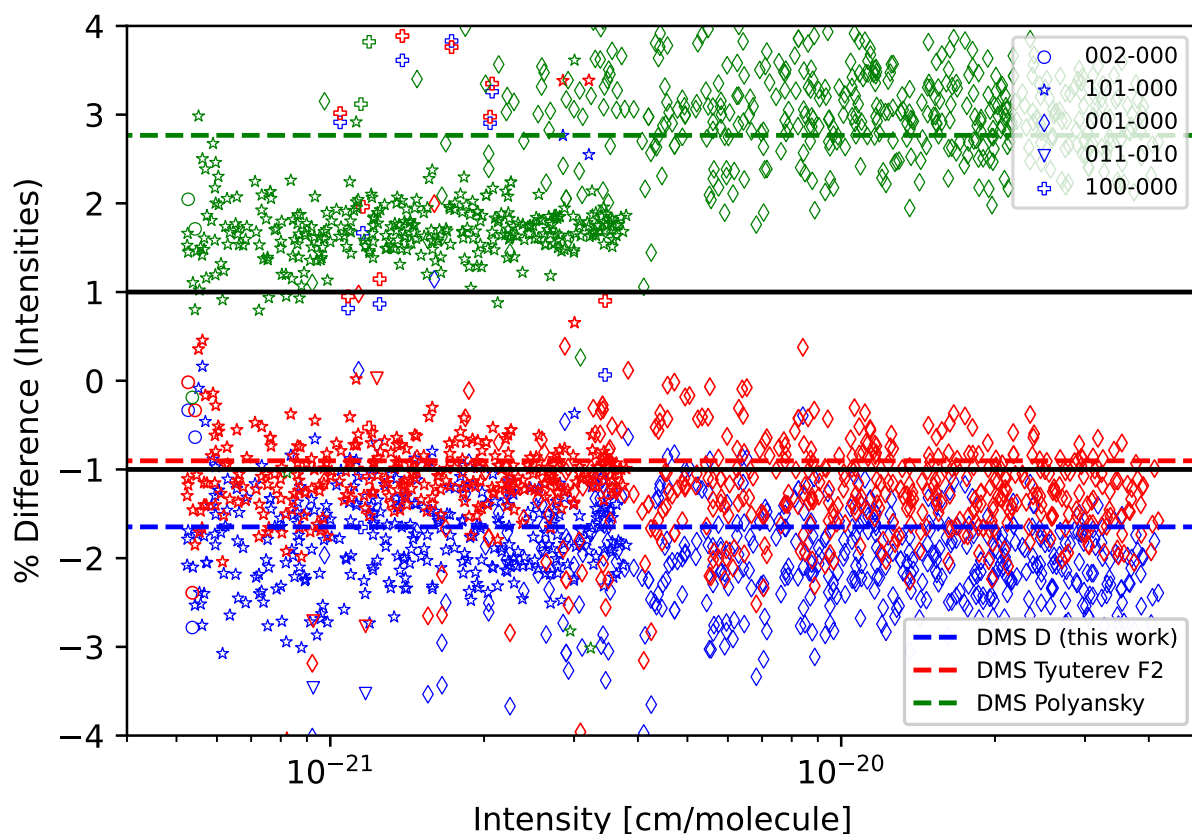


Figure 6.14: Comparison of calculated intensities of $^{16}\text{O}_3$ (from three different dipole moment surfaces) with measured intensities from Jacquemart et al [79] across five strong and weak bands. The three DMSs being compared are: DMS D (this work), DMS F2 (Tyuterev et al [150]) and DMS Polyansky (Polyansky et al [119]). All three sets of calculations use the potential PES1 from Polyansky et al [119]. All calculations are compared against intensity measurements from Jacquemart et al [79]. Different shaped markers indicate different vibrational bands. Dashed horizontal lines indicate mean % difference value for each particular DMS (actual values are given in Table 6.3). The sub 1% region is also visualised using solid horizontal guidelines at $\pm 1\%$.

Figure 6.14 compares intensities of three DMSs against intensity measurements of Jacquemart et al [79]. These intensity measurements of several strong and weak ro-vibrational bands of ozone in the infrared region by Jacquemart et al [79] have a relative standard uncertainty of 1.1×10^{-2} . According to the authors this level of precision has been achieved for the first time [79]. As shown

in Figure 6.14 DMS D (this work) in comparison with DMS Polyansky [119] shows significant improvement in accuracy of intensities across several strong and weak bands. The DMS F2 of Tyuterev et al [150] is the best performing DMS out of the three DMSs being compared in Figure 6.14 across all the five vibrational bands with a mean % difference of -0.90% .

It is also insightful to compare the intensities of weak and strong bands separately as illustrated in Figures 6.15 and Figure 6.16 respectively.

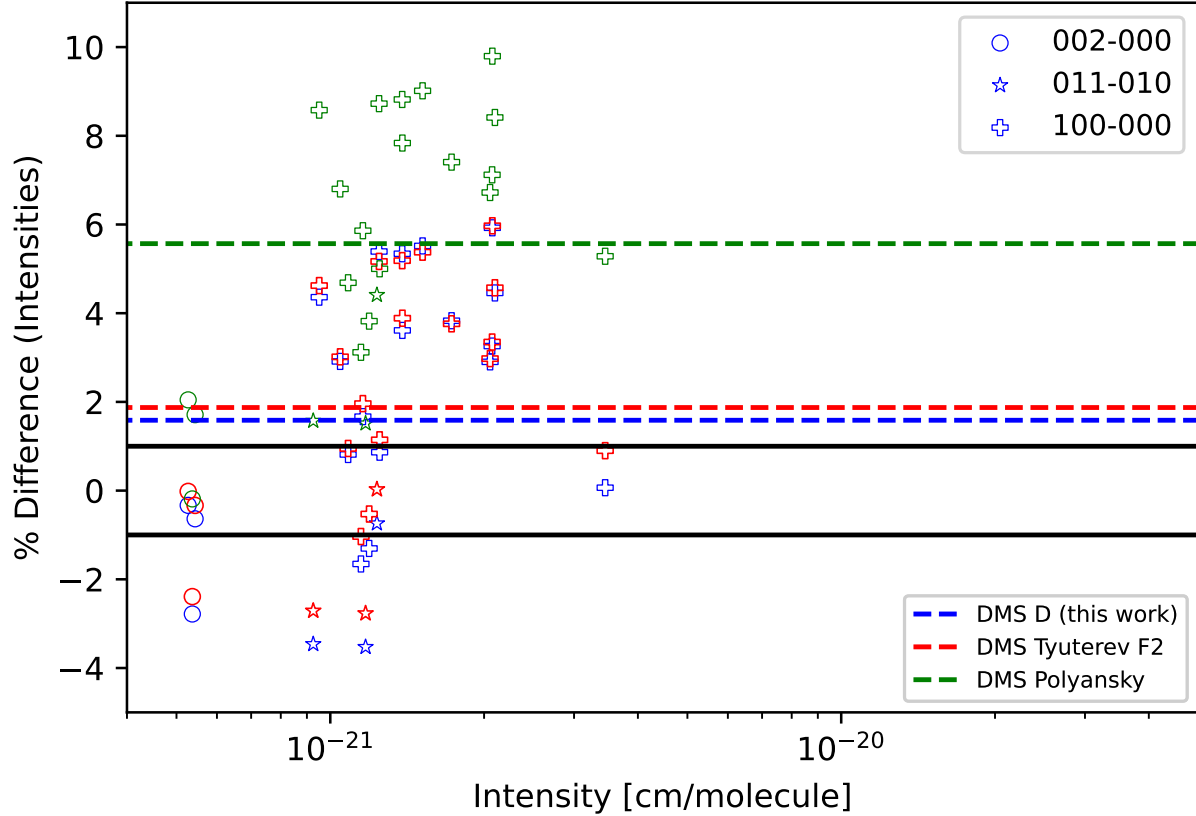


Figure 6.15: Comparison of calculated intensities of $^{16}\text{O}_3$ (from three different dipole moment surfaces) with measured intensities from Jacquemart et al [79] for weak bands only. The three DMSs being compared are: DMS D (this work), DMS F2 (Tyuterev et al [150]) and DMS Polyansky (Polyansky et al [119]). All three sets of calculations use the potential PES1 from Polyansky et al [119]. All calculations are compared against intensity measurements from Jacquemart et al [79]. Different shaped markers indicate different vibrational bands. Dashed horizontal lines indicate mean % difference value for each particular DMS (actual values are given in Table 6.3). The sub 1% region is also visualised using solid horizontal guidelines at $\pm 1\%$.

When considering weak bands only, our comparisons in Figure 6.15 show that (when used with PES1 of Polyansky et al [119]) DMS D (this work) performs better than DMS F2 of Tyuterev et al and DMS Polyansky with a mean % difference of 1.59%. Please see Table 6.3 and Figure 6.15.

When considering strong bands only, our results show that (when used with PES1 of Polyansky et al [119]) DMS F2 of Tyuterev et al [150] performs better than DMS D (this work) and DMS Polyansky with a mean % difference of -1.20% . Please see Table 6.3 Figure 6.16.

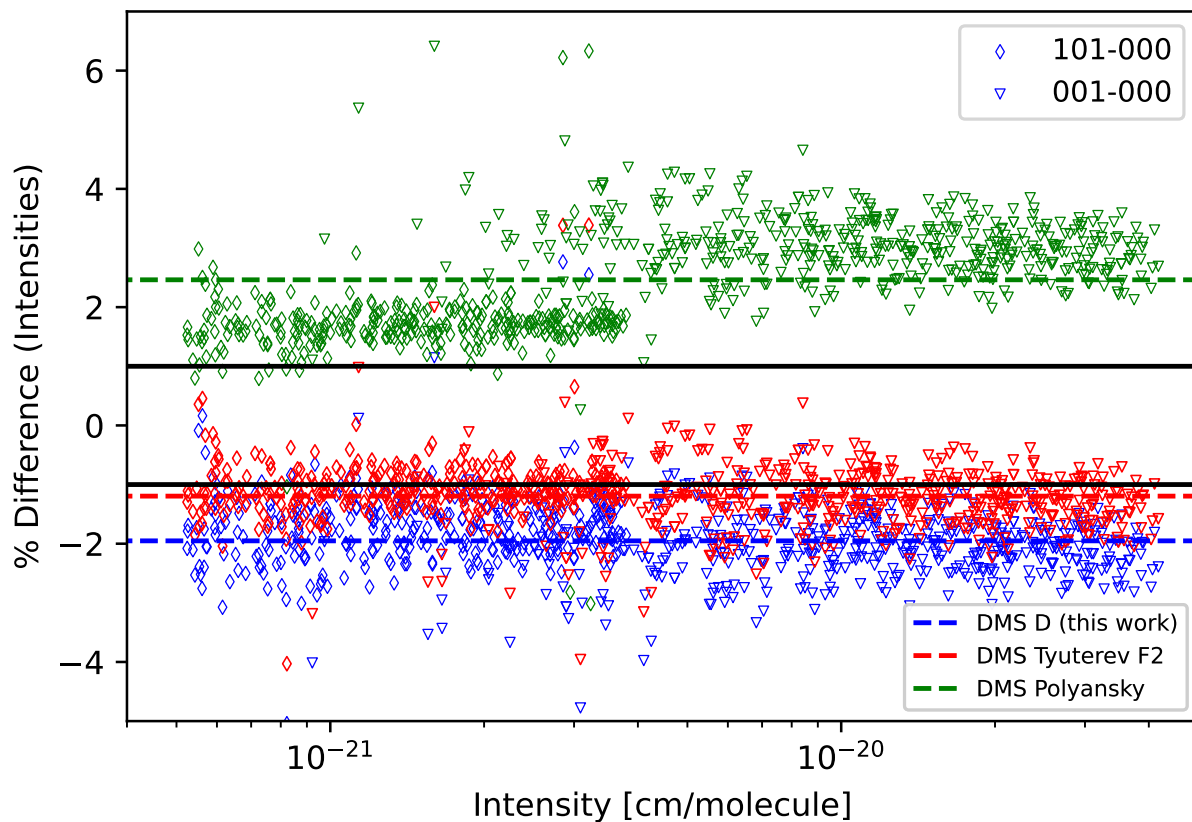


Figure 6.16: Comparison of calculated intensities of $^{16}\text{O}_3$ (from three different dipole moment surfaces) with measured intensities from Jacquemart et al [79] for strong bands only. The three DMSs being compared are: DMS D (this work), DMS F2 (Tyuterev et al [150]) and DMS Polyansky (Polyansky et al [119]). All three sets of calculations use the potential PES1 from Polyansky et al [119]. All calculations are compared against intensity measurements from Jacquemart et al [79]. Different shaped markers indicate different vibrational bands. Dashed horizontal lines indicate mean % difference value for each particular DMS (actual values are given in Table 6.3). The sub 1% region is also visualised using solid horizontal guidelines at $\pm 1\%$.

Figure 6.17 compares nine datasets of calculated and published intensities (from eight different DMSs) with intensity measurements from Jacquemart et al [79], across five strong and weak bands.

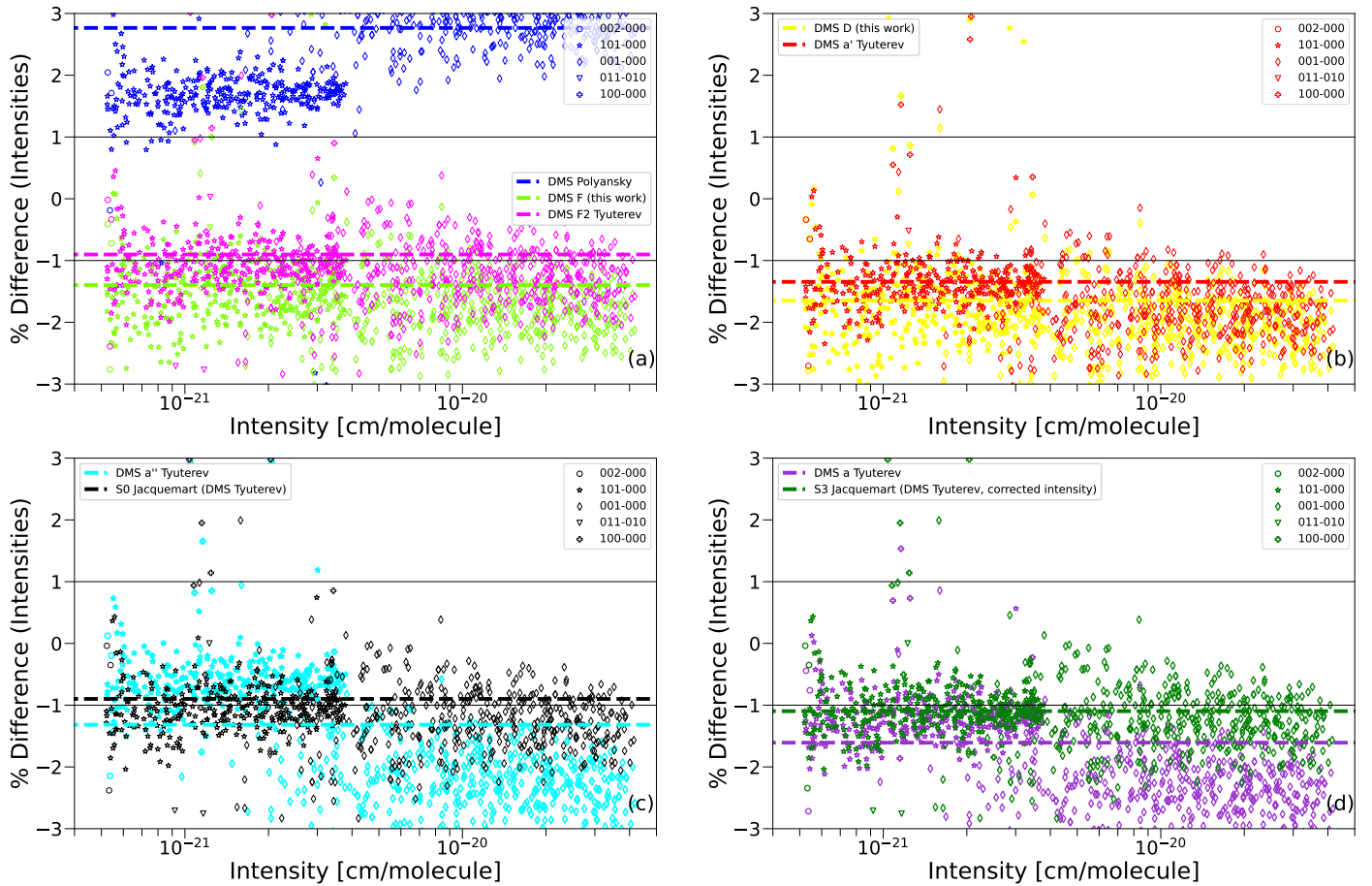


Figure 6.17: Comparison of nine calculated and published intensities of $^{16}\text{O}_3$ (from eight different dipole moment surfaces) with measured intensities from Jacquemart et al [79] across five strong and weak bands. The nine different sets of calculations being compared are: Panel (a) – DMS F (this work), DMS F2 Tyuterev [150], DMS Polyansky [119]. Panel (b) – DMS D (this work), DMS a' Tyuterev [147]. Panel (c) – S0 Jacquemart [80] (DMS Tyuterev [147, 150]), DMS a'' Tyuterev [147]. Panel (d) – S3 Jacquemart [80] (DMS Tyuterev, corrected intensity [147, 150]), DMS a Tyuterev [147]. All nine sets of data use the potential PES1 from Polyansky et al [119]. All calculations are compared against intensity measurements from Jacquemart et al [79]. Different shaped markers indicate different vibrational bands. Dashed horizontal lines indicate mean % difference value for each particular dataset (actual values are given in Table 6.3). The sub 1% region is also visualised using solid horizontal guidelines at $\pm 1\%$.

Table 6.3 compares the performance of DMSs calculated in this work (DMS D and DMS F) against those published in literature, by comparing the mean percentage difference values for each DMS across strong and weak bands.

It is interesting to note that DMS F is better than DMS D in the “strong + weak” and “strong only” categories of vibrational bands. Although DMS F does not properly account for core-valence electron correlation (and DMS D does not account for it at all) we think the results of DMS F

Table 6.3: Summary of DMS comparison statistics. Values of the mean % difference of intensities are shown for all DMSs considered in this work. Potential energy surface PES1 of Polyansky et al [119] is used in combination with all DMSs listed in this table. All calculated values are compared against measurements of Jacquemart et al [79].

Type of vibrational band	[1]*	[2]*	[3]*	[4]*	[5]*	[6]*	[7]*	[8]**	[9]**
Strong + Weak	-0.90	2.77	-1.65	-1.40	-1.61	-1.35	-1.32	-0.90	-1.10
Strong only	-1.20	2.46	-1.95	-1.70	-	-	-	-	-
Weak only	1.87	5.57	1.59	1.70	-	-	-	-	-
[1]*: DMS F2 Tyuterev [150]									
[2]*: DMS Polyansky [119]									
[3]*: DMS D (this work)									
[4]*: DMS F (this work)									
[5]*: DMS a Tyuterev [147]									
[6]*: DMS a' Tyuterev [147]									
[7]*: DMS a'' Tyuterev [147]									
[8]**: S0 Jacquemart [80] (DMS Tyuterev [147, 150])									
[9]**: S3 Jacquemart [80] (DMS Tyuterev, corrected intensity [147, 150])									
Strong bands: [(101-000),(001-000)]									
Weak bands: [(002-000),(011-010),(100-000)]									
* indicates a dataset calculated in this work using DVR3D.									
** indicates a dataset taken from literature.									

are better in these categories because it uses the aug-cc-pwCV5Z basis set which has additional variational parameters by virtue of the 'w' in the basis set used to calculate the DMS.

From Table 6.3 we can see that for all DMSs considered in this work, the only DMS to achieve sub 1% accuracy (when used with PES1 of Polyansky et al [119]) is the DMS F2 of Tyuterev et al [150] across five strong and weak bands in comparison with intensity measurements of Jacquemart et al [79].

6.2 Normal intensity distribution

Recent work carried out by Medvedev et al [102] (in which I am a co-author) concerns the empirical determination of the so called 'normal' intensity distribution (NID) in triatomic molecules using line list calculations. NID is analytically derived and already well established for high overtone vibrational transitions in diatomic molecules [101]. High overtones transitions refer to transitions in which the vibrational quantum number changes by an amount more than one, where the transition is occurring from the ground vibrational ($v = 0$) state. The intensity of these transitions is very weak however they are important in atmospheric studies because some regions of the spectrum are dominated by them e.g. the $7\nu_1$ band of water dominates the region around 450 nm and will be used in the TEMPO mission [164]. Hence this study [102] attempts to 'observe' the manifestation of NID and its properties in triatomic systems.

The NID states that for a vibrational transition, between two upper and lower states E' and E'' respectively, the logarithm of the oscillator strength (or intensity or Einstein A coefficient) is a linear function of the square root of the upper state energy. Another concept that originates from the theory of NID, is that of the 'effect of the repulsive wall' (ERW henceforth) on the NID. According to ERW, the rate of decrease of vibrational band intensity up to dissociation is dependent primarily on the steepness of the repulsive branch of the potential energy surface, and marginally on the dipole moment surface [100]. Hence the intensities of the weak high overtone transitions are mostly affected by changes in the steepness of the repulsive wall, at geometries far away from the equilibrium.

To test whether weak high overtone transitions follow the NID in ozone, line list calculations

are run for $J = 0 - 1$ and $J = 1 - 0$ transitions for all vibrational states of ozone up to dissociation. Ozone is special in the sense that it is a weakly bound triatomic molecule with a low dissociation threshold (around 8500 cm^{-1}) compared to other triatomic molecules like water or carbon dioxide. This means that the number of high upper energy transitions is low, compared to other triatomic molecules, and therefore it is interesting to see whether the NIDL has room to manifest in ozone.

We use the PES and DMS of Polyansky et al [119] for our $J = 0 - 1$ line list calculations and plot the logarithm of the Einstein A coefficients against upper level energy scaled with $\omega = 1580 \text{ cm}^{-1}$ which is the fundamental frequency of ground state oxygen O_2 . We assigned normal mode quantum numbers to our transitions based on the HITRAN line list. We also assigned local mode quantum numbers to our transitions according to the paper by [165]. Labelling transitions close to dissociation is a challenging task due to the density of vibrational states being very high.

Our results are illustrated in our paper [102] and Figure 6.18 which shows logarithm of the Einstein A coefficients of all transitions occurring from the fixed lower ground vibrational state with $E = 700.95 \text{ cm}^{-1}$. A line of best fit is fitted to the scatter in Figure 6.18 to illustrate the orders of magnitude drop in intensities as overtones of higher vibrational quanta increases.

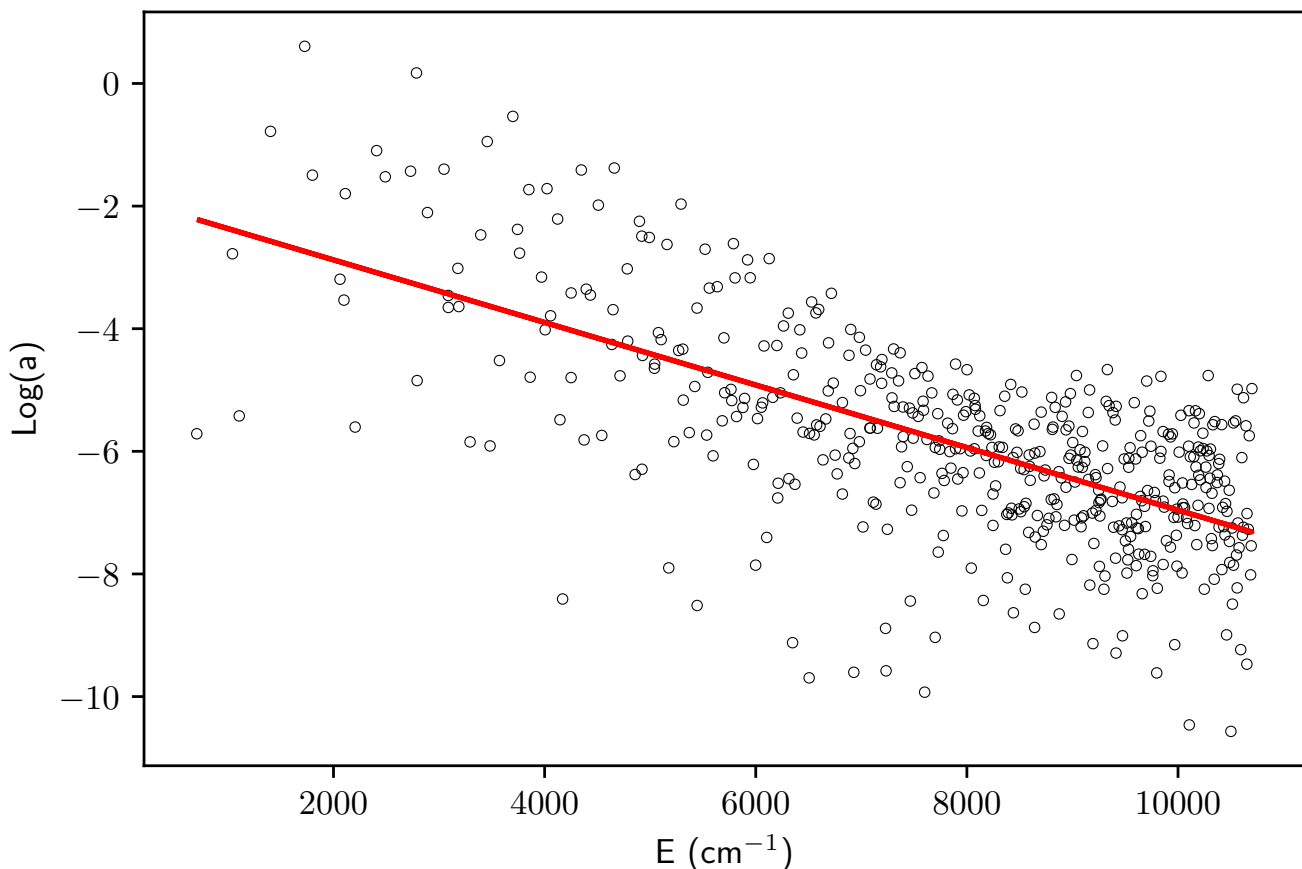


Figure 6.18: Plot of the logarithm of Einstein A coefficients against upper energy, from the fixed lower state vibrational energy level $1\nu_2(010)$ with energy $E = 700.95 \text{ cm}^{-1}$. The fitted red line has a slope of -0.000510 cm .

The work presented in this section also has consequences for accurate intensity calculations of ozone because it suggests that an accurate PES (especially around the repulsive wall) could improve the accuracy of intensities, especially for weak intensity bands which often tend to struggle in accuracy. Perhaps making the grid of geometries denser around the repulsive wall of the potential in electronic structure calculations will aid in getting more accurate intensities. Towards achieving more accurate intensities of weak bands, the following chapter on MARVEL is indeed aimed at not only improving the accuracy of line positions, but also line intensities via accurate wavefunctions by fitting a highly accurate PES to the MARVEL energy levels.

6.3 Rotation vibration spectrum of $^{18}\text{O}_3$ isotopologue

A new potential energy surface for the $^{18}\text{O}_3$ isotopologue of ozone is constructed using an empirically refined potential of $^{16}\text{O}_3$ and the diagonal Born Oppenheimer correction (DBOC) surfaces of the $^{16}\text{O}_3$ and $^{18}\text{O}_3$ isotopologues. The surfaces are tested by using them as input into the nuclear motion program DVR3D to calculate ro-vibrational energies of the $^{18}\text{O}_3$ isotopologue. The energy levels, line positions and intensities of $^{18}\text{O}_3$ are compared to values in the SMPO database.

6.3.1 Diagonal Born Oppenheimer correction and PES construction

Under the Born Oppenheimer approximation the molecular wavefunction is written as the product of electronic and nuclear parts:

$$\Phi \approx \Phi_{el}(\mathbf{r}_i; \mathbf{r}_\alpha) \Phi_N(\mathbf{r}_\alpha) \quad (6.16)$$

Upon substituting this equation into the full Schrodinger equation we arrive at the following equation:

$$\begin{aligned} & \frac{-\hbar^2}{2} \sum_{\alpha} \Phi_N \frac{\nabla_{\alpha}^2 \Phi_{el}}{M_{\alpha}} - \hbar^2 \sum_{\alpha} \frac{(\nabla_{\alpha} \Phi_{el}) \cdot (\nabla_{\alpha} \Phi_N)}{M_{\alpha}} - \frac{-\hbar^2}{2} \sum_{\alpha} \Phi_{el} \frac{\nabla_{\alpha}^2 \Phi_N}{M_{\alpha}} \\ & - \frac{-\hbar^2}{2m_e} \sum_i \Phi_N \nabla_i^2 \Phi_{el} + V \Phi_{el} \Phi_N = E \Phi_{el} \Phi_N \end{aligned} \quad (6.17)$$

If we neglect the first two terms of Equation 6.17 entirely, the equation separates into the electronic and nuclear Schrodinger equations respectively. However, when we account for the first two terms of Equation 6.17 we are considering the effect of the breakdown of the Born Oppenheimer approximation. The diagonal correction is considered a first or leading order correction to the Born Oppenheimer approximation[24].

The DBOC correction ΔE_{DBOC} is given by

$$\Delta E_{DBOC} = \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(0)} \rangle \quad (6.18)$$

where in the perturbation theory treatment $\hat{H}^{(1)}$ (comprising the first two terms from Equation 6.17) is the perturbation and ΔE_{DBOC} is the first order correction to the energy. The zeroth order wavefunctions $\psi^{(0)}$ and energies $E^{(0)}$ are the Born-Oppenheimer wavefunctions and energies respectively.

The ΔE_{DBOC} values as a function of r_1 , r_2 and θ are computed in a study by Tajti et al [131] and also subsequently fitted to the functional form of Equation 6.19:

$$\begin{aligned} \Delta V_{DBOC}(r_1, r_2, \alpha) = & [C - a \times \exp \left(-b \left(\left(\frac{r_1}{r_e} - 1 \right)^2 + \left(\frac{r_2}{r_e} - 1 \right)^2 + \left(\frac{\cos \alpha}{\cos \alpha_e} - 1 \right)^2 \right) \right) \\ & - \sum_{0 \leq i+j+k \leq n} d_{ijk} [(r_1 - r_e)^i (r_2 - r_e)^j + (r_1 - r_e)^j (r_2 - r_e)^i] (\cos \alpha - \cos \alpha_e)^k] \quad (6.19) \\ & \times \exp \left(-c \left(\left(\frac{r_1}{r_e} - 1 \right)^2 + \left(\frac{r_2}{r_e} - 1 \right)^2 + \left(\frac{\cos \alpha}{\cos \alpha_e} - 1 \right)^2 \right) \right) \end{aligned}$$

The parameters of $\Delta V_{DBOC}(r_1, r_2, \alpha)$ for several symmetric isotopologues of ozone are provided in the supplementary information to the Tajti et al [131] article. Using these parameters the $\Delta V_{DBOC}(r_1, r_2, \alpha)$ function for different isotopologues can be constructed as shown in Figure 6.19.

We construct the potential energy surface of $^{18}\text{O}_3$ (V^{888}) by the following formula 6.20:

$$V^{888} = [V_{\text{empirical}}^{666} - \Delta V_{DBOC}^{666}] + \Delta V_{DBOC}^{888} \quad (6.20)$$

$V_{\text{empirical}}^{666}$ represents the empirically refined potential energy surface of $^{16}\text{O}_3$ which automatically accounts for the breakdown of Born Oppenheimer approximation because it is fitted to empirical energy levels. This is why V_{DBOC}^{666} is subtracted from $V_{\text{empirical}}^{666}$ so that the correct DBOC (V_{DBOC}^{888}) can be added. The DBOC function introduces mass dependence into the PES of the isotopologues.

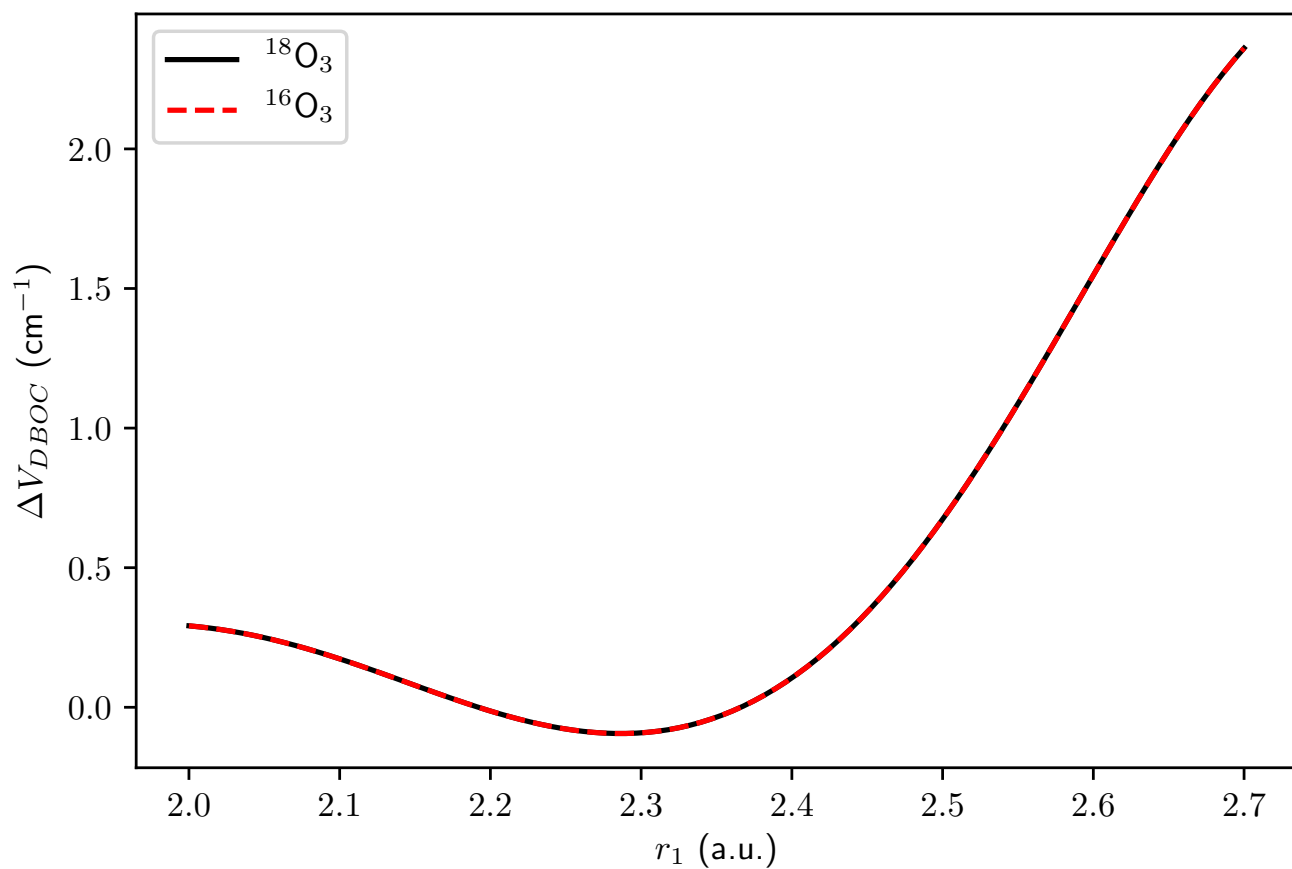


Figure 6.19: One dimensional slice of the $\Delta V_{DBOC}(r_1, r_2, \alpha)$ DBOC function for $^{16}\text{O}_3$ and $^{18}\text{O}_3$

The precision of the PES of $^{18}\text{O}_3$ is tested by using it as input into DVR3D to calculate energy levels, line positions and transition intensities.

6.3.2 Computing and comparing the spectra of $^{18}\text{O}_3$

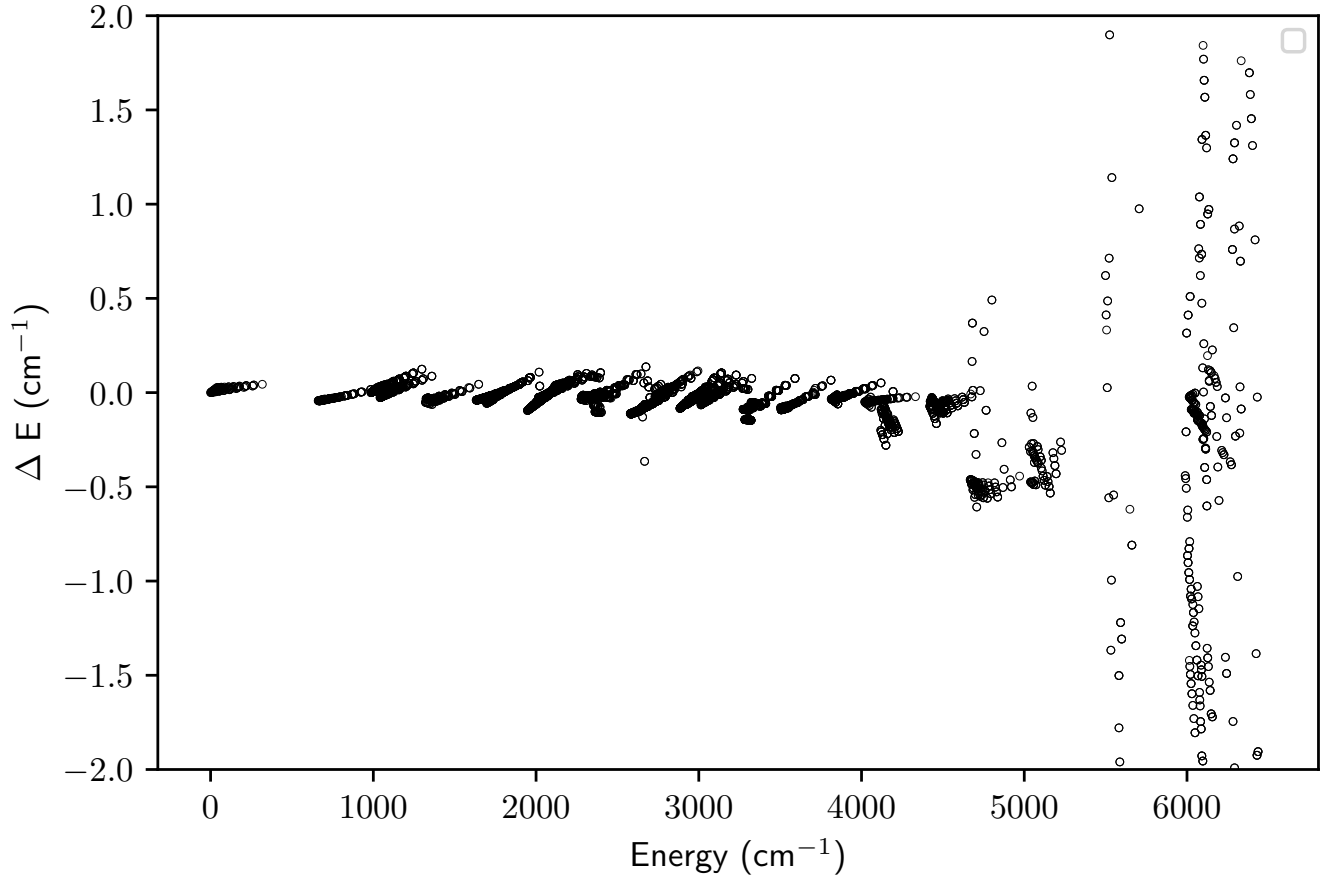


Figure 6.20: Comparison of variationally calculated energy levels (DVR3D) of $^{18}\text{O}_3$ with energies taken from the SMPO_20d line list [3]

Figure 6.20 shows the comparison of variationally calculated energies of $^{18}\text{O}_3$ (using the DVR3D program and the PES for $^{18}\text{O}_3$ constructed in this work) with energy levels in the SMPO_20d line list obtained from the S&MPO database [3]. In Figure 6.20 6742 energy levels are compared with a mean energy difference ΔE_{mean} of -0.127 cm^{-1} and standard deviation 0.775 cm^{-1} . ΔE in Figure 6.20 becomes large at high energies because the PES is not refined to empirical energies in the high energy region.

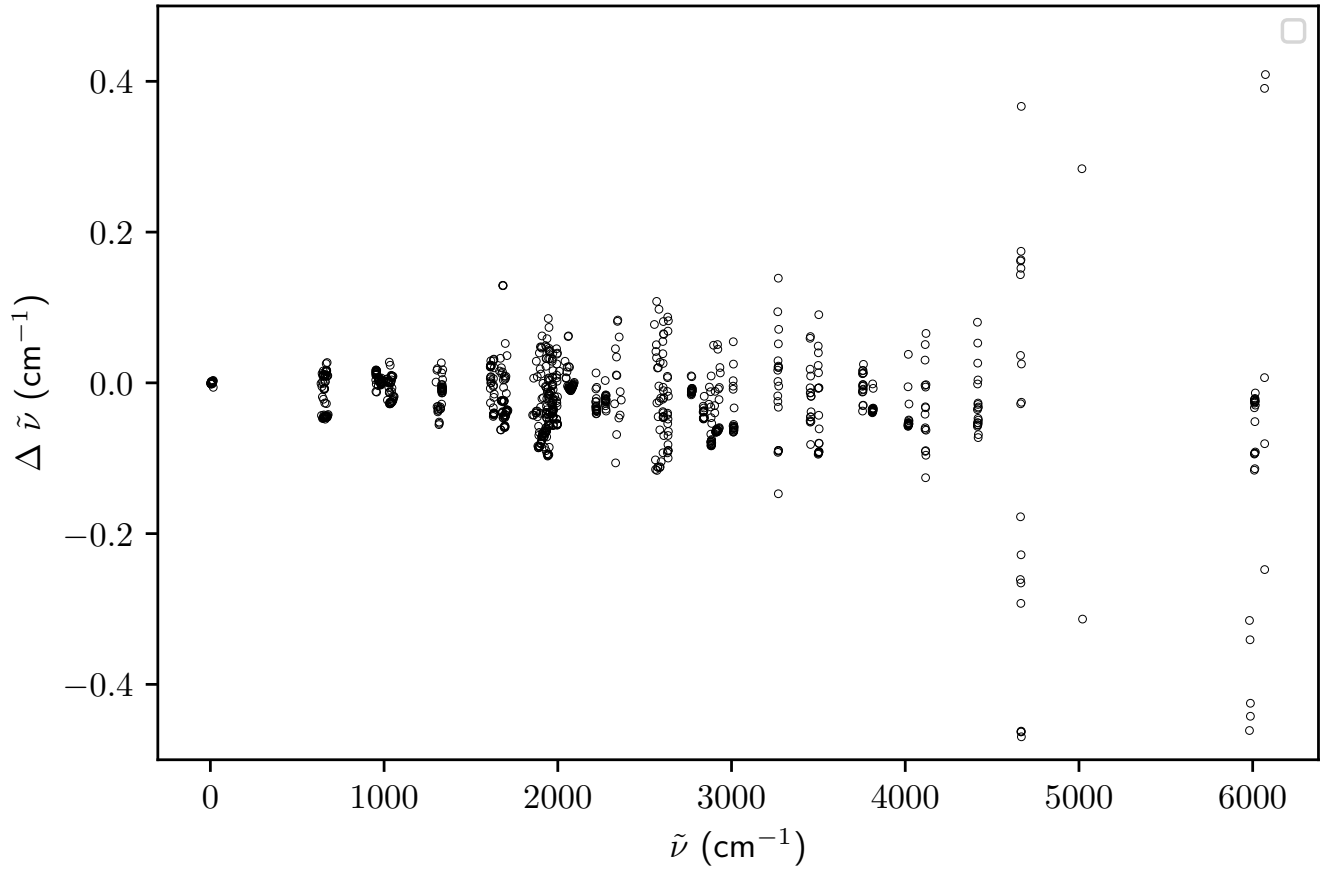


Figure 6.21: Comparison of variationally calculated line positions (DVR3D) of $^{18}\text{O}_3$ with SMPO_20d line list.

Line positions of 966 transitions are compared in Figure 6.21 with a mean line position difference $\Delta\tilde{\nu}_{mean}$ of -0.060 cm^{-1} and standard deviation 0.283 cm^{-1} showing good agreement between variationally calculated energies of $^{18}\text{O}_3$ (using DVR3D and the PES for $^{18}\text{O}_3$ constructed in this work) with those in the S&MPO database [3].

Figure 6.22 compares variationally calculated transition intensities of $^{18}\text{O}_3$ (using DVR3D, the PES for $^{18}\text{O}_3$ constructed in this work and DMS D computed in this work) with data in the S&MPO database [3] showing good agreement.

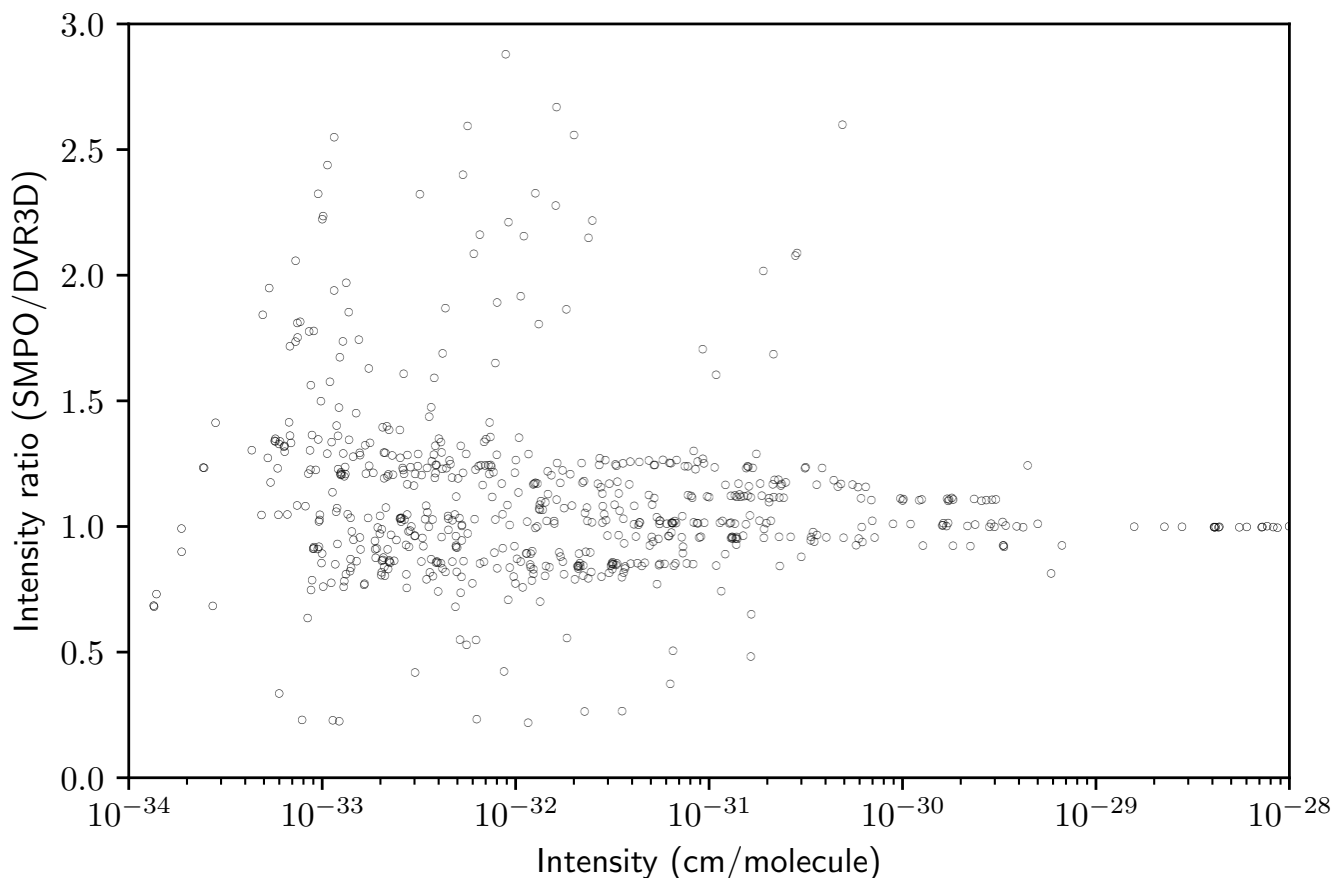


Figure 6.22: Comparison of variationally calculated line intensities (DVR3D) of $^{18}\text{O}_3$ with SMPO_20d line list.

6.4 Summary

Ab-initio electronic structure calculations of a new potential energy surface (PES) of $^{16}\text{O}_3$ are performed in MOLPRO. A new empirically refined PES is fitted to the ab-initio points for $^{16}\text{O}_3$ and compared against existing PES from literature. The new empirically refined PES (this work) shows excellent agreement with existing data compilations such as HITRAN database.

Two new DMSs are calculated using MOLPRO (DMS D and DMS F) and tested against high accuracy intensity measurements showing excellent agreement. Eight different DMSs are tested (either by performing ro-vibrational transition intensity calculations using DVR3D or obtaining intensities data from literature) by comparing to high accuracy intensity measurements. Our analysis shows DMS F2 Tyuterev from Tyuterev et al [150] is the only DMS to reach sub 1% accuracy out

of all DMSs considered in this work.

A new PES for $^{18}\text{O}_3$ isotopologue is constructed using DBOC functions. Energy levels, line positions and intensities show excellent agreement with data on the S&MPO database.

Chapter 7

Conclusion

This thesis tackles the challenge of developing a theoretical spectroscopic model of ozone, which can predict molecular properties (transition intensities, energies and line positions) accurate enough to resolve the ozone atmospheric retrieval problem. The theoretical framework and methodologies we employ to build the model and make predictions include ab-initio quantum mechanics, semi-empirical methods and numerical simulation. Because the model predictions need to be validated against accurate experiments, this accurate model building exercise is particularly arduous for ozone for which historically there has not been a benchmark for certain molecular properties such as experimental transition intensities, although recent measurements [79, 81] are very encouraging in terms of achieving sufficient accuracy to be able to validate theoretical models.

Towards improving the accuracy of our theoretical model, MARVEL analysis of measured ozone line positions is performed, to obtain empirical MARVEL energy levels of ozone ($^{16}\text{O}_3$). The results of this work are published in our paper [153]. See Chapter 5 of this thesis and our paper [153] for further details.

Electronic structure calculations of the potential energy surface (PES) and dipole moment surfaces (DMSs) of the ground electronic state X^1A' of the main isotopologue of ozone ($^{16}\text{O}_3$) are performed using the MOLPRO program [157]. As a result, a new empirically refined PES for $^{16}\text{O}_3$ and two new DMSs are calculated (the fitting parameters of all three surfaces are provided in Appendix A and Appendix B of this thesis). All three surfaces have been extensively tested, compared and validated in this thesis (see Chapter 6). The resulting energy levels and line positions from

the new refined PES (this work) show good agreement with data in the HITRAN database. The resulting intensities from DMSs calculated in this work (called DMS D and DMS F) are tested against high accuracy intensity measurements showing good agreement. Other DMSs published in literature are also compared to high accuracy intensity measurements with DMS F2 from the study of Tyuterev et al [150] the only DMS (out of all DMSs considered in this thesis) to register a sub 1% mean % difference of intensities. The comparisons of all DMSs considered in this work are summarised in Table 6.3. See Chapter 6 of this thesis for further computational and comparison details.

We perform a study of overtone transitions of ozone ($^{16}\text{O}_3$) and find that these transitions are sensitive to the repulsive wall region of the potential energy surface, at small inter-nuclear geometries, far from equilibrium geometry. This work indicates that to achieve better accuracy of weak bands, more attention should be paid to smaller inter-nuclear geometries in ab-initio electronic structure calculations, perhaps by using a denser grid of geometries in that region. The results of this work are published in our paper [102]. See Chapter 6 of this thesis for further details.

A new PES for $^{18}\text{O}_3$ isotopologue of ozone is constructed using diagonal Born Oppenheimer correction functions. The resulting line list of $^{18}\text{O}_3$ is compared with existing data in literature showing good agreement (see Chapter 6 of this thesis).

Future work will include developing a spectroscopic model for the excited electronic states of ozone and calculating line lists involving these excited electronic states.

Appendix A

Table 7.1: Non zero fitting parameters d_{ijk} of the new refined potential energy surface of Equation 6.2(this work).

d_{ijk}	$ixjxk$	d_{ijk}	$ixjxk$	d_{ijk}	$ixjxk$
-0.730479419366D+03	0x0x0	+0.509602522457D+06	2x0x2	+0.146814194024D+06	1x2x1
-0.209315428360D+04	0x0x1	-0.189792152626D+07	2x2x0	+0.101484036976D+06	0x6x0
+0.955726946981D+04	1x0x0	-0.271979311201D+06	3x0x1	-0.102347071407D+05	1x0x3
+0.627283101686D+05	0x0x2	+0.115240649592D+06	4x0x0	+0.266954035714D+05	0x0x6
-0.410380564138D+05	0x2x0	+0.239173222689D+05	0x0x5		
-0.446665396462D+05	1x0x1	+0.117735912153D+06	0x2x3		
+0.103140763190D+06	2x0x0	-0.540935353436D+06	0x4x1		
-0.243145356799D+04	0x0x3	-0.156570928779D+05	1x0x4		
+0.559502337561D+05	0x2x1	-0.964801390724D+06	1x2x2		
-0.211063504578D+06	1x0x2	+0.338470086697D+07	1x4x0		
+0.171805705239D+06	1x2x0	-0.321272879678D+06	2x0x3		
+0.160031204642D+06	2x0x1	+0.209690115670D+06	2x2x1		
-0.378426806873D+05	3x0x0	-0.875215711457D+05	3x0x2		
+0.591922976654D+05	0x0x4	+0.223790390346D+07	3x2x0		
+0.209399613437D+06	0x2x2	-0.270515746825D+06	4x0x1		
-0.755068754515D+06	0x4x0	+0.624738913041D+06	5x0x0		

Appendix B

Table 7.2: Non zero fitting parameters of DMS D of Equation 6.8 for the μ_x component (this work).

c_{ijk}^x	$ixjxk$	c_{ijk}^x	$ixjxk$	c_{ijk}^x	$ixjxk$
-1.140493154110E+00	0x1x0	-2.888763699320E-01	2x1x4	-4.985202675190E+00	1x5x0
5.620090389260E-01	0x1x1	-1.394160211720E+01	2x3x2	-2.075390922230E-01	1x1x4
2.501401924570E+00	1x1x0	6.274839976890E+00	2x5x0	1.166747160100E+01	1x3x2
6.298995685340E-01	0x1x2	-5.620727109940E-01	3x1x3	-2.298793618480E+00	2x1x3
-3.242199739850E+00	0x3x0	1.747581386180E+01	3x3x1	-1.500753344420E+01	2x3x1
5.501070260850E-01	1x1x1	5.405165216430E-01	4x1x2	2.520560596300E+00	3x1x2
-1.591314980680E+00	2x1x0	9.810848708370E+00	4x3x0	-1.351402368760E+01	3x3x0
9.349940598660E-02	0x1x3	3.650707341130E-01	5x1x1	-2.870183233870E-01	4x1x1
-9.183237424350E-01	0x3x1	5.590473519870E+00	1x5x1	-1.242896551370E+00	5x1x0
-4.675370324160E-01	1x1x2	3.430843313160E+00	1x3x0	5.086094293670E-01	0x1x6
-1.399921953020E+00	2x1x1	-7.735149222520E-01	3x1x0	-1.474088009000E+00	0x3x4
2.802992291200E-01	0x1x4	-4.010769317600E+00	0x3x2	7.262381096060E+00	0x5x2
7.968181204860E+00	0x5x0	1.662097746390E+00	1x1x3	-9.608302080430E+00	0x7x0
1.248003010020E+00	1x3x1	-1.827175662270E+00	2x1x2	-8.282758168980E-01	1x1x5
2.944877085120E+00	2x3x0	4.744987586630E-01	3x1x1	-1.401518596730E+00	1x3x3
1.992327919780E+00	4x1x0	3.329621355380E-01	0x1x5		
-1.860691687010E+00	0x3x3	-3.380775577860E-01	0x5x1		

Table 7.3: Non zero fitting parameters of DMS D of Equation 6.9 for the μ_y component (this work).

c_{ijk}^y	$ixjxk$	c_{ijk}^y	$ixjxk$	c_{ijk}^y	$ixjxk$
-1.140493154110E+00	0x1x0	-3.380775577860E-01	0x5x1	-2.075390922230E-01	1x1x4
5.620090389260E-01	0x1x1	1.166747160100E+01	1x3x2		
2.501401924570E+00	1x1x0	-2.298793618480E+00	2x1x3		
6.298995685340E-01	0x1x2	2.520560596300E+00	3x1x2		
-3.242199739850E+00	0x3x0	-2.870183233870E-01	4x1x1		
5.501070260850E-01	1x1x1	5.086094293670E-01	0x1x6		
-1.591314980680E+00	2x1x0	7.262381096060E+00	0x5x2		
9.349940598660E-02	0x1x3	-8.282758168980E-01	1x1x5		
-9.183237424350E-01	0x3x1	5.590473519870E+00	1x5x1		
-4.675370324160E-01	1x1x2	-1.394160211720E+01	2x3x2		
3.430843313160E+00	1x3x0	-5.620727109940E-01	3x1x3		
-1.399921953020E+00	2x1x1	5.405165216430E-01	4x1x2		
-7.735149222520E-01	3x1x0	3.650707341130E-01	5x1x1		
2.802992291200E-01	0x1x4	9.810848708370E+00	4x3x0		
-4.010769317600E+00	0x3x2	1.747581386180E+01	3x3x1		
7.968181204860E+00	0x5x0	6.274839976890E+00	2x5x0		
1.662097746390E+00	1x1x3	-2.888763699320E-01	2x1x4		
1.248003010020E+00	1x3x1	-1.401518596730E+00	1x3x3		
-1.827175662270E+00	2x1x2	-9.608302080430E+00	0x7x0		
2.944877085120E+00	2x3x0	-1.474088009000E+00	0x3x4		
4.744987586630E-01	3x1x1	-1.242896551370E+00	5x1x0		
1.992327919780E+00	4x1x0	-1.351402368760E+01	3x3x0		
3.329621355380E-01	0x1x5	-1.500753344420E+01	2x3x1		
-1.860691687010E+00	0x3x3	-4.985202675190E+00	1x5x0		

Table 7.4: Non zero fitting parameters of DMS F of Equation 6.8 for the μ_x component (this work).

c_{ijk}^x	$ixjxk$	c_{ijk}^x	$ixjxk$	c_{ijk}^x	$ixjxk$
-2.151605385740E-01	0x0x0	-8.988314959210E-01	3x0x2	3.893023702260E+00	3x2x0
-2.923004388720E-01	0x0x1	1.664314428960E+00	0x2x4	9.902707741140E-02	0x4x2
3.052674470110E-01	1x0x0	-7.810905874920E-01	0x6x0	2.134569905910E-01	1x2x3
1.145800097630E-01	0x0x2	2.481912853120E+00	1x4x1	1.010543364040E+01	2x2x2
-4.945849092730E-01	0x2x0	-6.633714316720E+00	2x4x0	-7.121621440350E-01	3x0x3
2.379094589280E-01	1x0x1	6.488440322560E+00	4x0x2		
1.994582044650E-01	0x0x3	8.661240995150E+00	6x0x0		
-1.758640330780E-01	0x2x1	-6.059280448010E-01	0x6x1		
4.100162673010E-01	1x2x0	2.714485503820E+00	1x4x2		
4.714227029840E-01	2x0x1	-3.061519436680E-01	2x2x3		
-1.350439099980E-01	3x0x0	-7.599354081520E-01	3x0x4		
-2.851891893400E-01	0x2x2	4.694070894350E+00	3x4x0		
-3.000634958590E-02	0x4x0	2.028693144750E-01	4x0x3		
1.094913030100E+00	1x2x1	1.074920583010E+00	5x2x0		
-5.866138810520E-01	2x0x2	-1.099662568100E+01	7x0x0		
-5.355861227360E-01	2x2x0	6.299966824440E-01	6x0x1		
-4.822316563180E-01	3x0x1	-5.144806792730E+00	5x0x2		
-9.255109070620E-01	4x0x0	1.319402757220E+00	4x2x1		
1.838287294260E-02	0x2x3	-2.079569516210E+01	3x2x2		
-4.947190063060E-01	0x4x1	-1.951031192560E+00	2x4x1		
-6.655115680510E-01	1x2x2	-4.255597437180E-01	1x6x0		
3.766312421690E+00	1x4x0	-1.444167982670E+00	1x2x4		
3.421392387840E-02	2x0x3	1.512261308950E-01	0x2x5		
-2.194048611560E+00	2x2x1	-6.056992017120E+00	4x2x0		

Table 7.5: Non zero fitting parameters of DMS F of Equation 6.9 for the μ_y component (this work).

c_{ijk}^y	$ixjxk$	c_{ijk}^y	$ixjxk$
-1.140655675700E+00	0x1x0	1.201914594430E+01	1x3x2
5.607321075680E-01	0x1x1	-2.199890340390E+00	2x1x3
2.501622587980E+00	1x1x0	3.384499424040E+00	3x1x2
6.320626277080E-01	0x1x2	-3.986742364120E-01	4x1x1
-3.219173717420E+00	0x3x0	-1.528342570260E+00	0x3x4
5.528169504070E-01	1x1x1	-9.545817451630E+00	0x7x0
-1.563773023910E+00	2x1x0	5.818659170880E+00	1x5x1
1.356186864020E-01	0x1x3	2.476560207810E+00	2x5x0
-9.151082790340E-01	0x3x1	1.790190883310E+01	3x3x1
-5.142993695500E-01	1x1x2	6.607521965180E+00	4x3x0
3.366413875490E+00	1x3x0	8.004019699190E-01	5x1x1
-1.393686894350E+00	2x1x1	-1.168839761340E+00	4x1x2
-8.100177259490E-01	3x1x0	-6.060156855440E-01	3x1x3
3.101925797860E-01	0x1x4	-1.451912203300E+01	2x3x2
-4.042884428910E+00	0x3x2	-1.523749388540E+00	1x3x3
7.681799598770E+00	0x5x0	7.439175835980E+00	0x5x2
1.568177995030E+00	1x1x3	-6.887403238040E-01	5x1x0
1.210964857800E+00	1x3x1	-9.910468036420E+00	3x3x0
-1.890060659300E+00	2x1x2	-1.532079526700E+01	2x3x1
2.085266637770E+00	2x3x0	-2.899427288150E+00	1x5x0
4.680495893720E-01	3x1x1		
1.709079797630E+00	4x1x0		
-1.889512986800E+00	0x3x3		
-2.936846415440E-01	0x5x1		

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