

ExoMol line lists – LXVIII. Rotation–vibration–electronic spectroscopy of potassium hydride (KH)

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ABSTRACT

Comprehensive line lists for three potassium hydride (KH) isotopologues, ^{39}KH , ^{40}KH , and ^{41}KH , applicable at high temperatures are presented. *Ab initio* potential energy curves (PECs), non-adiabatic couplings (NACs), spin-orbit curves, electronic angular momentum curves, and (transition) dipole moment curves ((T)DMCs) are generated for the $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$, $C^1\Sigma^+$, $a^3\Sigma^+$, $c^3\Sigma^+$, and $b^3\Pi$ states of KH using the MRCI method. Empirical energy levels are determined for the $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$ states using the MARVEL (Measured Active Rotation Vibration Energy Levels) procedure, and are used to refine the corresponding *ab initio* PECs of $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$. These PECs and (T)DMCs are used to calculate energies, Einstein *A* coefficients, lifetimes and partition functions up to 10 000 K covering wavenumbers below $40\,000\text{ cm}^{-1}$ ($\geq 250\text{ nm}$) and rotational excitations with $J \leq 130$. Calculated energies and state lifetimes are generally in good agreement with experimental values. Emission to unbound $X^1\Sigma^+$ states contributes significantly to lifetimes of $A^1\Sigma^+$ rovibronic states. This study should facilitate detections of KH in exoplanet and stellar atmospheres. The Khan line lists are available from the ExoMol data base at www.exomol.com.

Key words: molecular data – opacity – planets and satellites: atmospheres – stars: atmospheres – ISM: molecules.

1 INTRODUCTION

Potassium hydride (KH) is a molecule of interest in astrophysical sources, particularly in the study of exoplanetary atmospheres. The spectra of cool stars are known to be dominated by molecular absorption, with metal hydrides accounting for a significant portion. As the atmospheres of hot Jupiters are similar to those of cool stars, it is reasonable to expect that metal hydrides will represent a sizeable fraction of the planet's atmospheric composition. This is supported by recent detections of Chromium Hydride (CrH) in the atmosphere of WASP-31b (L. Flagg et al. 2023). Theoretical investigations into atmospheric molecular abundances suggest K bearing species to be the most abundant of the Group Ia elements within the temperature range 1000–5000 K, with KH predicted to be the most abundant K bearing species at temperatures representative of ultrahot Jupiters ($T > 2000\text{ K}$) (T. Tsuji 1973). In practice, K and Na often occur together; T. Rivlin et al. (2015) computed a line list for NaH. This line list has allowed modelling of NaH spectra and opacity contribution in cool stars (H. R. A. Jones et al. 2023; Y. P. Lyubchik et al. 2022). NaH is found to be important in the radiative zones in the molecular hydrogen envelopes of Jupiter and Saturn (L. Siebenaler et al. 2025), where KH is also likely to be important but has yet to be considered due to the lack of a suitable line list. Similarly it has been suggested that NaH may play an important role in thermal inversion in hot Jupiter exoplanets (S. Gandhi & N. Madhusudhan 2019). Recently there has been a tentative detection of NaH

in exoplanet HAT-P-70b (B. Guo et al. 2026). These studies all suggest that a KH line list similar to that provided by ExoMol for NaH by T. Rivlin et al. (2015) should be an important addition to the database.

KH could also serve a role in characterizing the atmospheres of smaller terrestrial planets. Theoretical studies into the atmospheric composition of ultra-hot rocky planets as a function of increasing H pressure show that a substantial proportion of volatiles are extracted from surface magma with only a small addition of H to the atmosphere (S. Charnoz et al. 2023). This results in a significant fraction of the atmosphere being composed of H bearing metal species, including KH, thereby increasing their susceptibility to atmospheric escape processes and depleting their presence in the planet's composition. The depletion of K could have a number of effects on the planet's evolution, especially considering the majority of a planet's early internal heat budget is governed by the radioactive decay of ^{40}K (V. Murthy, W. van Westrenen & Y. Fei 2003; C. O'Neill, A. Jellinek & A. Lenardic 2007). Hence, the detection of KH can provide useful information regarding a planet's environment and evolution, underscoring the need for an accurate spectroscopic line list.

A comprehensive review of early experimental studies of KH was performed by W. C. Stwalley, W. T. Zemke & S. C. Yang (1991). The experiments included in this review primarily cover transitions between the $X^1\Sigma^+$ and $A^1\Sigma^+$ states. A study by N. N. Haese, D.-J. Liu & R. S. Altman (1984) covered transitions within low lying vibrational levels of the $X^1\Sigma^+$ state, with more recent studies analysing pure rotational transitions within the $X^1\Sigma^+$ state (H. Odashima et al. 1995; T. Okabayashi & M. Tanimoto 2000; M. A. Brewster & L. M. Ziurys 2001). Investigations into

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higher excited states and radiative lifetimes are scant, with a single study investigating transitions involving the $B^1\Pi$ state (A.-Y. Lee & W.-T. Luh 2009), and a single experimental study reporting radiative lifetimes for the $A^1\Sigma^+$ state ($v = 5, 7, 10, 13, 17, 19, 22$; M. Giroud & O. Nedelec 1982).

A number of theoretical investigations have been performed, with D. Watson, R. Stewart & A. Dalgarno (1976) deriving excitation energies and oscillator strengths for transitions from the $X^1\Sigma^+$ state to excited $^1\Sigma^+$ and $^1\Pi$ states. R. W. Numrich & D. G. Truhlar (1975) used a one-electron pseudopotential method to develop potential energy curves (PECs) for the $^1\Sigma^+$ states ($X-D$), $^3\Sigma^+$ states ($a-d$), $B^1\Pi$ state and $^3\Pi$ states ($b-c$), although their estimates for dissociation energy and bond lengths are not in agreement with experimental data for the $X^1\Sigma^+$ state.

Improvements were made by H. S. Lee, Y. S. Lee & G. H. Jeung (2000) who generated PECs for the lowest ten $^1\Sigma^+$ and seven $^3\Sigma^+$ states. Extensive calculations have also been performed by N. Khelifi, B. Oujia & F. X. Gadea (2002), presenting adiabatic and diabatic PECs for $^1\Sigma^+$ states ($X-I$) along with curves for $^3\Sigma^+$ states ($a-i$), and adiabatic PECs for $^1\Pi$, $^3\Pi$, $^1\Delta$, and $^3\Delta$ states. Their results for bond distances and dissociation energies are in agreement with experimental data for $X^1\Sigma^+$ and $A^1\Sigma^+$ states, noting that the parameter for hydrogen electron affinity was particularly important for correcting bond distance estimates in the $A^1\Sigma^+$ state. Comparisons for higher excited states cannot be made due to the lack of experimental data, but predictions from their *ab initio* calculations are in agreement with those of H. S. Lee et al. (2000).

Theoretical investigations into dipole and radiative properties have also been performed by S. R. Langhoff, C. W. Bauschlicher & H. Partridge (1986), reporting dipole moment functions, vibrationally averaged dipole moments, Einstein A coefficients and radiative lifetimes for purely vibrational transitions in the $X^1\Sigma^+$ state ($v \leq 9$). J. J. Camacho et al. (1998) provide transition probabilities between the $X^1\Sigma^+$ state ($v' = 0 - 23, J' = 5, 7$) and $A^1\Sigma^+$ state ($v' = 7, J' = 6$), with their theoretical relative intensities showing good agreement with experiment. N. Khelifi et al. (2002) present permanent dipole moments for the eight lowest lying $^1\Sigma$ and $^3\Sigma$ states as a function of internuclear distance. They also report adiabatic and diabatic transition dipole moments for $X-A$, $X-C$, $A-C$, and $C-D$ singlet transitions (N. Khelifi et al. 2002), as well as radiative transition probabilities for $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ and $C^1\Sigma^+ \rightarrow X^1\Sigma^+$ transitions from $0 \leq v' \leq 35$ and $0 \leq v' \leq 55$, respectively (N. Khelifi et al. 2007).

In this work, a systematic analysis of the available experimental transition data for ^{39}KH has been performed, and an empirical set of energy levels has been derived. These energy levels are obtained using the MARVEL (Measured Active Rotational Vibrational Energy Levels) procedure (T. Furtenbacher, A. G. Császár & J. Tennyson 2007; T. Furtenbacher & A. G. Császár 2012) by inverting the experimental transition data available in the literature (G. M. Almy & C. D. Hause 1932; N. N. Haese et al. 1984; H. Odashima et al. 1995; T. Okabayashi & M. Tanimoto 2000; M. A. Brewster & L. M. Ziurys 2001; A.-Y. Lee & W.-T. Luh 2009) to obtain a self-consistent set of energy levels. These energy levels are used to refine *ab initio* PECs of $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$ which are used in conjunction with *ab initio* dipole moment curves (DMCs) and transition dipole moment curves (TDMCs) to construct molecular line lists for ^{39}KH , ^{40}KH , and ^{41}KH covering transitions between the lowest four singlet electronic states X , A , B and C . The underlying theory and methods will be presented in the next sections, followed

by a discussion of the resulting line lists, lifetimes and partition functions.

2 METHOD

A full description of the scope and methodology of the ExoMol project is provided by J. Tennyson & S. N. Yurchenko (2012), with a short description provided here. Briefly, *ab initio* calculations are performed to determine PECs, couplings, and (T)DMCs. Once the PECs have been determined, solutions to the Schrödinger equation for nuclear motion can be used to calculate rovibronic energies and wavefunctions. These wavefunctions are then used in conjunction with the DMCs to calculate intensities, which combined with the rovibronic energies result in the molecular line list.

In this study, the program DUO (S. N. Yurchenko et al. 2016) is used to solve systems of coupled Schrödinger equations for KH covering the four lowest singlet electronic states $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$, and $C^1\Sigma^+$ up to $40\,000\text{ cm}^{-1}$ enabling interactions between electronic states to be accounted for. DUO initially solves the Schrödinger equations on a fixed radial grid for $J = 0$ for each electronic state independently yielding a set of vibrational eigenfunctions that serve as a vibrational basis for subsequent calculations. DUO then constructs rovibronic Hamiltonian matrices for each J in question which incorporates PECs, coupling terms, Born–Oppenheimer breakdown terms etc. forming the so-called spectroscopic model. These matrices are diagonalized to obtain fully coupled, variational nuclear-motion eigenvalues and eigenstates of the diatomic molecule; these are then used in the intensity (line list) calculations.

Generally, line intensities calculated using *ab initio* (T)DMCs will be reasonably accurate, however, *ab initio* PECs computed using state-of-the-art electronic structure methods usually cannot deliver rovibronic energies with sufficient accuracy. Hence, PECs are refined empirically by least-squares fitting to experimentally determined energies. During the fitting procedure, it is important to ensure that the shapes of the PECs remain realistic, hence an additional constraint was imposed which requires that the refined PECs remain similar in shape to the *ab initio* PECs.

Experimental energies can be obtained from spectroscopic studies which report transition wavenumbers or frequencies between various rovibronic states of a given molecule. The MARVEL procedure outlined by T. Furtenbacher et al. (2007) provides a comprehensive protocol for extracting energy levels from experimental data, and DUO is used to fit analytical PECs to these determined energies. Once the PECs have been refined, these are used in DUO to generate files containing energy levels, transition energies and Einstein A values, which are subsequently used in the programme EXOCROSS (S. N. Yurchenko, A. F. Al-Refaie & J. Tennyson 2018) to calculate lifetimes and cross sections at different temperatures, as well as the partition function. This process enables line lists to be constructed which are accurate across a range of temperatures.

By default, DUO treats the system as fully bound. However, it can also generate continuum spectra as bound–unbound transitions, see M. Pezzella, S. N. Yurchenko & J. Tennyson (2021). This can be achieved by analysing wavefunctions at large bond lengths and selecting unbound states, i.e. non-vanishing at the asymptote. This can be monitored either via an integrated density at large distances or via an expectation value of the molecular bond length (T. Uhlíková et al. 2025). A

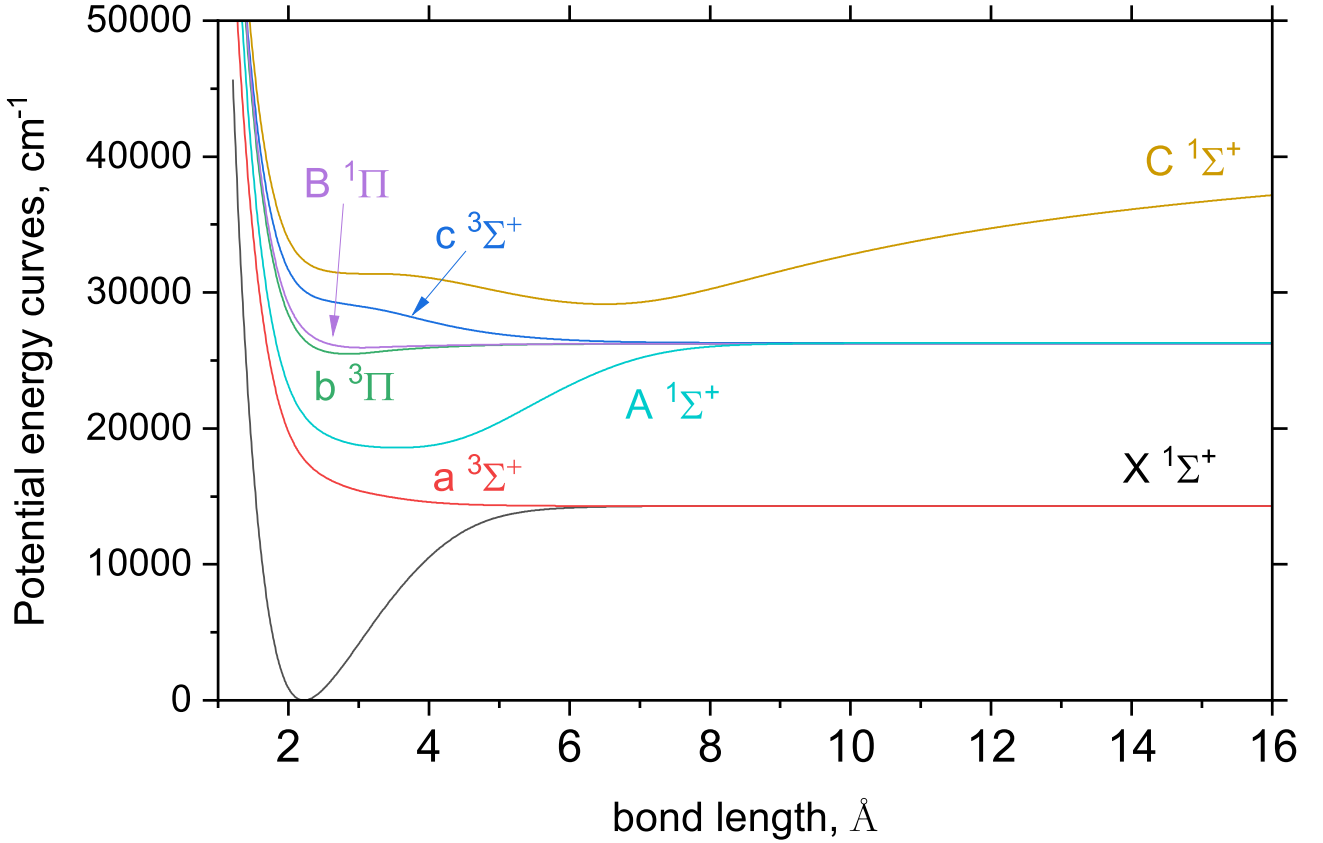


Figure 1. Potential energy curves generated ab initio for $X^1\Sigma^+$, $A^1\Sigma^+$, $C^1\Sigma^+$, $a^3\Sigma^+$, $c^3\Sigma^+$, $B^1\Pi$, and $b^3\Pi$ states of KH.

full description of the theory and functionality behind DUO is provided by S. N. Yurchenko et al. (2016) (see also <https://duo.readthedocs.io/>).

2.1 Ab initio calculations

Internally contracted multi-reference configuration interaction (icMRCI) *ab initio* calculations for the lowest 7 singlet and triplet electronic states of KH correlating to the $K(4s)+H$, $K(4p)+H$, and ionic K^++H^- dissociation limits were performed using MOLPRO (H.-J. Werner et al. 2020) with aug-cc-pVQZ-X2C basis sets, using molecular orbitals obtained from state-averaged complete active space self-consistent field (CASSCF) calculations. Under the C_{2v} point group symmetry, all *ab initio* calculations were done using the occupied orbital space (8,3,3,0) across the A_1 , B_1 , B_2 , and A_2 irreducible representations, respectively, with corresponding closed orbitals (5,1,1,0). Using this level of theory, PECs (Fig. 1), (T)DMCs (Figs 2 and 3), spin-orbit couplings (SOCs) (Fig. 4), electron angular momentum curves (EAMCs) and non-adiabatic couplings (NACs) (Fig. 5) were generated on a dense grid of 2000 bond lengths ranging from 1.21 to 20 Å. These cover the $X^1\Sigma^+$, $A^1\Sigma^+$, $C^1\Sigma^+$, $a^3\Sigma^+$, $c^3\Sigma^+$, $B^1\Pi$ and $b^3\Pi$ states, as shown in Fig. 1.

PECs: Fig. 1 reveals that, except for the $a^3\Sigma^+$ and $c^3\Sigma^+$ states, which have clear unbound character, the remaining five states considered here are bound. The $B^1\Pi$ and $b^3\Pi$ states exhibit very shallow potential wells, and are therefore expected to support few bound rovibrational states. A general feature of our PECs is that they extend significantly at large bond lengths, common

in diatomic hydrides. An avoided crossing structure is observed in the $^1\Sigma^+$ manifold, where the ground state appears ionic. The diabatic counterpart of this state extends towards the ionic limit in the $C^1\Sigma^+$ state. These avoided crossings are indicative of a charge-transfer process, leading to the progression from ionic to neutral character in $X^1\Sigma^+$, contributing to the wide extension of these potentials. Additionally, three NACs between states of the $[X^1\Sigma^+, A^1\Sigma^+, C^1\Sigma^+]$ system were computed at the CASSCF level of theory using the DDR (derivative couplings) procedure as implemented in MOLPRO and are illustrated in Fig. 5. The NACs appear to be weak, where analogous diabatic couplings are expected to be large (R. P. Brady et al. 2024). We can expect the adiabatic representation to be a sensible choice for constructing efficient contracted vibronic basis sets for nuclear motion calculations.

(T)DMCs: Figs 2 and 3 illustrate the computed (T)DMCs for the singlet and triplet states of KH, respectively. Of note is the $\langle C^1\Sigma^+ | \mu_z | C^1\Sigma^+ \rangle$ DMC, which becomes linear in bond length, consistent with the ionic nature of the $C^1\Sigma^+$ state in this region. Generally, the DMCs are large, which is a feature of the ionic nature of the KH electronic structure; the non-zero asymptotes correspond to strong atomic transitions in the potassium atom or dissociation into ions.

SOCs: Fig. 4 shows only one non-zero diagonal SO_z term, which couples the $b^3\Pi$ state. It is clear that the SOCs appear to be simple functions of bond length, and correlate to different asymptotes corresponding to the spin-orbit interaction in the atomic fragments. The spin-orbit interactions are weak for KH, and so minimal spin-orbit splitting is expected.

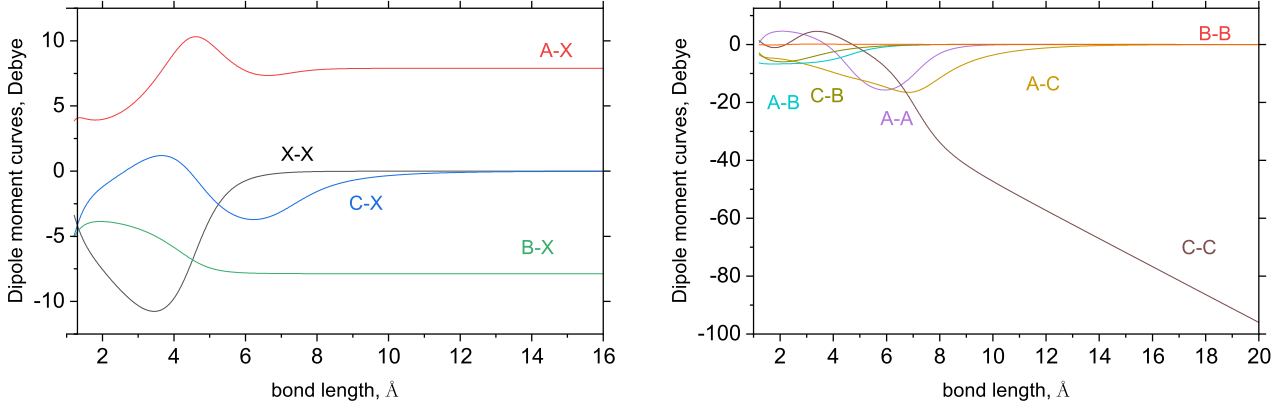


Figure 2. Ab initio permanent and transition dipole moment curves for singlet states of KH, $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$, and $C^1\Sigma^+$.

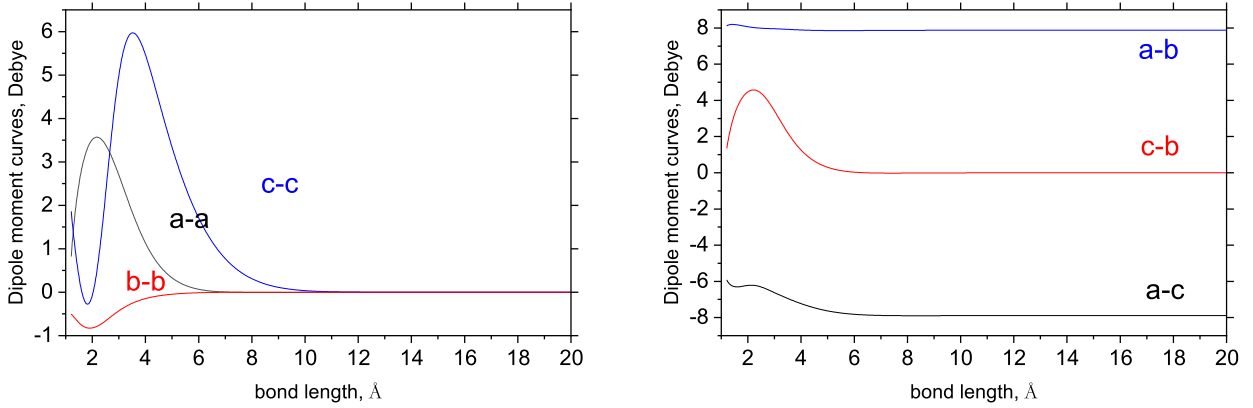


Figure 3. Ab initio permanent (left panel) and transition (right panel) dipole moment curves for triplet states of KH $a^3\Sigma^+$, $b^3\Pi$, and $c^3\Sigma^+$.

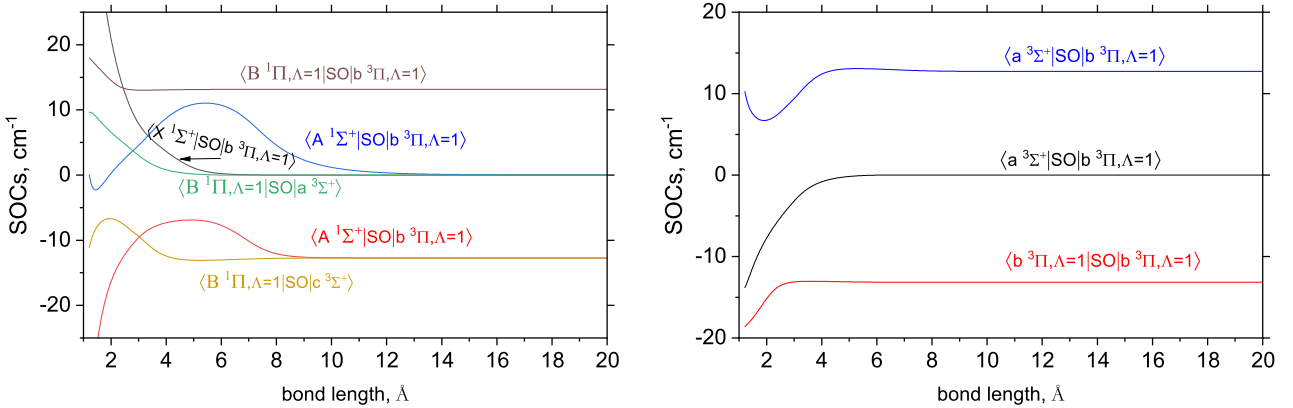


Figure 4. Ab initio spin-orbit coupling curves of KH.

EAMCs: Fig. 5 illustrates the computed $\hat{L}_+$ -component of the (non-diagonal) EAMCs of the KH states considered here, which correlates to different asymptotes corresponding to the EAM of the atomic fragments.

2.2 MARVEL

The MARVEL programme (T. Furtenbacher et al. 2007) is used to produce a self-consistent set of empirical energies from experimentally observed transition data. It works by constructing spectroscopic networks (SNs) in which nodes represent energy

levels and edges represent observed transitions, each weighted by their associated uncertainties. Within each SN, a vector of observed transition energies is assembled, alongside a vector of unknown energy levels to be determined and a matrix defining their linear relationships. MARVEL then performs a weighted least-squares optimization procedure to solve for the energy levels that best reproduce the experimental transitions, with weights derived from the inverse squares of the transition uncertainties. Transitions that produce residuals exceeding a specified threshold, based on their uncertainties, are flagged as inconsistent and may be excluded from the final analysis. Such inconsistencies

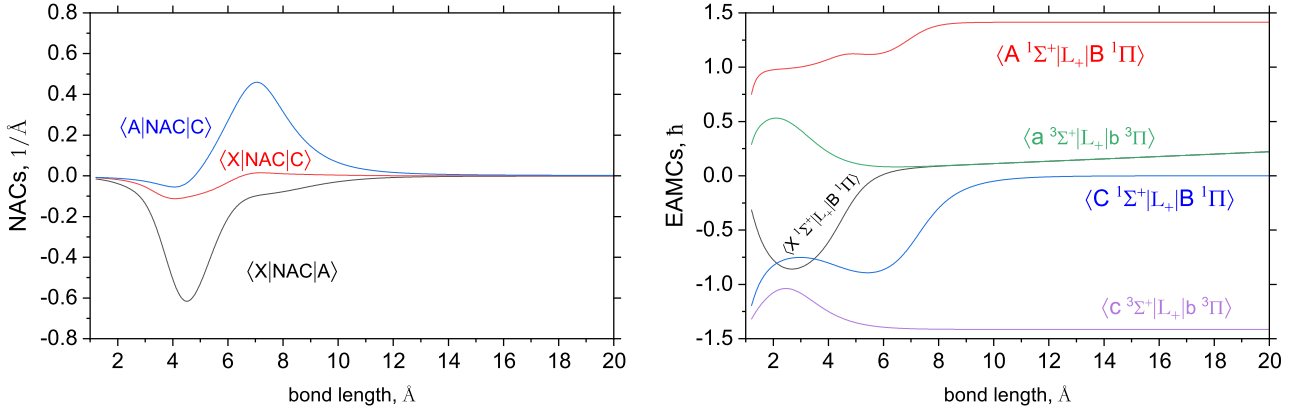


Figure 5. Ab initio non-adiabatic couplings and electron angular momentum curves of KH.

often arise from experimental misassignments or labelling errors in the reported transitions. The following sections will describe the data sources relevant to KH (full breakdown shown in Table 1) and expand upon the procedure. Full input and output files used in the MARVEL analysis are provided in Supplementary Data.

2.2.1 Data sources

32AlHa (G. M. Almy & C. D. Hause 1932) was the first investigation into the spectrum of KH. It contains data on 1227 transitions between $X^1\Sigma^+$ ($v'' = 0 - 4$) and $A^1\Sigma^+$ ($v' = 2 - 18$) states. Note that the vibrational levels of the $A^1\Sigma^+$ state are incorrectly assigned in this paper and need to be increased by 2 (I. R. Bartky 1966). Transitions that were omitted from analysis due to conflicting assignments are still present in the provided data set (Supplementary Material) and given a negative value to signify their omission as per the MARVEL procedure.

84HaLi (N. N. Haese et al. 1984) provide data on 73 transitions within the $X^1\Sigma^+$ state ($v = 0 - 2$). 46 of these transitions were measured in ^{39}KH with the remaining 27 in ^{41}KH . This analysis focused on the spectrum of ^{39}KH , hence only the corresponding 46 transitions were included. Energies for lower vibrational levels ($v = 0 - 4$, $J = 0 - 31$) were reconstructed from their spectroscopic constants. These cover the same vibrational levels in the $X^1\Sigma^+$ state from 32AlHa to provide stability when running MARVEL and assist in minimizing uncertainties.

95OdWa (H. Odashima et al. 1995) provide data on 13 rotational transitions in the $X^1\Sigma^+$ state ($v = 0$, $J = 0 - 12$).

00OkTa (T. Okabayashi & M. Tanimoto 2000) provide data on 3 hyperfine components in the $X^1\Sigma^+$ state ($v = 0$; $J = 0 \rightarrow 1$). These were considered as 3 individual transitions, with the differences lying within the uncertainty range.

01BrZi (M. A. Brewster & L. M. Ziurys 2001) provide data on 6 transitions involving hyperfine components of $X^1\Sigma^+$ state ($v = 0$; $J = 0 \rightarrow 1$, $J = 1 \rightarrow 2$ and $v = 1$; $J = 1 \rightarrow 2$).

09LeLu (A.-Y. Lee & W.-T. Luh 2009) provide data on 42 transitions between the $X^1\Sigma^+$ state ($v'' = 0 - 1$, $J'' = 0 - 8$) and $B^1\Pi$ state ($v' = 0$, $J' = 1 - 7$).

86HuEf (K. Hussein et al. 1986) describe experimentally observed transitions between the $X^1\Sigma^+$ state ($v'' = 0, 1, 2, 4, 5, 7, 13 - 23$) and $A^1\Sigma^+$ state. Transition energies are not quoted in their paper, but are reconstructed from their

derived spectroscopic constants. Uncertainties of 0.1 cm^{-1} were assumed.

93RaAl (M. Rafi et al. 1993) describe experimental observations of transitions between the $X^1\Sigma^+$ and $A^1\Sigma^+$ state, particularly involving higher vibrational bands in the $A^1\Sigma^+$ state: (24, 0) – (34, 0) and (27, 1) – (38, 1). Experimental transition energies are not quoted in their paper, but are reconstructed from their derived spectroscopic constants. Uncertainties of 0.1 cm^{-1} were assumed.

96RaAl (M. Rafi, R. Al-Tuwirqi & Fayyazuddin 1996) present a set of spectroscopic constants along with their semi-empirically constructed PEC of the $A^1\Sigma^+$ state. These constants were used to reconstruct energies at lower vibrational levels as there is limited transition data available in this region. Uncertainties of 0.3 cm^{-1} were assumed.

2.2.2 Procedure

The first step was to compile the available transition energies and uncertainties into a MARVEL input file, along with quantum numbers that uniquely define each transition. In this case, State, v , J , e/f were sufficient to identify experimentally observed transitions for KH covering $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ states. Finally, a unique identifier formed from a combination of the last two digits of the relevant paper's publication year, first two letters of the authors surnames and a number index is applied to each transition. An excerpt from the input file used in this MARVEL analysis is shown in Table 2 for reference.

For the three electronic states $^1\Sigma^+$ of KH with experimental data available, the parity is determined by $(-1)^J$, and DUO constructs a Hamiltonian matrix separately for each parity block, with each block being diagonalized independently. For the transitions to the $B^1\Pi$ state, their parities e/f are determined via the known selection rules of the dipole transitions: for the Q-branch transitions ($\Delta J = 0$), $e \leftrightarrow f$ and for the P- and R-branch transitions ($\Delta J = \pm 1$), $e \leftrightarrow e$ or $f \leftrightarrow f$.

Along with a correctly structured input file, MARVEL4 (J. Tenynson et al. 2024a) used here also requires a segment file which informs the program of which data sources exist in the input file as well as the transition frequency/wavenumber unit used by each source. This segment file, plus the input transitions file and output energy file are given in the supporting materials.

Alongside MARVEL, when some transitions are flagged as incorrect, for example the transitions from **32AlHa** (G. M. Almy &

Table 1. Breakdown of the available data sources used in this MARVEL analysis. Each data source with its corresponding electronic band, vibrational band, J range and energy range is shown. A/V refers to the number of available and validated transitions, respectively. Sources with an * were used to reconstruct semi-empirical energies from spectroscopic constants.

Data source	Electronic states	Vibrational bands	J range	Energy range (cm^{-1})	A/V
32AlHa	$X^1\Sigma^+ - A^1\Sigma^+$	$\nu' = 6 \dots 18,$ $\nu'' = 0 \dots 4$	0–33	15071.7–22855.6	1227/1181
84HaLi	$X^1\Sigma^+ - X^1\Sigma^+$	(1,0), (2,1)	0–24	20.26–3748.66	46/46
84HaLi*	$X^1\Sigma^+ - X^1\Sigma^+$	(0,0), (1,0), (2,0), (3,0), (4,0)	0–31	6.75–6515.34	159/159
95OdWa	$X^1\Sigma^+ - X^1\Sigma^+$	(0,0)	0–12	6.747–86.304	13/13
00OkTa	$X^1\Sigma^+ - X^1\Sigma^+$	(0,0)	0–1	6.75–6.75	3/3
01BrZi	$X^1\Sigma^+ - X^1\Sigma^+$	(0,0), (1,0)	0–2	6.75–13.50	3/3
09LeLu	$X^1\Sigma^+ - B^1\Pi$	(0,0), (0,1)	0–8	26081.36–27194.08	42/42
86HuEf*	$X^1\Sigma^+ - X^1\Sigma^+$	$\nu' = 0 \dots 23, \nu'' = 0$	0–10	6.75–14307.14	164/164
93RaAl*	$X^1\Sigma^+ - A^1\Sigma^+$	(24,0), (34,0)	0–10	25322.1–27687.5	121/121
96RaAl*	$X^1\Sigma^+ - A^1\Sigma^+$	(0,0) - (10,0)	0–10	18683.94–21554.0	121/121

Table 2. Extract from the MARVEL input file. Unc. is the experimental uncertainty with an additional column provided for MARVEL to update.

Frequency (cm^{-1})	Unc. (cm^{-1})	Unc. (cm^{-1})	State'	ν'	J'	e/f	State''	ν''	J''	e/f	Line ID
27593.4	0.5	0.5	A	34	2	e	X	0	0	e	93RaAl.113
27598.9	0.5	0.5	A	34	3	e	X	0	0	e	93RaAl.114
27606.1	0.5	0.5	A	34	4	e	X	0	0	e	93RaAl.115
27615.1	0.5	0.5	A	34	5	e	X	0	0	e	93RaAl.116
27626	0.5	0.5	A	34	6	e	X	0	0	e	93RaAl.117
27638.7	0.5	0.5	A	34	7	e	X	0	0	e	93RaAl.118
27653.1	0.5	0.5	A	34	8	e	X	0	0	e	93RaAl.119
27669.4	0.5	0.5	A	34	9	e	X	0	0	e	93RaAl.120
27194.084	0.05	0.05	B	0	1	e	X	0	0	e	09LeLu.14
27187.306	0.05	0.05	B	0	1	f	X	0	1	e	09LeLu.21
26218.602	0.05	0.05	B	0	1	e	X	1	2	e	09LeLu.34
26238.248	0.05	0.05	B	0	1	e	X	1	0	e	09LeLu.35
26231.644	0.05	0.05	B	0	1	f	X	1	1	e	09LeLu.42
27159.644	0.05	0.05	B	0	2	e	X	0	3	e	09LeLu.11

C. D. Hause (1932) ($A^1\Sigma^+ - X^1\Sigma^+$ band), the Combination Differences (CD) technique was used. This approach involves reconstructing energy levels of an upper rovibronic state using measured transition energies and known energy levels of a lower state. If multiple transitions are available that terminate on the same upper state level, each one provides an independent estimate of that level's energy. If the reconstructed energies from different transitions disagree significantly, it indicates that at least one of the transitions is likely misassigned, mislabelled, or otherwise inaccurate. This technique provides an effective way of identifying and handling inaccurate transitions, however, it does rely on the assumption that energy levels of the lower state are already known or that a reliable reference set can be generated.

For these CD tests, lower state energies were generated from spectroscopic constants provided by N. N. Haese et al. (1984). In cases where multiple transitions yielded consistent values for a given upper-state energy level while a smaller subset produced discrepant values, the minority transitions were assumed to be erroneous and discarded. However, if the conflicting transitions were evenly split, with equal numbers supporting incompatible energy values, then all transitions involved were discarded due to the ambiguity in identifying the source of error. Experimental uncertainties were used as the threshold for determining con-

sistency between calculated upper state energies. This process resulted in 46 transitions being removed from the G. M. Almy & C. D. Hause (1932) data source, and re-running MARVEL with the updated input file yielded a consistent set of empirical energy levels. An extract from the final energy file is shown in Table 3 for reference.

2.3 Rovibronic calculations

We use DUO to solve a coupled system of Schrödinger equations on a sinc-DVR grid of 1001 points ranging from 0.25 to 20 Å. Prior to calculating a line list for KH (Einstein A coefficients), we used DUO to refine PECs of the $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ states against experimentally derived (MARVEL) energies.

2.3.1 Pre-processing

Before performing the fitting process, the content from the MARVEL output file must be reformatted to be compatible with DUO. Energy levels are identified based on J , parity p , ν , Λ , Σ , and Ω (S. N. Yurchenko et al. 2016). In the fittings, each energy level is assigned a weight, indicating the degree of confidence with which the empirical energy has been determined. Weights were

Table 3. Extract from MARVEL output file showing derived rovibronic energy levels for electronic states with uncertainties and a correlation to the DUO quantum numbers and weights. N transitions refers to the number of experimental transitions that were used to derive each energy level.

State	v	J	e/f	$\tilde{E}$ (cm ⁻¹)	Unc. (cm ⁻¹)	N_{trans}	Λ	Σ	Ω	Weight
A	30	1	e	26741.1	0.7	1	0	0	0	1.20
A	31	1	e	26959.2	0.8	1	0	0	0	1.12
A	32	1	e	27170.2	0.8	1	0	0	0	1.12
B	0	1	f	27194.09583	0.1118	2	1	0	1	598.15
B	0	1	e	27194.12924	0.05	4	1	0	1	1788.85
A	33	1	e	27381	0.6	1	0	0	0	1.29
A	34	1	e	27589.8	0.5	1	0	0	0	1.41
X	0	2	e	20.25668768	0.07071	28	0	0	0	10529.74
X	1	2	e	975.5738728	0.07071	10	0	0	0	37.61
X	2	2	e	1901.166801	0.1	2	0	0	0	6.32
X	3	2	e	2795.971915	3	3	0	0	0	1.73
X	4	2	e	3665.329703	0.1	4	0	0	0	12.65
X	5	2	e	4505.0014	0.1	1	0	0	0	3.16
X	7	2	e	6101.931	0.1	1	0	0	0	3.16

taken to be the product of the number of transitions used to determine each energy level by MARVEL and the inverse uncertainty. These weights are then normalized by DUO prior to performing calculations. Table 3 shows an example of the correlation used in the DUO input file for the refinement.

2.3.2 Fitting

DUO is able to support the fitting of multiple analytical functions to supplied energies. The PECs of A and B are represented using the Extended Morse Oscillator (EMO; E. G. Lee et al. 1999):

$$V(r) = T_e + (A_e - T_e) [1 - e^{-\beta_{\text{EMO}}(r)(r-r_e)}]^2, \quad (1)$$

where $V(r)$ is the potential function, T_e is the energy of the PEC minimum, A_e is the asymptotic energy, r and r_e are bond length and equilibrium bond length respectively, and β_{EMO} is a power series:

$$\beta_{\text{EMO}} = \sum_{i=0}^N a_i y_p^e(r)^i \quad (2)$$

in the reduced Šurkus variable:

$$y_p^e = \frac{r^p - r_e^p}{r^p + r_e^p}, \quad (3)$$

where a_i are expansion coefficients and p is a parameter controlling the behaviour of y_p^e . This set-up ensures that at equilibrium bond length $r = r_e$, $V = T_e$, at large bond distances $r \rightarrow \infty$, $V = A_e$ and at short bond distances $r \rightarrow 0$, $V \rightarrow \infty$ with a_i and p parameters controlling behaviour and shape of the function between these limits. A different number of expansion coefficients a_i can be specified for regions to the left and right of the minimum. As the shape of the function is generally more complex for $r > r_e$, additional parameters to the right of the minimum can be used to capture this behaviour.

For X, the Morse/Lennard–Jones oscillator (MLJ) potential energy function is used (P. G. Hajigeorgiou & R. J. Le Roy 2000; Y. Huang & R. J. Le Roy 2003)

$$V(r) = D_e \left[1 - \left(\frac{r}{r_e} \right)^n e^{-\phi(r)z} \right]^2, \quad (4)$$

with D_e the dissociation energy. The polynomial function $\phi(r)$ and the reduced variable z ensure the function has the correct long-range behaviour,

$$\phi(r) = f_{\text{sw}}(r) \sum_{i=0}^{N_\phi} \phi_i z^i + (1 - f_{\text{sw}}(r)) \phi(\infty), \quad (5)$$

$$z = \frac{2(r - r_e)}{r + r_e}, \quad (6)$$

$$f_{\text{sw}}(r) = [1 + e^{\delta(r-r_{1/2})}]^{-1}, \quad (7)$$

where $\phi(\infty)$ is the asymptotic value of $\phi(r)$ assumed to be constrained to

$$\phi(\infty) = \frac{1}{2} \ln \left(\frac{2D_e r_e^n}{C_n} \right)$$

with C_n as a leading coefficient. Here we use the value C_6 for K from W. C. Stwalley et al. (1991). The MLJ improves on the well-known Morse potential by accounting for the long-range behaviour of molecular potential energy surfaces.

Born–Oppenheimer breakdown (BOB) rotational corrections were modelled using a polynomial decay expansion by L. Prajapat et al. (2017) (see also M. Semenov et al. 2022; S. N. Yurchenko et al. 2023)

$$F(r) = \sum_{i=0}^{N_B} B_i z^i (1 - \xi_p) + \xi_p B_\infty, \quad (8)$$

where ξ_p is the Šurkus variable defined by

$$\xi_p = \frac{r^p - r_{\text{ref}}^p}{r^p + r_{\text{ref}}^p}. \quad (9)$$

with p as an exponent chosen as part of the fit and z is taken as the damped coordinate

$$z = (r - r_{\text{ref}}) e^{-\beta_2(r-r_{\text{ref}})^2 - \beta_4(r-r_{\text{ref}})^4}, \quad (10)$$

where β_2 and β_4 are two damping parameters and r_{ref} is taken close to the associated equilibrium value.

The refining procedure involves least-squares fitting of the analytical functions to provided energy levels using a set of initial parameters. DUO will then iteratively adjust parameters and repeat the least-squares fit until convergence has been reached. This procedure was initially performed for $J = 0$ to speed up computation,

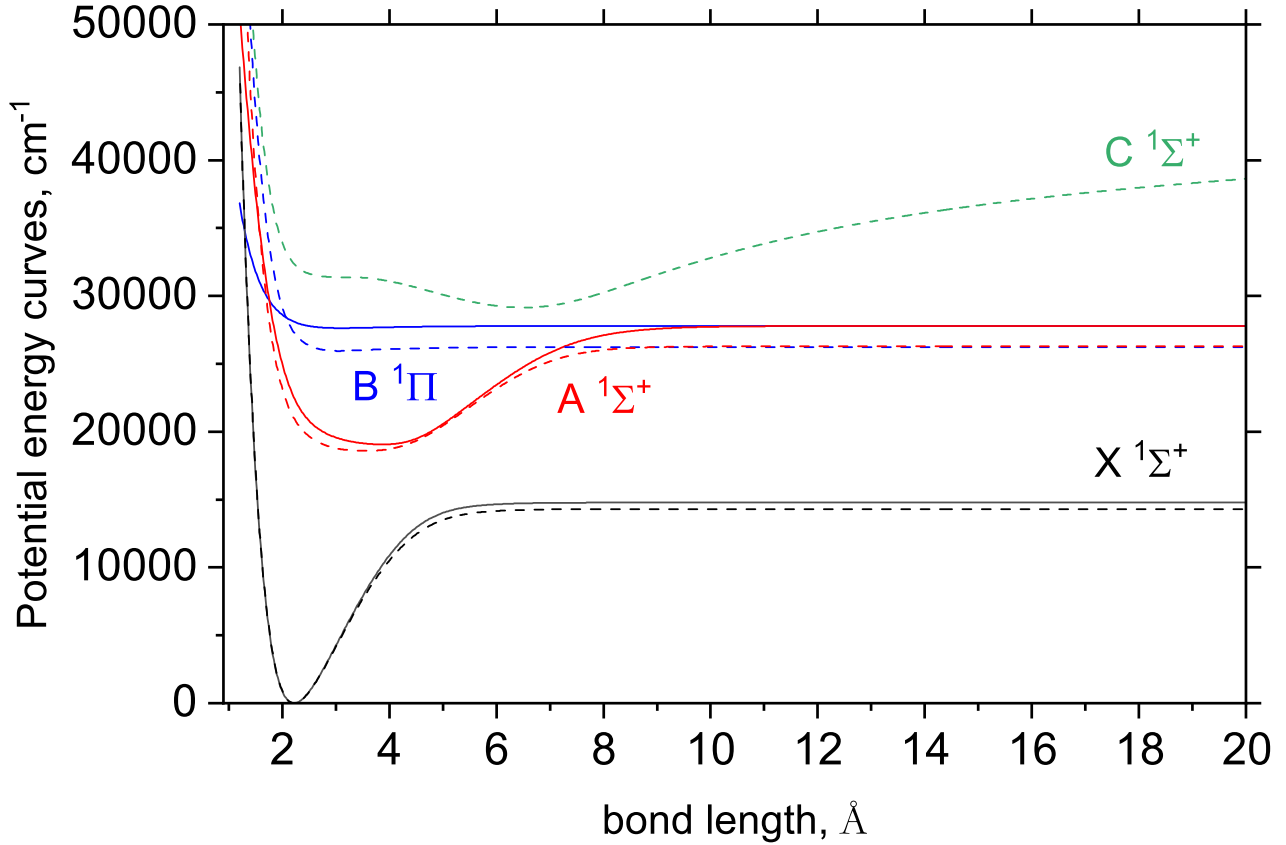


Figure 6. Comparison between *ab initio* (dashed lines) and refined (solid lines) PECs for $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ states of KH. Lower middle and top PECs correspond to $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ states, respectively.

followed by the addition of values up to $J = 33$, as this was the maximum level observed in experiment. Weights were adjusted on the fly by using Watson’s robust weighting procedure (J. K. G. Watson 2003).

A value for the dissociation energy $D_e = 14772.7 \text{ cm}^{-1}$ of the $X^1\Sigma^+$ state was taken from experiment (W. T. Zemke & W. C. Stwalley 1988). The dissociation energy of the $A^1\Sigma^+$ was estimated from this D_e , the vertical electronic excitation energy (T_e) and the energy of the $K 4p^2P^o$ state taken from NIST (National Institute of Standards and Technology; A. Kramida et al. 2020). An estimate for r_e in the $X^1\Sigma^+$ state was taken from the *ab initio* potential of 2.22 Å . Initial estimates for r_e and T_e in the $A^1\Sigma^+$ state were taken from the *ab initio* potential. Initial estimates for parameters of the $B^1\Pi$ state were taken from the experimental work by A.-Y. Lee & W.-T. Luh (2009). Final fitted parameters used for PECs of $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ states are provided as Supplementary Data in the form of a DUO input file.

In order to reduce the numerical errors commonly appearing in simulations of spectra of high overtones, see E. S. Medvedev et al. (2016), the *ab initio* DMC of $X^1\Sigma^+$ was modelled using the expansion

$$\mu(r) = (1 - \xi_p) \sum_{k=0}^N C_k z^k + \xi_p C_\infty, \quad (11)$$

where z is taken as the damped-coordinate z from equation (10). The expansion centre r_{ref} was chosen to be close to the equilibrium value of the ground electronic state.

Refined potentials for the $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ states are shown in Fig. 6. The fitted potential for the $X^1\Sigma^+$ state is similar to the *ab initio* curve, with the asymptotic energy shifted downwards slightly. For the $A^1\Sigma^+$ fit, the attempt to use the high v energy levels reconstructed from the spectroscopic constants from M. Rafi et al. (1996) led either to a distorted shape with a sharp step-like dissociation or to an unphysical large barrier. We therefore decided to exclude these empirical energies from the fit.

The $A^1\Sigma^+$ state has a shifted minimum, although determining an accurate location and shape is difficult given the lack of experimental data for lower vibrational levels. This lack of data is possibly due to the widened shape of the potential causing the Franck–Condon factor between wavefunctions in the $X^1\Sigma^+$ state being smaller with lower vibrational levels of the $A^1\Sigma^+$ state, making these transitions more difficult to observe. The fitted $B^1\Pi$ state potential is similar in shape to the *ab initio* curve, but shifted upwards in accordance with experimental data of A.-Y. Lee & W.-T. Luh (2009).

3 LINE LIST

Using the spectroscopic model defined above, consisting of three empirical PECs of $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$, an *ab initio* PEC of $C^1\Sigma^+$ (see Fig. 6), two BOB rotational curves of $X^1\Sigma^+$ and $A^1\Sigma^+$, and nine *ab initio* (T)DMCs associated with these four lowest singlet electronic states (see Fig. 2), hot line lists for three potassium hydride (KH) isotopologues, ^{39}KH , ^{40}KH , and ^{41}KH were computed. The line lists, named Khan, cover all transitions

Table 4. Parameters for uncertainty estimation using equation (13).

State	C_0	C_1	C_2
$X^1\Sigma^+$	0	0.1	0.001
$A^1\Sigma^+$	0.0001	0.1	0.001
$B^1\Pi$	0.001	0.1	0.001
$C^1\Sigma^+$	100	2	0.02

between bound and quasi-bound rovibronic states belonging to four lowest singlet electronic states $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$, and $C^1\Sigma^+$ for the wavenumber range up to $40\,000\text{ cm}^{-1}$ ($\lambda \geq 250\text{ nm}$) and for the rotational excitations up to $J_{\text{max}} = 130$. The bond-length integration range was selected as $[0.25 \dots 20]\text{ \AA}$; therefore, the realistic wavenumber cut-off is about $37\,000\text{ cm}^{-1}$ where the $C^1\Sigma^+$ state hits the long range boundary, see Fig. 6. We used the sinc-DVR method implemented in DUO to obtain vibrational basis functions for each electronic term $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$, and $C^1\Sigma^+$ independently by solving uncoupled Schrödinger equations on a grid of 1001 integration points. The selection of bound from unbound states was performed based on the criterion for the expectation value of the bond-length $\langle r \rangle$ for a given rovibronic state (T. Uhlíková et al. 2025). First, states with the expectation value of $\langle r \rangle$ larger than $9\text{ \AA}$ (for $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$) or $16\text{ \AA}$ (for $C^1\Sigma^+$) were assigned unbound. Additionally, we check whether they have non-zero density across a region $\Delta r = 2\text{ \AA}$ adjacent to the outer border $r_{\text{max}} = 20\text{ \AA}$ against the threshold value $\epsilon_{\text{max}} = 10^{-2}$, see discussion by S. N. Yurchenko et al. (2023), S. N. Yurchenko et al. (2024):

$$\epsilon = \int_{18\text{ \AA}}^{20\text{ \AA}} |\psi_\lambda(r)|^2 dr > 10^{-2}, \quad (12)$$

where the value of $\epsilon_{\text{max}} = 10^{-2}$ was selected based on an initial analysis.

The Khan line lists contain transitions between bound (or quasi-bound) states only, while bound-unbound and unbound-bound transitions can be used to evaluate continuum photoabsorption cross sections using EXOCROSS (G. B. Mitev et al. 2025; A. Sokolov et al. 2025).

The energies in the States file were improved through the so-called MARVELization procedure, where the calculated (Ca) values are replaced with the empirical, MARVEL, values (Ma), wherever available. Uncertainties of the MARVELized states are taken from the associated MARVEL values, otherwise they are estimated using the following expression:

$$\sigma_{\text{calc.}} = C_0^{\text{State}} + C_1^{\text{State}}v + C_2^{\text{State}}J(J+1), \quad (13)$$

where $\sigma_{\text{calc.}}$ is the uncertainty, v and J are the vibrational and rotational numbers of the corresponding energy level, with C_i^{State} representing parameters adjusted to vary the level of certainty with which calculations were performed listed in Table 4. These were purposely selected to overestimate the uncertainty, as the calculated energies require experimental verification. Table 5 shows an extract from the Khan.states file, containing energy term levels calculated from the refined spectroscopic model. Column headings are also shown for clarity, but these are not shown in the states file.

A further comparison between observed and calculated energies is shown in Fig. 7, which displays the difference between these energies as a function of J . In the range $J = 0\text{--}10$, the largest errors consistently occur between energies of the $A^1\Sigma^+$ state

with $v = 29 \dots 33$. These data were reconstructed from spectroscopic constants in the M. Rafi et al. (1993) data source, hence errors may reflect a systematic difference between models.

3.1 Partition function

The partition functions of KH isotopologues were calculated using the Khan line lists by counting Boltzmann-weighted contributions from bound states within the $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$ electronic states up to a temperature of $10\,000\text{ K}$. Fig. 8 shows a comparison of the Khan partition function of ^{39}KH to data from P. S. Barklem & R. Collet (2016) as well as A. J. Sauval & J. B. Tatum (1984) between $T = 1000\text{--}9000\text{ K}$, as this is the applicable temperature range for data from A. J. Sauval & J. B. Tatum (1984). Following the ExoMol and HITRAN convention, the ^{39}KH partition function includes the nuclear spin statistical weight of $g_{\text{ns}} = 8$. We therefore scaled the two external partition functions shown in Fig. 8 by this factor.

From Fig. 8, data from each source are in agreement at lower temperatures (below $\sim 3000\text{ K}$), but diverge at higher temperatures. This work consistently predicts a lower partition function than the other two sources, suggesting fewer accessible energy states at higher temperatures. P. S. Barklem & R. Collet (2016) present the highest values throughout the plotted range, while A. J. Sauval & J. B. Tatum (1984) lies between the two. Although the values from A. J. Sauval & J. B. Tatum (1984) are lower than those of P. S. Barklem & R. Collet (2016) up to 9000 K , the steeper gradient of their curve implies a crossover point beyond this temperature range.

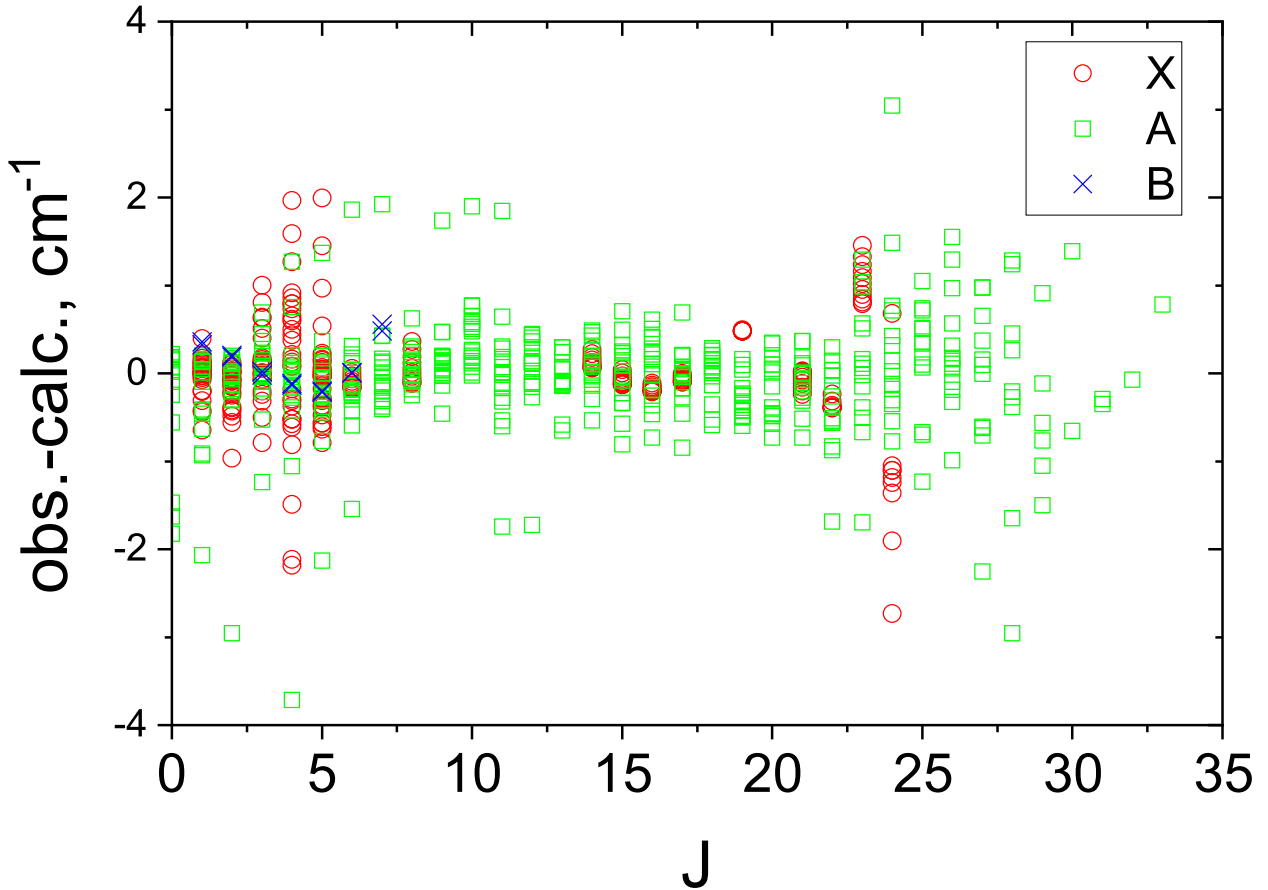
The partition function by A. J. Sauval & J. B. Tatum (1984) was determined using semi-empirical energies calculated from spectroscopic constants collated by K. P. Huber & G. Herzberg (1979). There is no explicit mention of constraints imposed on vibrational and rotational levels used in their calculations, hence unphysical or quasi-bound states may have been included. This could result in an overestimation of available states at high temperatures. Calculations from P. S. Barklem & R. Collet (2016) also relied on spectroscopic constants from K. P. Huber & G. Herzberg (1979), but their calculations involved a direct summation of states over each rovibronic state. They imposed truncation criteria for each electronic state such that vibrational levels are only considered bound if their contribution to the vibrational energy is no more than half of the previous one. In cases where this could not be applied (e.g. missing constants), the maximum level was set to $v = 100$. Additionally, the results from P. S. Barklem & R. Collet (2016) predict the lowest number of available states for KH to be 2, despite the ground state being singlet. The source of this factor of 2 was unclear from their methodology, hence their values were divided by 2.

Although both sources (A. J. Sauval & J. B. Tatum 1984; P. S. Barklem & R. Collet 2016) constructed partition functions from the same spectroscopic constants, differences in methodology are reflected in the varying shapes of their functions. Moreover, the spectroscopic constants compiled by K. P. Huber & G. Herzberg (1979) for KH originated from older experimental studies by G. M. Almy & C. D. Hause (1932), G. M. Almy & A. C. Beiler (1942), T. Hori (1933) and I. R. Bartky (1966) which cover the $X^1\Sigma^+$ and $A^1\Sigma^+$ states. These are not the most up-to-date constants available in literature, and tend to underestimate energies when compared to more accurate *ab initio* calculations.

Table 5. Extract from the Khan.states file for ^{39}KH containing energy term values (cm^{-1}), state applied alongside the collisional v degeneracies, uncertainties (cm^{-1}) and associated quantum numbers.

i	$\tilde{E}_i, \text{cm}^{-1}$	g_i	J	Unc. cm^{-1}	τ	+ / - e/f	State	v	Ω	Ca/Ma	$\tilde{E}_i^{(\text{Ca})}$
137	37297.883603	8	0	252.000000	2.1929E-07	+ e	C1Sigma +	76	0	Ca	37297.883603
138	37369.332863	8	0	254.000000	2.2335E-07	+ e	C1Sigma +	77	0	Ca	37369.332863
139	27194.059217	24	1	0.050000	1.3671E-08	+ f	B1Pi	0	1	Ma	27193.771792
140	27266.482550	24	1	0.103000	1.7373E-0811	+ f	B1Pi	1	1	Ca	27266.482550
141	27294.736132	24	1	0.203000	2.2471E-08	+ f	B1Pi	2	1	Ca	27294.736132
142	6.747407	24	1	0.000100	4.4775E+02	- e	X1Sigma +	0	0	Ma	6.746542
143	962.421028	24	1	0.070710	2.1059E-02	- e	X1Sigma +	1	0	Ma	962.392474
144	1888.340591	24	1	0.100000	1.1033E-02	- e	X1Sigma +	2	0	Ma	1888.209174
145	2784.447000	24	1	3.000000	7.7152E-03	- e	X1Sigma +	3	0	Ma	2784.968680
146	3653.161690	24	1	0.100000	6.0755E-03	- e	X1Sigma +	4	0	Ma	3653.197917
147	4493.154900	24	1	0.100000	5.1063E-03	- e	X1Sigma +	5	0	Ma	4493.323152
148	5305.738452	24	1	0.602000	4.4706E-03	- e	X1Sigma +	6	0	Ca	5305.738452
149	6090.716900	24	1	0.100000	4.0229E-03	- e	X1Sigma +	7	0	Ma	6090.823314
150	6848.925104	24	1	0.802000	3.6896E-03	- e	X1Sigma +	8	0	Ca	6848.925104

Notes. i : state counting number; $\tilde{E}_i$: state energy term values in cm^{-1} , MARVEL or calculated (DUO); g_i : total statistical weight, equal to $g_{\text{ns}}(2J+1)$; J : total angular momentum; unc: uncertainty, cm^{-1} ; τ : lifetime (s); +/−: total parity; e/f: rotationless parity; State: electronic state; v : state vibrational quantum number; Ω : projection of the total angular momentum; Label: ‘Ma’ is for MARVELized and ‘Ca’ is for Calculated; $\tilde{E}_i^{(\text{Ca})}$: Calculated state energy term values in cm^{-1} .

**Figure 7.** Difference between calculated ^{39}KH energies in DUO and MARVEL energies as a function of J .

4 KH SPECTRAL ILLUSTRATIONS

Fig. 9 shows spectra (absorption cross sections) of ^{39}KH at $T=300$ and 1000 K computed using the Khan line list with the contributions from bound-bound and continuum (bound-

unbound) transitions. ExoCROSS (S. N. Yurchenko et al. 2018) is used to produce these cross sections. Contributions to the spectrum largely arise from transitions within the $X^1\Sigma^+$ state below 8000 cm^{-1} , $A^1\Sigma^+ - X^1\Sigma^+$ band in the $9000\text{--}28\,000\text{ cm}^{-1}$ range

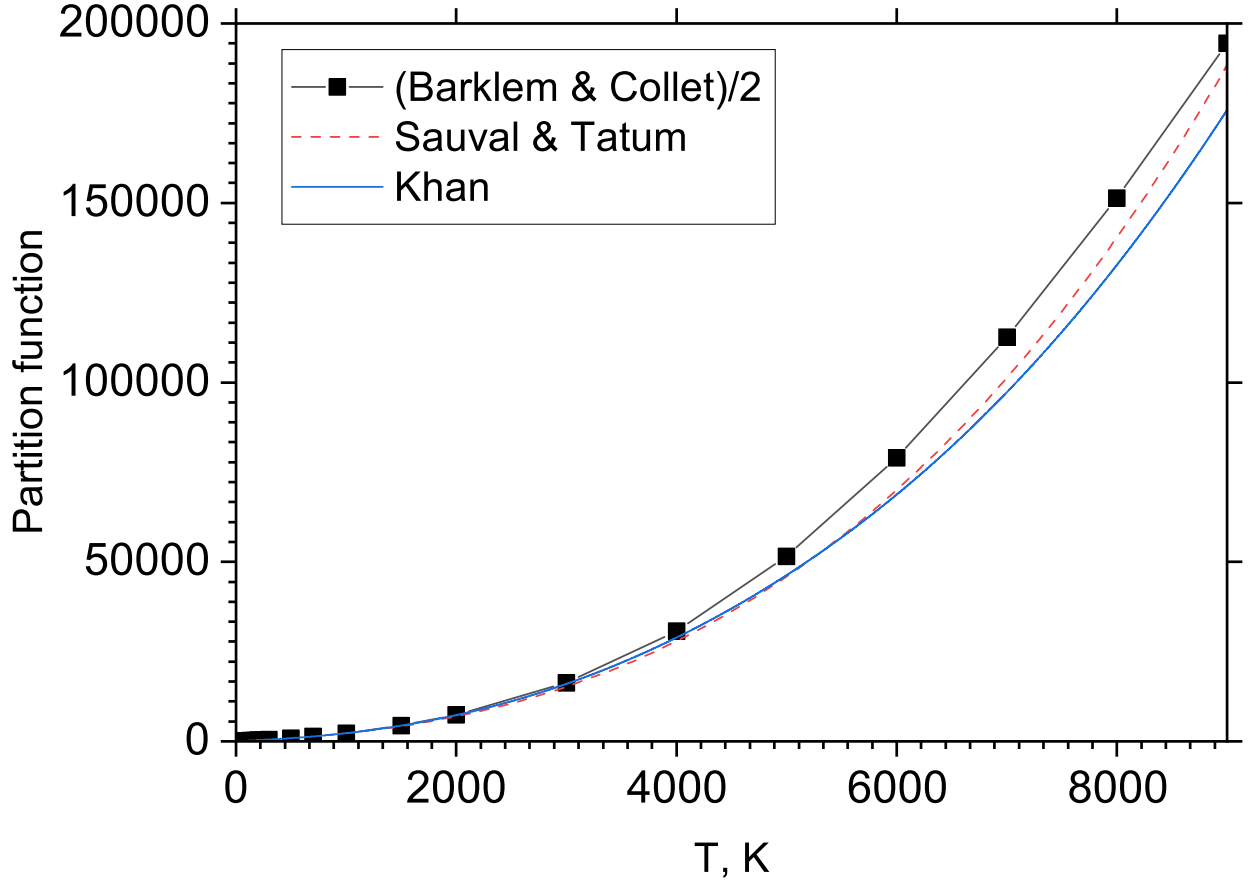


Figure 8. Partition function for ^{39}KH calculated in the range $T = 1000\text{--}9000\text{ K}$, compared against data from P. S. Barklem & R. Collet (2016) and A. J. Sauval & J. B. Tatum (1984).

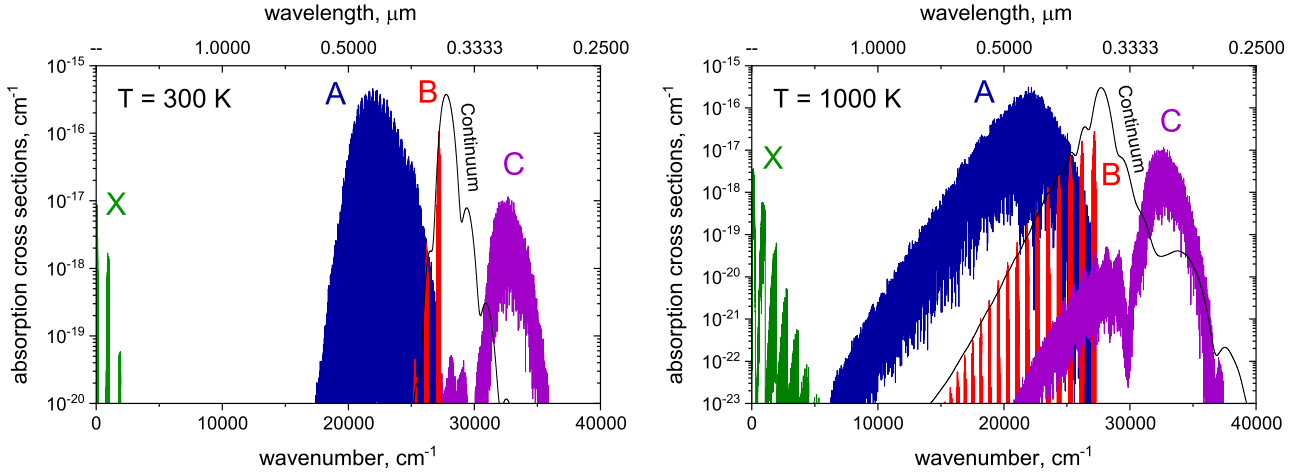


Figure 9. ^{39}KH absorption cross sections in the region $0\text{--}40\,000\text{ cm}^{-1}$ for $T = 300$ and 1000 K with contributions from individual bands and the total spectra shown.

and $\text{B}^1\Pi - \text{X}^1\Sigma^+$ band in the $15\,000\text{--}28\,000\text{ cm}^{-1}$ range and $\text{C}^1\Sigma^+ - \text{X}^1\Sigma^+$ band in the $30\,000\text{--}40\,000\text{ cm}^{-1}$ range. Here, cross sections for bound transitions were generated using a Gaussian line profile with EXOCROSS:

$$f_{\tilde{\nu}_{fi}, \alpha_G}^G(\nu) = \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\alpha_G} \exp\left(-\frac{(\tilde{\nu} - \tilde{\nu}_{fi})^2 \ln 2}{\alpha_G^2}\right) \quad (14)$$

where $f_{\tilde{\nu}_{fi}, \alpha_G}^G(\tilde{\nu})$ is the Gaussian, $\tilde{\nu}$ is the wavenumber, $\tilde{\nu}_{fi}$ is the wavenumber at the peak of the Gaussian, α_G is the half-width at half-maximum (HWHM). The continuum spectrum from bound-unbound transitions was also calculated using a Gaussian profile, but with a larger HWHM of 200 cm^{-1} to produce a smooth spectrum, see M. Pezzella et al. (2021). The continuum is dominant beyond $28\,000\text{ cm}^{-1}$.

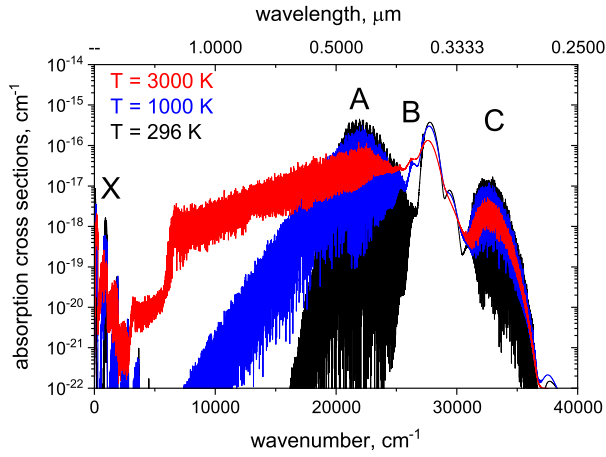


Figure 10. ^{39}KH spectrum in the 0–40 000 cm^{-1} range for $T = 300, 1000$, and 3000 K . Cross sections are calculated using a Gaussian profile with a HWHM of 1 cm^{-1} for the bound–bound transitions and HWHM = 200 cm^{-1} for the bound–unbound (upper) transitions.

Table 6. Number of lines and states in the Khan line lists for ^{39}KH , ^{40}KH , and ^{41}KH , their isotopic abundances (NIST) and the nuclear statistical weights g_{ns} .

Iso	N_{states}	N_{trans}	g_{ns}	Abundance
^{39}KH	13081	887976	8	93.2474%
^{40}KH	13089	888998	18	0.0117%
^{41}KH	13096	889318	8	6.7012%

Fig. 10 shows absorption cross sections of ^{39}KH in the 0–40 000 cm^{-1} range for $T = 300, 1000$, and 3000 K . As an illustration, a continuum contribution for $T = 3000\text{ K}$ is also shown. The $\text{B}^1\Pi\text{--X}^1\Sigma^+$ band is weaker than $\text{A}^1\Sigma^+\text{--X}^1\Sigma^+$ with at least two distinct bands clearly visible beyond the $26\,000\text{ cm}^{-1}$ region, most prominently in higher temperature spectra. This state giving rise to fewer bands is to be expected given the shallow nature of its PEC (Fig. 1). Interestingly, in the experimental study by A.-Y. Lee & W.-T. Luh (2009), only emission from $v' = 0$ of $\text{B}^1\Pi$ was observed and it was initially predicted that the $\text{B}^1\Pi$ state may only sustain one bound state. However, after investigation they note the energy of the $v' = 0$ state is significantly lower than the calculated dissociation energy so an additional bound state may be present. The additional bands seen in the calculated spectra indicate the presence of bound states with $v' = 1$.

The Khan line lists for ^{39}KH , ^{40}KH , and ^{41}KH contain bound transitions only, which just over 13 000 states and nearly 900 000 transitions each, see Table 6, which also lists their terrestrial abundances and nuclear spin degeneracies. The distribution of the bound and quasi-bound rovibronic levels retained in the line lists is illustrated in Fig. 11 through their expectation values of bond length, $\langle r \rangle$, overlaid on the $\text{X}^1\Sigma^+$, $\text{A}^1\Sigma^+$, $\text{B}^1\Pi$, and $\text{C}^1\Sigma^+$ potential energy curves. The photodissociation as well as the predissociation effects from the repulsive triplet electronic states is a goal of the future work and will be reported in due course.

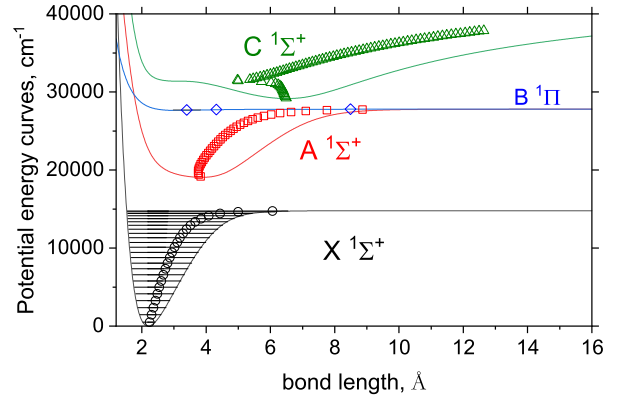


Figure 11. Expectation values $\langle r \rangle$ (Å) of ^{39}KH computed for different rovibronic states shown as circles, squares, triangles, and diamonds in X, A, B, and C, respectively.

4.1 Radiative lifetimes

Radiative lifetimes of KH were obtained from the Einstein A coefficients of the Khan line list using EXOCROSS. For each upper bound rovibronic state i , the radiative lifetime was computed from the total spontaneous-emission rate,

$$\tau_i = \frac{1}{\sum_{\tilde{E}_j < \tilde{E}_i} A_{i \rightarrow j}}, \quad (15)$$

where the sum runs over all energetically accessible lower states j with $\tilde{E}_j < \tilde{E}_i$ and $A_{i \rightarrow j}$ denotes the spontaneous-emission Einstein coefficient for the transition $i \rightarrow j$.

In many diatomic systems the lifetime is dominated by bound–bound decay and contributions involving unbound lower levels are often neglected. For KH, however, radiative decay from $\text{A}^1\Sigma^+$ to $\text{X}^1\Sigma^+$ includes a substantial bound–unbound (bound–free) component. This is a direct consequence of the unusual ordering of dissociation limits and the large separation between the bound regions of $\text{X}^1\Sigma^+$ and $\text{A}^1\Sigma^+$ (Fig. 11), which opens a broad continuum of energetically allowed final states in $\text{X}^1\Sigma^+$. The impact of this channel is illustrated in the left-hand panel of Fig. 12, where the partial lifetimes obtained by restricting the sum in equation (15) to bound–bound transitions only are compared with the full lifetimes including bound–free contributions. For the simulation box of r ranging from 0.25 to 20 Å , DUO identified 60–86 such unbound vibrational states for each J multiplet. While the bound–free term is negligible for low vibrational excitation, it increases rapidly with v and becomes comparable to the bound–bound contribution for $v \simeq 10\text{--}25$, demonstrating that continuum emission plays an essential role in shaping the vibrational dependence of the $\text{A}^1\Sigma^+$ radiative lifetimes.

Table 7 and the right-hand panel of Fig. 12 compare our $\text{A}^1\Sigma^+$ lifetimes with the experimental measurements of M. Giroud & O. Nedelec (1982) (for $J = 8, 9$ and $v = 5\text{--}22$) which have an uncertainty of about 10 percent (see fig. 9 of M. Giroud & O. Nedelec (1982)). Also shown are the theoretical results of N. Khelifi et al. (2007). Our values not only agree more closely with experiment, but also reproduce the observed vibrational trend, which we attribute to the explicit inclusion of bound–free decay in equation (15). We therefore suggest that the underestimation of the bound–free contribution is a primary reason why the calculations of N. Khelifi et al. (2007) do not capture the experimental vibrational dependence. The remaining differences between our lifetimes and the experimen-

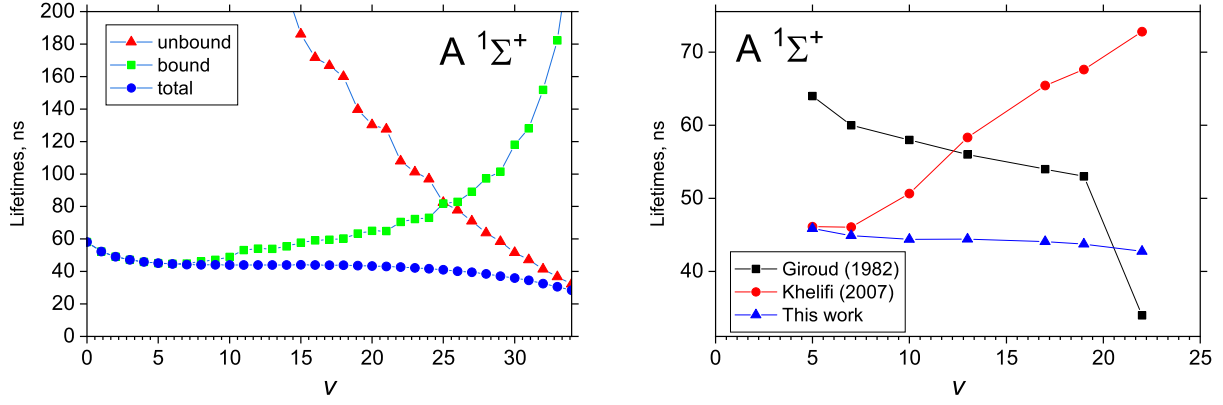


Figure 12. Left panel: Contributions from bound and unbound states to the lifetimes of $A^1\Sigma^+$ for $J=0$ as a function of v . Right panel: Comparison between experimentally measured $A^1\Sigma^+$ lifetimes of ^{39}KH from M. Giroud & O. Nedelec (1982) ($v = 5, 7, 10, 13, 17, 19, 22$ and $J = 8, 9$ as in Table 7), theoretical calculations from N. Khelifi et al. (2007) ($J=0$) and this work ($J=8, 9$).

Table 7. Comparison of experimental (M. Giroud & O. Nedelec 1982), theoretical (N. Khelifi et al. 2007) and calculated lifetimes τ of ^{39}KH from this work for a selection of levels in the $A^1\Sigma^+$ state. Lifetimes are in nanoseconds, ns.

v	J	τ M. Giroud & O. Nedelec (1982)	τ (N. Khelifi et al. 2007)	τ (This work)
5	9	64	46.13	45.88
7	9	60	46.06	44.91
10	8	58	50.67	44.40
13	9	56	58.33	44.42
17	8	54	65.43	44.10
19	8	53	67.62	43.76
22	9	34	72.80	42.77

tal values appear largely systematic, consistent with a modest overall scaling of the $A^1\Sigma^+-X^1\Sigma^+$ transition dipole moment; matching the measurements would require reducing the corresponding transition dipole moment by approximately a factor of ~ 1.14 .

M. Giroud & O. Nedelec (1982) noted that the sudden decrease in lifetime at $v = 22$ may be the result of a perturbation by another state. They suspected a perturbation by the $a^3\Sigma^+$ state given interactions in similar systems such as sodium hydride (NaH) and lithium hydride (LiH). From the *ab initio* PECs in Fig. 1, vibrational resonance between wavefunctions of the dissociative $a^3\Sigma^+$ state and higher vibrational levels of the $A^1\Sigma^+$ state could enable non-radiative decay pathways which are not accounted for in these radiative lifetime calculations. This could explain the significant overestimation for $v = 22$.

4.2 Predissociative lifetimes

In addition to the bound rovibronic levels supported by the $X^1\Sigma^+$ and $A^1\Sigma^+$ potential energy curves, KH also admits a small number of quasi-bound (shape-resonance) levels with energies lying above the dissociation limit. These states can be temporarily stabilized at very high total angular momentum by the centrifugal (rotational) barrier in the effective potential. They are therefore metastable and decay predominantly via tunnelling through the barrier, i.e. by predissociation. For KH this effect is relevant only

at very high J , where the barrier becomes sufficiently large to support resonant levels above dissociation.

To estimate predissociation rates for such rotationally stabilized levels we employ the program LEVEL (R. J. Le Roy 2017), using the $X^1\Sigma^+$ and $A^1\Sigma^+$ PECs determined in this work. LEVEL evaluates quasi-bound levels and their predissociation widths, Γ , using a uniform semiclassical procedure of J. Connor & A. Smith (1981) through the centrifugal barrier. For the majority of rovibronic levels the computed widths are zero within numerical precision, indicating truly bound character. Non-zero widths are found only for the highest- J resonances, specifically for $J \gtrsim 85$ in $X^1\Sigma^+$ and $J \gtrsim 125$ in $A^1\Sigma^+$, where quasi-bound levels occur above the dissociation threshold. The corresponding predissociation lifetime is obtained from the width as

$$\tau_{\text{prediss}} = \frac{1}{2\pi c \gamma_{\text{prediss}}}, \quad (16)$$

where γ_{prediss} is the predissociation width in cm^{-1} returned by LEVEL.

Radiative decay provides an additional loss channel for these metastable levels. We therefore combine the radiative lifetime in the Khan.states files, τ_{rad} , computed from the Einstein A coefficients, with the predissociation lifetime by adding the rates,

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{\text{rad}}^{\text{b-b}}} + \frac{1}{\tau_{\text{rad}}^{\text{b-f}}} + \frac{1}{\tau_{\text{prediss}}}, \quad (17)$$

where $\tau_{\text{rad}}^{\text{b-b}}$ and $\tau_{\text{rad}}^{\text{b-f}}$ are the associated lifetimes through bound-bound and bound-free transitions (if applicable), respectively. This procedure yields effective lifetimes for the quasi-bound levels that can be used consistently alongside the radiative lifetimes reported for the bound spectrum. For example, these lifetimes can then be used to evaluate the line broadening of the predissociated lines by inverting τ_{total} for the HWHM γ_{total} and applied alongside the collisional value of γ_{col} (S. N. Yurchenko et al. 2024; J. Tennyson et al. 2024b).

5 DISCUSSION AND CONCLUSION

Generating reliable spectra at high temperatures is of particular importance for the study of exoplanets, where recent observations have detected hot Jupiters of over 4000 K in the case of KELT-9 b (B.-O. Demory et al. 2016), and rocky terrestrial planets up to 2700 K in the case of 55 Cancri e (K. Jones et al. 2022). Accurate KH spectra will be valuable in both cases, as prior studies by T. Tsuji (1973) predict KH to be the most abundant K-bearing species at temperatures above 2000 K in bodies with solar-like compositions, and investigations by S. Charnoz et al. (2023) predict the presence of KH in hydrogen-rich atmospheres of ultra-hot rocky exoplanets.

This investigation into the KH system has revealed interesting avenues for further research, involving the three vibrational bands originating from $B^1\Pi-X^1\Sigma^+$ transitions, which are most prominent in the $T = 3000$ K spectrum (Fig. 10). As already mentioned, it was initially predicted by A.-Y. Lee & W.-T. Luh (2009) that the $B^1\Pi$ state may only sustain a single vibrational level. However, they noted that their measurement of the energy at $v' = 0$ was significantly below the expected dissociation energy and predicted the presence of an additional vibrational level. The results of this study support that prediction and further indicate vibrational levels up to $v' = 1$. A follow-up experimental study to measure the energies of these vibrational levels would aid in characterizing the $B^1\Pi$ state in more detail, and could be used to further refine PECs used in this study to improve the accuracy of the line list.

One of the limitations when investigating the KH system was the lack of available experimental data. The majority of empirical transition energies originated from G. M. Almy & C. D. Hause (1932), generating a broad emission spectrum using a potassium arc operating in hydrogen. Subsequent studies used more accurate techniques such as laser-induced fluorescence and Fourier transform spectroscopy, but covered a much narrower range of transitions. A number of these studies did not report the raw transition energy data, instead providing the spectroscopic constants derived from their experimental observations. Hence, in order to produce SNs dense enough for the MARVEL procedure to work effectively, a range of transition energies were reconstructed from these spectroscopic constants. This was particularly important for modelling the PEC of the $A^1\Sigma^+$ state where experimental data do not cover $v' = 0, 1, 2$. Reconstructing energies in this manner introduces an additional source of uncertainty, as the resulting semi-empirical data depend on the choice and assumptions of the underlying spectroscopic model. Further high-resolution experimental data on the spectrum of KH covering a broader range of transitions, as well as low-lying $A^1\Sigma^+$ states, would be valuable in generating a more accurate line list.

Finally, it is important to note that in addition to the radiative and non-radiative decays considered here for the singlet states,

the predissociation through spin-orbit coupling to triplet dissociative states can become important. This non-radiative pathway needs to be considered in calculations to avoid overestimating lifetimes, as seen in the prediction for $v \leq 18$ in the $A^1\Sigma^+$ state (Fig. 12). A follow-up study which incorporates these effects will need to be performed in order to produce more accurate lifetimes.

To conclude, Khan line lists for three KH isotopologues, ^{39}KH , ^{40}KH , and ^{41}KH covering the four lowest singlet electronic states $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$, and $C^1\Sigma^+$ were constructed using a refined spectroscopic model with X, A and B PECs fitted to reproduce experimentally derived (MARVEL) energies. As there is currently no high-temperature line list is available for KH, the goal of this study was to produce such line lists. These line lists are available from www.exomol.com. The results of this study should assist future studies aiming to characterize exoplanet atmospheres from spectroscopic information, many of which are high temperature environments.

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DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

The data discussed in this paper are freely available from the ExoMOL website <https://exomol.com> and the supporting materials.

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SUPPORTING INFORMATION

Supplementary data are available at *MNRAS* online.

The Supplementary material includes:

- (i) ab initio PECs and DMCs and refined curves as a DUO input file for ^{39}KH .
- (ii) MARVEL input file for ^{39}KH .
- (iii) MARVEL output file for ^{39}KH .
- (iv) MARVEL segment file for ^{39}KH .

The line lists and partition functions are available at www.exomol.com.

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