ExoMol: molecular line lists for exoplanet and other atmospheres

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ABSTRACT

The discovery of extrasolar planets is one of the major scientific advances of the last two decades. Hundreds of planets have now been detected and astronomers are beginning to characterize their composition and physical characteristics. To do this requires a huge quantity of spectroscopic data most of which are not available from laboratory studies. The ExoMol project will offer a comprehensive solution to this problem by providing spectroscopic data on all the molecular transitions of importance in the atmospheres of exoplanets. These data will be widely applicable to other problems and will be used for studies on cool stars, brown dwarfs and circumstellar environments. This paper lays out the scientific foundations of this project and reviews previous work in this area.

A mixture of first principles and empirically tuned quantum mechanical methods will be used to compute comprehensive and very large rotation–vibration and rotation–vibration–electronic line lists. Methodologies will be developed for treating larger molecules such as methane and nitric acid. ExoMol will rely on these developments and the use of state-of-the-art computing.

Key words: molecular data – opacity – astronomical data bases: miscellaneous – planets and satellites: atmospheres – stars: low-mass.

1 INTRODUCTION

Most information on the Universe around us has been gained by astronomers studying the spectral signatures of astronomical bodies. Interpreting these spectra requires access to appropriate laboratory spectroscopic data as does the construction of associated radiative transport and atmospheric models. For hot bodies the quantities of atomic and molecular data involved can be very substantial: beyond that which is easily harvested using only laboratory experiments. This problem led, for example, to the establishment of the Opacity Project (The Opacity Project Team 1994, 1995; Seaton 2005) some 35 years ago with the explicit aim of calculating all the necessary radiative data involving atomic ions which could be of importance for models of (hot) stars. This project was introduced by papers laying the scientific (Seaton 1987) and computational (Berrington et al. 1987) background for the project.

Stars cooler than our own Sun have significant quantities of molecules in their outer atmospheres. These molecules have spectra which are, in general, much richer than those of atoms and atomic ions. Thus, they both dominate the spectral signature of the cool stars and provide their major opacity sources which, in turn, determine their atmospheric structures. There are even cooler objects which are neither stars nor planets, called brown dwarfs. These objects are largely characterized and classified according to the

molecular features in their atmospheres. The last decade has also witnessed a rapid escallation in the number of planets orbiting other stars (exoplanets) that have been identified. This number is still increasing rapidly. So far spectroscopic studies of exoplanets are limited in the number, their wavelength coverage and, in particular, their resolution. However, it is already apparent from those studies available, which are so far largely confined to hot gas giant planets, that analysing their results will place similar demands on molecular line lists to the requirements of cool stars and brown dwarfs. Modelling and interpreting the spectra of these objects requires data appropriate for temperatures up to about 3000 K.

Since the first detection of sodium in an exoplanet (Charbonneau et al. 2002), exoplanet spectroscopy has made rapid advances. However, even with a rather limited set of molecules detected in exoplanet atmospheres, there remain serious problems with laboratory data. For example, methane was detected in HD189733b by Swain, Vasisht & Tinetti (2008), who lacked the necessary data to determine its quantity; even the presence of methane in other objects remains controversial (Stevenson et al. 2010; Beaulieu et al. 2011).

Planets and cool stars share some common fundamental characteristics: they are faint, their radiation peaks in the infrared and their atmosphere is dominated by strong molecular absorbers. Modelling planetary and stellar atmospheres is difficult as their spectra are extremely rich in structure and their opacity is dominated by molecular absorbers, each with hundreds of thousands to many billions of spectral lines which may be broadened by high-pressure

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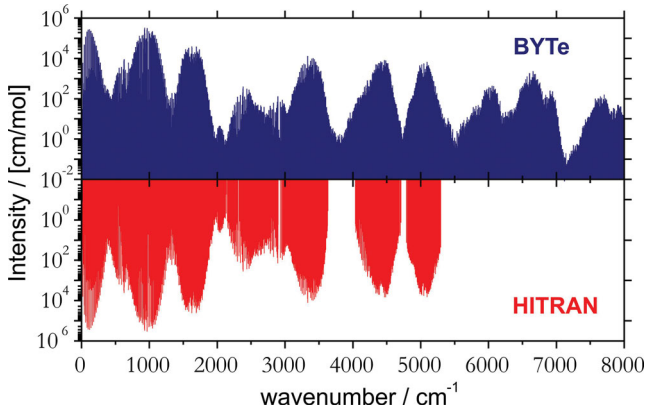
Figure 1. Room temperature ($T = 296$ K) comparison of the laboratory measured spectrum of ammonia, as taken from the HITRAN data base, with the line list calculated using the program 'TROVE' by Yurchenko, Barber & Tennyson (2011a) (2009).
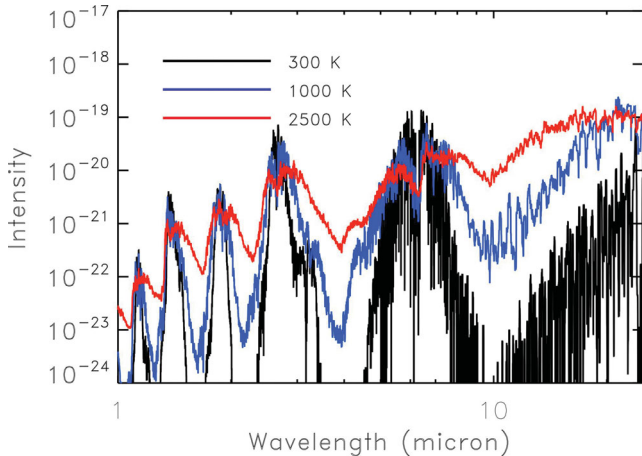
Figure 2. Absorption spectra of H_2O given by BT2 (Barber et al. 2007) for $T = 300$, 1000 and 2500 K.

and temperature effects. Despite many attempts and some successes in the synthesis of transition lists for molecular absorbers, reliable opacities for many important species are still lacking.

Determining line lists for hot molecules experimentally is difficult because of (a) the sheer volume of data (maybe billions of lines), (b) the difficulty in obtaining absolute line strengths in many cases, (c) the need to have assigned spectra in order for the correct temperature dependence to be reproduced and (d) the need for completeness, which requires a large range of wavelengths; even at room temperature experimental line lists are often far from complete, see Fig. 1 for an example. All this means that a purely empirical strategy is problematic. Instead the plan is to build a reliable theoretical model for each molecule of importance, based on a combination of the best possible ab initio quantum mechanical treatment which is then validated by and, in most cases, tuned using experimental data.

Molecular spectra, particularly for polyatomic species, rapidly become extraordinarily rich at elevated temperatures, meaning that the data requirement for a single triatomic molecule can outstrip the entire Opacity Project data set. Fig. 2 illustrates the strong temperature dependence of the spectrum of water which requires many millions of lines to simulate at higher temperatures. Considerable effort has been expended in constructing spectroscopic data bases, such as HITRAN (Rothman et al. 2009) and GEISA (Jacquinet-

Husson et al. 2011), which provide lists of molecular transitions important at about 296 K. These are appropriate for modelling the atmosphere of our planet and those of the other members of our Solar system. However, the construction of accurate and complete data bases for higher temperatures has been much more partial with most high-accuracy studies concentrating on a single species. The present status of this data is reviewed below.

This paper lays out the scientific foundations of a new project, called ExoMol, which aims to systematically provide line lists for molecules of key astronomical importance. These molecules have been selected to be those most likely to be present in the atmospheres of extrasolar planets. In practice they are of importance in many other hot astronomical environments, particularly brown dwarfs and cool stars. The ExoMol project aims to provide a comprehensive data base for these objects too. The following section summarizes the presently available line lists and illustrates the importance of these line lists by considering some of the problems they have been applied to. Section 3 considers the requirements for providing comprehensive data. The molecules concerned are categorized on physical grounds and appropriate methodologies are suggested for each class of problem. Section 4 gives conclusions and perspectives.

2 THE CURRENT SITUATION

Astronomers interested in molecular line lists use a number of collected data sources. Besides HITRAN and GEISA mentioned above, the JPL (Pickett et al. 1998) and CDMS (Müller et al. 2005) data bases provide comprehensive molecular line lists for wavelengths longer than 30 μm. However, these data bases are aimed at the cool interstellar medium rather than hot sources. HITEMP in both its original (Rothman et al. 1995) and recently updated (Rothman et al. 2010) editions carries data appropriate for modelling molecular spectra at elevated temperatures, but only for five species. Kurucz has extended his well-used atomic opacity tables with data for a number of molecules (Kurucz 2011) but the data for the majority of molecules are approximate and the list of molecules far from complete. Similarly there are partial lists of diatomic opacities provided by the UGAMOP data base at the University of Georgia (see www.physast.uga.edu/ugamop/) and the RADEN databank at Moscow State University (Hefferlin & Kuznetsova 1999). The SCAN data base also contains line lists for a few diatomics and triatomics (Jørgensen 1996). In summary, while there are a number of sources of molecular line list data, none of them can be considered complete, especially for work at elevated temperatures.

In their review of brown dwarf and very low mass star atmospheres, Allard et al. (1997) found that the majority of molecular opacities available were based on statistical or similarly approximate treatments. Indeed they quote no case where they considered the available molecular line lists to be adequate. This situation has improved somewhat since 1997; Tables 1 and 2 summarize what we believe to be the current situation for line lists of hot diatomic and polyatomic species, respectively.

2.1 Diatomics

Table 1 lists diatomic line lists which are published, available and fairly complete. Thus, for example, we have omitted the HF line list used by Uttenthaler et al. (2008) as there is no source for these data or, indeed, any details on how it was calculated. Similarly the recent AlO line list of Launila & Berg (2011) contains accurate, measured line frequencies but no transition intensities. In addition,

Table 1. Recommended available line lists for hot diatomic molecules. Given are the main reference; method: experimental (expt), ab initio (ai) or semi-empirical (semi); isotopologues other than the main one; completeness up to a given estimated temperature (T^{max}); number of lines in the line list (N) and the electronic source of the data, if available.

Molecule	Reference	Method	Isotopologues	$T^{\mathrm{max}\,c}$	N	Available[d]
C_2	Kurucz (2011)	semi		5200 K	3 459 595	Kurucz
CH	Kurucz (2011)	semi		3000 K	71 591	Kurucz
CN	Kurucz (2011)	semi		5000 K	1 644 597	Kurucz
CO	Rothman et al. (2010)	expt		4000 K	113 631	HITEMP
CaH	Weck, Stancil & Kirby (2003d)	semi		3500 K	89 970	UGAMOP
CrH	Burrows et al. (2002)	semi	^{50}Cr,^{53}Cr,^{54}Cr	1300 K	13 824	Bernath
FeH	Bernath and co-workers[a]	semi	^{54}Fe,^{57}Fe,^{58}Fe	1600 K	116 300	Bernath
HD$^+$	Coppola, Lodi & Tennyson (2011)	ai		All	10 120	ExoMol
HeH$^+$	Engel et al. (2005)	ai	All[e]	All	8 573	ExoMol
LiCl	Weck et al. (2004)	semi		4000 K	3 357 811	UGAMOP
LiH	Coppola et al. (2011)	ai		All	18 981	ExoMol
LiH$^+$	Coppola et al. (2011)	ai		All	329	ExoMol
MgH	Weck and co-workers[b]	semi		1300 K	23 315	UGAMOP
OH	Rothman et al. (2010)	expt		4000 K	41 577	HITEMP
NH	Kurucz (2011)	semi		3000 K	36 163	Kurucz
NO	Rothman et al. (2010)	expt		4000 K	115 610	HITEMP
SiH	Kurucz (2011)	semi		3000 K	78 286	Kurucz
SiO	Langhoff & Bauschlicher (1993)	semi				
SiO	Kurucz (2011)	semi		5300 K	1 827 047	Kurucz
TiH	Burrows et al. (2005)	semi		1800 K	199 073	Bernath
TiO	Schwenke (1998)	semi		6200 K	37 744 499	Kurucz

[a]Dulick et al. (2003), Wende et al. (2010) and Hargreaves et al. (2010)
[b]Weck et al. (2003a,b), Skory et al. (2003) and Weck, Stancil & Kirby (2003c)
[c]T^{max} should be considered as a guide indicating the completeness of a line list in question, estimated from the maximal energy E^{max} of the line list and the following condition on the Boltzmann factor: $\exp(-E^{\mathrm{max}}/kT^{\mathrm{max}}) = 5 \times 10^{-7}$. The latter is an empirical threshold that corresponds to T^{max} and E^{max} of the BT2 line list (Barber et al. 2006) (see Table 2). 'All' indicates that all bound–bound transitions within the ground electronic state are given.
[d]Data sources:
Bernath: http://bernath.uwaterloo.ca/XY, where XY is the chemical formula of the molecule
CDSD databank: ftp://ftp.iao.ru/pub/CDSD-4000
ExoMol project: www.exomol.com
HITEMP: http://www.cfa.harvard.edu/hitran/HITEMP.html
Kurucz CDs, http://kurucz.harvard.edu/
UGAMOP project: http://www.physast.uga.edu/ugamop/
[e]'All' means all possible stable isotopologues.

Table 2. Recommended available line lists for hot polyatomic molecules. All line lists are theoretical and designed to be complete up an estimated maximum temperature, T^{max}; the number of lines in millions for the main isotopologue only. For data sources see footnote d in Table 1.

Molecule	Reference	Isotopologues	T^{max}	$10^{-6}N$	Available
H_3^+	Neale, Miller & Tennyson (1996)	H_2D^+ (Sochi & Tennyson 2010)	3000 K	12	ExoMol
H_2O	Barber et al. (2006)	HDO (Voronin et al. 2010)	3000 K	503	ExoMol
HCN/HNC	Harris et al. (2006)	$H^{13}CN$ (Harris et al. 2008)	3000 K	240	ExoMol
C_3	Jørgensen, Almlöf & Siegbahn (1989)		3100 K		
CO_2	Tashkun & Perevalov (2011)	All	5000 K	626	CDSD
NH_3	Yurchenko et al. (2011a)		1500 K	1014	ExoMol

the MARCS model atmosphere code (Gustafsson et al. 2008) contains unpublished molecular line opacities for a number of diatomic species.

It is interesting to consider some of the diatomics that have been treated. Only in a minority of cases, specifically CO, OH and NO which all form part of the HITEMP data base (Rothman et al. 2010), have the line lists been constructed essentially on the basis of experimental data, see for example Goorvitch (1994) and Bernath & Colin (2009). A more typical and demanding situation is given by TiO.

TiO is a major opacity source in cool, oxygen-rich stars (Allard et al. 1997). It is an open shell system with several low-lying electronic states which can absorb at near-infrared and red wavelengths, that are close to the radiation peak in a cool star. A number of theoretical studies provided at least partial line lists for this system (Jørgensen 1994; Alvarez & Plez 1998; Plez 1998). At the same time there have been several detailed experimental spectroscopic studies on the system (Gustavsson, Amiot & Verges 1991; Simard & Hackett 1991; Amiot et al. 1995; Kaledin, McCord & Heaven 1995; Ram, Bernath & Wallace 1996). Schwenke (1998) combined

these studies and data from earlier laboratory spectra (Linton 1974; Hocking, Gerry & Merer 1979; Galehouse, Brault & Davis 1980; Brandes & Galehouse 1985) with state-of-the-art ab initio calculations to give a comprehensive TiO line list containing 37 million lines. This line list and the corresponding TiO opacity was found to give a very good representation of the TiO absorption in cool stars (Allard, Hauschildt & Schwenke 2000) and is now widely used. Schwenke's TiO line list is the largest available list for a diatomic by more than an order of magnitude.

The next largest available diatomic line list is that for C_2 which is one of a number of diatomics species for which line lists have been provided by Kurucz. Recently, however, there have been several new experimental measurements on this system, including the characterization of entirely new, low-lying electronic bands (Kokkin et al. 2006; Joester et al. 2007; Tanabashi et al. 2007; Nakajima et al. 2009; Bornhauser et al. 2010, 2011). This work has been accompanied by significantly improved ab initio electronic structure calculations (Kokkin, Bacskay & Schmidt 2007; Schmidt & Bacskay 2007, 2011; Nakajima et al. 2009). Given its importance, C_2 is one of the species we aim to provide an updated line list for.

The important CN radical is represented only by the Kurucz (2011) data in Table 1, which is somewhat approximate. We should note the recent experimental efforts by Ram et al. (2010) and Ram & Bernath (2011) offering accurate but only partial information. More work is therefore needed on this species.

Before turning to larger molecules it is worth considering the FeH and MgH molecules. Both these molecules have been the subject of experimental studies which have provided partial line lists.

In the case of FeH, Dulick et al. (2003) present results on rotation–vibration–electronic (rovibronic) transitions within the $F^4\Delta$–$X^4\Delta$ electronic band. The available line list is based on measured transitions which give the spectroscopic constants of rotational levels belonging to the $v = 0$, 1 and 2 vibrational levels of the FeH X and F states; these are then extrapolated to $v = 3$ and 4, and for $J (= N + S)$ values up to 50.5, where v is the vibrational, J is the total angular momentum, N is the rotational and S is the spin quantum numbers. The line list for this band therefore consists of experimental and extrapolated term values for the 25 vibrational bands with $v \leq 4$. The line list of Dulick et al. (2003) was verified and corrected by scaling the Einstein A-coefficients, by Wende et al. (2010) using the high-resolution spectra of the red dwarf star GJ 1002. Hargreaves et al. (2010) provide a line list for the FeH $E^4\Pi$–$A^4\Pi$ electronic system near 1.58 μm which combined measured frequencies with ab initio calculation of the line strengths.

MgH, along with CrH, is of potential interest for measuring the presence of deuterium in brown dwarfs (Pavlenko et al. 2008), the so-called deuterium test (Béjar, Zapatero Osorio & Rebolo 1999). Extensive experimental studies of MgH electronic spectra have been performed by Weck et al. (2003b), Weck et al. (2003a) and Skory et al. (2003). These have been used to compute the complete line list for the $B'^2\Sigma^+$–$X^2\Sigma^+$ system of ^{24}MgH. The list includes transition energies and oscillator strengths over the 11 850–32 130 cm^{-1} wavenumber range, for all possible allowed transitions from the ground electronic state vibrational levels $v'' \leq 11$. This list was computed using the best available ab initio potential energies and dipole transition moment function, with the former adjusted to account for experimental data. The status of CrH is somewhat similar to this.

It is clear from the above that a mixed experimental and theoretical approach has been the most successful so far. Other experimental data sets are available; for example, a very extensive study on NiH

has recently been completed (Vallon et al. 2009; Ross et al. 2012), and these will provide an appropriate starting point for further line lists.

2.2 Polyatomic molecules

Table 2 summarizes the available line lists for polyatomic molecules. In the case where several line lists are available, only the recommended one is given.

For polyatomic molecules the main methodology has been theoretical. So far calculations have, of necessity, been performed piecemeal and molecule by molecule. For key molecules many line lists may be available; for example, at least seven lists are available for hot water (Wattson & Rothman 1992; Allard et al. 1994; Partridge & Schwenke 1997; Viti, Tennyson & Polyansky 1997; Schwenke & Partridge 2000; Jørgensen et al. 2001; Barber et al. 2006). Studies have shown significant differences between the use of different line lists (see Jones et al. 2002 for example). It is clear that use of complete and spectroscopically accurate line lists is important both for modelling hot astronomical objects and for interpreting their spectra.

The recent CDSD-4000 CO_2 line list of Tashkun & Perevalov (2011) extended their earlier work, which was used in the 2010 edition of HITEMP (Rothman et al. 2010), to higher temperatures. This line list was constructed using effective Hamiltonians parametrized using experimental data. Carbon dioxide is a more rigid molecule that the other polyatomics considered in Table 2 and thus is a good candidate for treatment using effective Hamiltonians. Very recent, high-temperature, emission experiments by Depraz et al. (2012) suggest that the CDSD-4000 line list is indeed the best available list at modelling high-temperature spectra but there remains some work to be done on this problem. We note that a new theoretical study using methods closer to those advocated here has recently started (Huang et al. 2012).

It is instructive to consider the breadth of applications of the calculated line lists, many of which could not have been anticipated prior to their construction. The polyatomic line lists summarized in Table 2 have all also been used to predict, analyse and assign laboratory spectra of the species, especially at elevated temperatures. These line lists also provide a source of cooling functions (Miller et al. 2010; Coppola et al. 2011) and high-temperature partition functions (Neale & Tennyson 1995; Vidler & Tennyson 2000; Barber, Harris & Tennyson 2002) which are important for a variety of astrophysics problems. In addition, other applications can be summarized as follows.

(1) H_3^+. The Neale et al. (1996) line list and related partition function (Neale & Tennyson 1995) have been used

(i) to give all transition intensities for interpreting astronomical observations since there are no laboratory absolute intensity measurements for the spectrum of H_3^+;

(ii) to significantly improve models of cool white dwarf stars (Bergeron, Ruiz & Leggett 1997);

(iii) to resolve issues with the Jovian energy budget (Miller et al. 2000);

(iv) to probe the role of H_3^+ in primordial cooling (Glover & Savin 2009);

(v) to provide stability limits for giant extrasolar planets orbiting near their star (Koskinen, Aylward & Miller 2007) and

(vi) to model non-thermal rotational distributions of H_3^+ both in the interstellar medium (Oka & Epp 2004) and in storage ring experiments (Krechel et al. 2002; Kreckel et al. 2004).

(2) Water. The BT2 line list (Barber et al. 2006) has been used

(i) to show an imbalance between nuclear spin and rotational temperatures in cometary comae (Dello Russo et al. 2004, 2005) and assign a new set of, as yet unexplained, high-energy water emissions in comets (Barber et al. 2009);

(ii) to detect and analyse water spectra in (a) Nova-like object V838 Mon (Banerjee et al. 2005), (b) atmospheres of brown dwarfs (Lyubchik et al. 2007) and (c) FU Orionis objects;

(iii) to calculate the refractive index of humid air in the infrared (Mathar 2007);

(iv) to detect water on transiting extrasolar planets, for which it was completely instrumental (Tinetti et al. 2007) as other available line lists did not contain good enough coverage of the many weak lines that become significant absorbers at high temperatures to make this detection securely;

(v) for high-speed thermometry (Kranendonk et al. 2007), tomographic (Ma et al. 2009) imaging in gas engines and burners and input for models of jet engines (Lindermeir & Beier 2012);

(vi) as input for an improved theory of line broadening (Bykov et al. 2008);

(vii) to model water spectra in the deep atmosphere of Venus (Bailey 2009) and

(viii) to validate the data used in models of the earth's atmosphere and in particular simulating the contribution of weak water transitions to the so-called water continuum (Chesnokova et al. 2009).

(3) HCN/HNC. Jørgensen et al. (1985) showed that including HCN opacity in their model of atmospheres of cool carbon-rich stars caused the modelled atmosphere to expand by a factor of 5 and lowered the gas pressure of the surface layers by one or two orders of magnitude. This finding did much to stimulate detailed work on molecular line opacities. Subsequent line lists (Harris, Polyansky & Tennyson 2002; Harris et al. 2006) have treated the isomerizing HCN/HNC as a single species. They have been used

(i) to detect HNC in the spectra of carbon stars (Harris et al. 2003);

(ii) to constrain C and N abundances in asymptotic giant branch stars (Matsuura et al. 2005);

(iii) for models of the thermochemistry of HCN (Barber et al. 2002);

(iv) to assign a particularly extensive set of hot, laboratory HCN (Mellau 2011a) and HNC (Mellau 2011b) spectra.

(4) HeH$^+$. This molecule had been neglected from standard models of helium-rich white dwarfs (which rather surprisingly included both H$_2^+$ and He$_2^+$, see for example Stancil 1994). The line list of Engel et al. (2005) has been used

(i) for models of the white dwarf stars, particularly helium-rich white dwarfs (Harris et al. 2004);

(ii) to study the effects of early chemistry on the cosmic ray background (Schleicher et al. 2008);

(iii) as a starting point for calculations of end effects in the upcoming Karlsruhe tritium neutrino experiment (KATRIN) neutrino mass measurement experiment (Doss et al. 2006).

To add context to the methods discussed below, it should be noted that while the H$_3^+$ and HeH$^+$ line lists are completely ab initio, those for water, HCN/HNC and NH$_3$ used laboratory measurements to improve the procedure. For water and ammonia this came via the use of a spectroscopically determined potential energy surface (PES), while the HCN/HNC calculations replaced the calculated ab initio energy levels with observed ones where known. Both of these procedures, plus other methods discussed below, take advantage of laboratory high-resolution spectra. In contrast, comparisons between dipole transition intensities computed using a completely ab initio dipole moment surface (DMS) and benchmark experimental studies have shown that intensities calculated ab initio are competitive with, and often more accurate than, laboratory intensity measurements even when they are available (Asvany et al. 2007; Lodi, Tennyson & Polyansky 2011).

2.3 Scope of the ExoMol project

A list of species that we plan to consider is given in Table 3. This list is based on current demands for models of exoplanets and brown dwarfs. However, it is necessary to be flexible since as the characterization of exoplanets improves additional molecular line lists are likely to be required.

Broadly speaking, it is possible to separate the spectroscopic demands for hot Jupiters, which have a reducing or hydrogen-rich chemistry, and super-earth-type exoplanets, which can be expected to be oxidizing or oxygen rich. In practice, there will be other categories of exoplanets, such as warm Neptunes; however, the above division should be sufficient to identify the species for which data are required.

Although the atmospheres of other exoplanets are now starting to be probed (Bean, Miller-Ricci Kempton & Homeier 2010; Beaulieu et al. 2011), those exoplanets that are currently the subject of spectroscopic analysis are largely hot Jupiters. For hot Jupiters there is already a major demand for a high-quality methane line list (Swain et al. 2008) and there are likely to be demands for line lists of other hydrogenated species such as H$_2$S, PH$_3$, acetylene, ethane and propane. For super-earths, that is planets with rocky cores, oxygen-bearing species such as ozone and oxides of nitrogen and sulphur are likely to be more important and will also provide bio-signatures (Des Marais et al. 2002). Simulated remote spectra of habitable planets (Kaltenegger et al. 2010) suggest that a variety of molecules including even nitric acid could provide a possible bio-signature. Finally, it is already known from models of cool stars

Table 3. ExoMol list of molecules: molecular line lists available, fuller lists are given in Tables 1 and 2, and planned categorized by chemistry.

	Primordial (Metal-poor)	Terrestrial planets (Oxidizing)	Giant-planets and cool stars (Reducing atmospheres)
Already available	H$_2$, HD$^+$, LiH, LIH$^+$, HeH$^+$, H$_3^+$, H$_2$D$^+$	OH, CO$_2$, O$_3$, NO, H$_2$O, NH$_3$	H$_2$, CN, CH, CO, CO$_2$, TiO, YO, HCN/HNC, H$_2$O, NH$_3$
ExoMol	BeH	O$_2$, CH$_4$, SO$_2$, HOOH, H$_2$CO, HNO$_3$	CH$_4$, PH$_3$, C$_2$, C$_3$, HCCH, C$_2$H$_6$, C$_3$H$_8$, VO, O$_2$, AlO, MgO, BeH, CrH, MgH, FeH, CaH, AlH, SiH, NiH, TiH

that open shell diatomics with low-lying electronic states have clear atmospheric signatures and can play an important role in determining the radiative transport properties of the atmosphere. So far only for TiO (Schwenke 1998) is there a satisfactory line list available.

Table 3 summarizes the molecules that are thought likely to be important in the atmospheres of extrasolar planets and cools stars. They are classified according to anticipated atmospheric chemistry, since it is radically different in systems which have no heavy elements (such as bodies formed in the very early universe), are oxygen rich or are carbon rich. These species are separated between those for which satisfactory line lists, extending to high temperature, are currently available, and those for which line lists are needed. It is clear that, except for primordial chemistries, the to-do list is much longer. Table 3 has been constructed from the literature (e.g. Sharp & Burrows 2007; Freedman, Marley & Lodders 2008) and as a result of extended discussions with several scientists involved directly or indirectly in characterizing exoplanets.

There are significant differences in the physical processes that need to be modelled for different molecules. These are addressed in the next section. Based on the underlying physics that needs to be considered, the problems can be classified as (1) diatomics, (2) triatomics, (3) tetratomics, (4) methane and (5) larger molecules. Special techniques will be required in each case. A final topic will focus on the content, construction and use of the ExoMol data base itself.

3 METHODOLOGY

Most of the molecules listed in Table 3 are chemically stable and only undergo electronic transitions in the ultraviolet. For these systems it is necessary to consider in detail pure rotational and vibration–rotation transitions within the ground electronic state. However, the list also contains a number of open shell diatomic species such as C_2 and FeH. These molecules undergo electronic transitions at near-infrared or visible wavelengths; for these systems it is necessary to consider electronic transitions and hence excited electronic states.

Within the Born–Oppenheimer approximation, the calculation of line lists of rotation–vibration transitions for a stable polyatomic molecule can essentially be broken down into the following steps: ground-state electronic structure calculations to give energies and electric dipoles at a series of geometries; interpolation between geometries to create the PES and DMS; nuclear motion calculations to provide energy levels and wavefunctions; calculation of transition dipoles using the wavefunctions and DMS. Predicted frequencies which arise from such a pure ab initio procedure are only accurate enough for present purposes for electronically very simple systems. It is therefore necessary to improve these frequencies using experimental data. This can be done in one of three ways.

(a) A priori by tuning the PES by comparison with the results of laboratory high-resolution spectroscopic studies. We have developed new procedures for this (Yurchenko et al. 2008, 2011b) which are both efficient and retain the predictive nature of the underlying ab initio PES.

(b) Post hoc by replacing calculated energy levels with observed ones. As energy levels are not observed directly we will rely on the Measured Active Rotation–Vibration Experimental Level (MARVEL) inversion procedure (Furtenbacher, Császár & Tennyson 2007) which has been successfully used for water isotopologues (Tennyson et al. 2009, 2010).
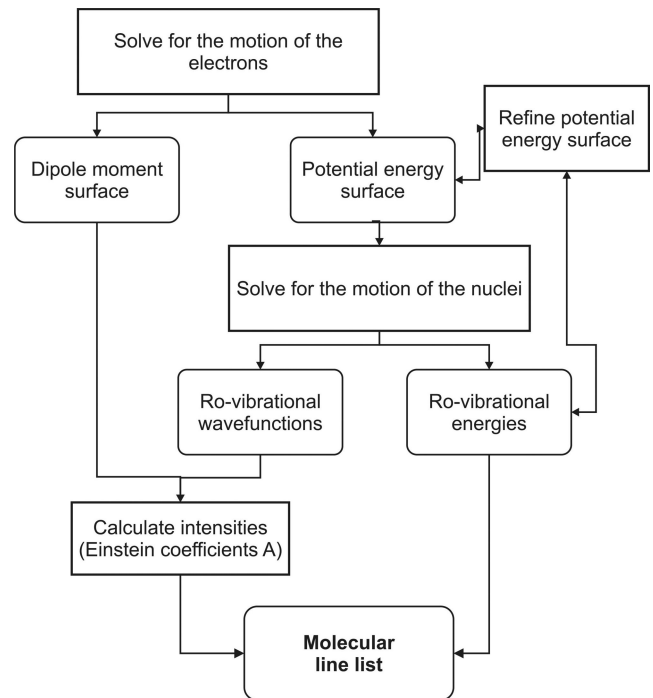
Figure 3. Schematic presentation of the general method that will be used to produce molecular line lists.

(c) During the calculation: since most of the error is in the vibrational and not the rotational energies (Polyansky et al. 1997), using empirical vibrational band origins can significantly improve predicted frequencies for all transitions in the band. The nuclear motion program TROVE (Yurchenko, Thiel & Jensen 2007) contains the facility to replace predicted band origins with empirical ones part way through the calculation. This facility was used in constructing the recent BYTe line list for NH_3 (Yurchenko et al. 2011a). In practice, all three methods will be used, often in combination. Fig. 3 summarizes our general methodology.

For each line list the following components are required:

(i) nuclear motion model, implemented in a computer program, for accurate calculations of rotation–vibration energies and wavefunctions;
(ii) accurate PES and DMS and
(iii) a computational procedure for intensity simulations based on the results of the nuclear motion calculations.

It is generally accepted that the ab initio DMS computed at high levels of theory provides very reasonable description of the intensities, better, for example, than that can be obtained by attempting to fit a DMS to measured intensities (Lynas-Gray, Miller & Tennyson 1995). Moreover, such properly obtained ab initio intensities are, in all but a few cases, superior to data provided by experiment (Lodi et al. 2011).

The ab initio PES, however, cannot deliver rotation–vibration energies with sufficiently high accuracy. It is therefore common to empirically refine ab initio PESs by least-squares fitting to experimental energies or frequencies to give a 'spectroscopic' PES; such potentials can provide theoretical line positions with near-experimental accuracy. When performing such fits it is important to prevent the refined surface from distorting into unrealistic shapes in regions not well characterized by the experimental data. To this end,

we impose an additional constraint requiring that the refined PES remains relatively close to the underlying ab initio PES (Yurchenko et al. 2008). Technically this is done by simultaneous fitting of the potential parameters function both to the experimental (rotation–) vibration energies and to the (lower weighted) ab initio energies (Yurchenko et al. 2003); this is an efficient and, as yet, not widely used procedure.

As mentioned above, the MARVEL procedure (Furtenbacher et al. 2007) provides a rigorous protocol for extracting experimental energy levels from the observed data. So far this protocol has largely been applied to water and the results are only just being incorporated into line lists (Lodi & Tennyson 2012). We will make extensive use of MARVEL during the ExoMol project; note that the 'Active' means that the results can be updated as more or improved laboratory measurements become available by simply including these measurements and re-running the process. The original HCN/HNC line list (Harris et al. 2002) was already updated in this fashion (Harris et al. 2006) and extended to $H^{13}CN/HN^{13}C$ (Harris et al. 2008) using empirical energy levels, although not the ones obtained using MARVEL. This procedure took advantage of our preferred data structure which separates the line lists into energy and transitions files, and which is discussed in Section 3.6.

There are essentially two different approaches to the construction of the rotation–vibration Hamiltonian. Hamiltonians based on use of an exact kinetic energy (EKE) operator for the nuclear motion of the molecule in question are expressed in terms of geometrically defined internal coordinates (Tennyson & Sutcliffe 1982). EKE calculations are potentially very accurate, since the EKE approach can provide an exact (within the Born–Oppenheimer approximation) evaluation of the corresponding matrix elements (Tennyson 2012). However, in order to achieve this high accuracy, very substantial computer resources may be needed. Consequently, the EKE approach is the method of choice for triatomics but its use has to be reviewed on a case-by-case basis for larger systems to ensure that the calculations are tractable.

As an alternative, the kinetic energy operator can be defined as a Taylor series in some vibrational coordinates with expansion parameters obtained numerically (Yurchenko et al. 2007). Such a non-EKE approach can be adopted for the larger molecules, some tetratomics and methane. The rotation–vibration coordinates are chosen to minimize the coupling between rotation and vibration. The vibrational coordinates are taken essentially as the Cartesian displacements of the nuclei from their positions when the molecule is at equilibrium. For molecules with large amplitude motions, such as HOOH, we can follow the HBJ method of Hougen, Bunker & Johns (1970) and expand the nuclear kinetic energy operator in terms of the small-amplitude vibrational coordinates from a flexible reference configuration, i.e. around the large-amplitude coordinate. In our extensions of the HBJ theory, the eigenvalues and eigenfunctions of the expanded Hamiltonians are determined variationally by numerical diagonalization of a matrix representation of the expanded Hamiltonian. This procedure is implemented in the program TROVE of Yurchenko et al. (2007).

For the largest molecules to be considered, those which have five or more atoms (apart from methane), nuclear motion calculations will be performed using new procedures. These will be based on the use of more approximate methods, such as MULTIMODE (Carter & Bowman 1998), DEWE (Mátyus et al. 2007) or an adaption of TROVE, which use normal coordinates and are more appropriate for fairly rigid molecules. These calculations will not be as accurate as those proposed for smaller systems and therefore extensive tuning to experimental data will be required. Furthermore, the potentially huge number of lines required to reproduce a line-by-line spectrum for these species at even moderately high temperature is likely to be prohibitive.

For diatomic and triatomic systems we will generate full line lists in which each rotation–vibration transition is explicitly calculated. For tetratomics and methane, this will also be done where computationally feasible. Otherwise vibrational band intensities and Hönl–London factors will be used to give transition intensities, while the calculated energy levels and hence frequencies will be obtained from calculated, vibrationally averaged rotational constants.

A number of steps will be undertaken to ensure the accuracy of our final line lists. For each system we will initially compute a less comprehensive, low-temperature line list which can be checked for reliability against available laboratory spectra. This step has proved to be fundamental to the success of our recent line list calculations. We note that in the case of methane there are extensive laboratory data, particularly in the near-infrared, which have so far defied analysis. It is to be anticipated that our line lists will help resolve these problems as has been the case previously for H_3^+, water and the HCN/HNC system.

3.1 Diatomics

For many diatomics it is necessary to consider electronic transitions. Best results will rely on the availability of laboratory frequency measurements. Such measurements are, of course, more reliable than we can calculate but are rarely complete, especially for elevated temperatures. Laboratory data are available for the majority of systems such as the extensive data set of NiH transition frequencies and associated energy levels that have recently become available (Ross et al. 2012). However, it is extremely difficult to construct a complete, high-temperature line list only from directly measured data; for example the cited NiH spectra contain no usable information on transition intensities. This makes the construction of a reliable theoretical model essential.

Treatment of the nuclear motion problem for diatomics case is relatively straightforward. For uncoupled electronic states, we will simply use the program LEVEL by Le Roy (2007). In more complicated cases, where strong coupling between different electronic states is important, it will be necessary to consider this coupling explicitly in the calculation. Marian (1995, 2001) has developed a practical theory for such calculations. A program to include couplings between electronic states already exists (Zaharova et al. 2009) but will need to be extensively generalized to cover the many different types of couplings that will be encountered during the project. Given this, the main issue determining the accuracy of the calculations is therefore the one of obtaining reliable potential energy curves, curve couplings and transition dipoles.

Our strategy here will be to start from high-grade ab initio methods: multireference configuration interaction (MRCI) expansions based on full-valence complete active space, self-consistent-field reference states utilizing large Gaussian basis sets such as aug-cc-pV6Z to resolve valence electron correlation effects. Core and core-valence correlations and scalar relativistic energy corrections will also be added. Such features are all standard in quantum chemistry programs such as MOLPRO (Werner et al. 2010), MOLCAS (Aquilante et al. 2010) and COLUMBUS (Lischka et al. 2001).

High-quality ab initio potential energy and interstate coupling curves will provide the starting point for further refinement. This will take two forms.

(i) Ab initio methods will be used to determine relativistic effects, and in particular relativistic spin orbit and other couplings between nearby curves.

(ii) Spectroscopic data will be used initially to test curves and then to refine them to give curves that reproduce observed spectra. Much of this can be done with program DPOTFIT (Le Roy 2006), although this procedure may need extending to deal with molecules whose electronic states are strongly coupled.

Work on diatomic line lists is actively underway and the following paper (Yadin et al. 2012) reports line lists for the $X\,^2\Sigma^+$ states of BeH, MgH and CaH.

3.2 Triatomics

As there are good line lists for the key triatomic species H_2O, CO_2, HCN/HNC and H_3^+, relatively few triatomic line lists are planned. Species to be considered include H_2S, C_3 and SO_2. The nuclear motion problem for these species will be solved using the EKE DVR3D triatomic code (Tennyson et al. 2004), which has already been extensively adapted for the requirement of generating large line lists. For example, the algorithm to compute dipole transition intensities was both reworked and parallelized to cope with the requirements of these calculations.

A very accurate spectroscopic H_2S PES was constructed by Tyuterev, Tashkun & Schwenke (2001); this will provide a good starting point although further work will be required to ensure that it remains reliable for higher lying states. Some work on the role of minor corrections to the PES has already been performed (Barletta et al. 2002). The DMS for H_2S is less straightforward as H_2S has a known feature that the dipole associated with the asymmetric stretch passes through zero close to the equilibrium geometry making the DMS very sensitive to the level of theoretical treatment used to model it. A DMS calculated by Cours, Rosmus & Tyuterev (2002) purports to deal with this problem, but in our tests it has not been found to be uniformly reliable. Therefore, a new higher level theoretical treatment will be needed to give a satisfactory solution to this problem. The procedures developed to produce an essentially exact DMS for water (Lodi et al. 2008, 2011) will be used to determine the level of treatment appropriate for H_2S. In particular, the DMS calculations will use finite differences rather than expectation values which will allow us to test the appropriate level at which to introduce relativistic and other 'minor' effects prior to launching a full determination.

A C_3 line list was produced by Jørgensen et al. (1989), one of the very early ones to be produced. However, this line list is no longer accurate by modern standards. C_3 is a complicated quasi-linear system with an exceptionally flat PES which supports many low-frequency bending modes (Spirko, Mengel & Jensen 1997). These have been probed via electronically excited states using stimulated emission pumping (Rohlfing & Goldsmith 1989; Northrup & Sears 1990; Rohlfing & Goldsmith 1990) or laser-induced fluorescence (Rohlfing 1989; Baker, Bramble & Hamilton 1993). Some preliminary work on constructing a new C_3 line list has been performed (Tennyson et al. 2007) which was based on measurements (Saha & Western 2006) and ab initio calculations (Ahmed, Balint-Kurti & Western 2004) performed in Bristol. A first task will be to improve our current PES by performing a new ab initio calculation and then tuning to the available data.

The third triatomic for which a line list will be computed is SO_2. This is a known constituent of Solar system planetary atmospheres (Na, Esposito & Skinner 1990).

3.3 Tetratomics

Two different codes will be used for treating the tetratomic nuclear motion problem. TROVE (Yurchenko et al. 2007) has already been used to compute an ammonia line list (Yurchenko et al. 2011a) and will be used for phosphine (PH_3) and formaldehyde (H_2CO). However, this code is not appropriate for systems which probe linear geometries such as the linear acetylene (HCCH). For this molecule the EKE code WAVR4 (Kozin et al. 2004) will be employed; indeed acetylene was one of the molecules the code was originally developed to treat (Kozin et al. 2005).

A preliminary acetylene line list was computed by Urru et al. (2010). This calculation gave reasonable results for spectra simulated using vibrational (i.e. $J = 0$) wavefunctions and vibrational band intensities (Le Sueur et al. 1992) with the rotational fine structure given by vibrational-state-dependent rotational constants, and intensities computed using Hönl–London factors. We will aim to produce an improved line list based on a fully coupled rotation–vibration calculation but first further work will be required on both the PES and DMS. In this context we note the recent emission spectra of hot acetylene obtained by Moudens et al. (2011). In addition, we will produce a line list for HOOH which is naturally treated using the diatom–diatom coordinate option available in WAVR4.

Phosphine should be amenable to the the same treatment as ammonia and has already been the subject of preliminary, low-temperature studies (Yurchenko et al. 2006; Ovsyannikov et al. 2008; Sousa-Silva, Yurchenko & Tennyson 2012). Formaldehyde is the final tetratomic planned. This has lower symmetry than the other tetratomics discussed so will be computationally the most demanding. However, a high-quality, spectroscopically determined PES has recently been developed for this molecule (Yachmenev et al. 2011) which will make an excellent starting point for a line list calculation.

3.4 Methane

The detection of methane in exoplanet HD189733b (Swain et al. 2008) was notable for the failure to determine the actual quantity due to the lack of appropriate laboratory data. Similar problems dogged studies of the impact of comet Shoemaker-Levy 9 with Jupiter (Dinelli et al. 1997), and also the interpretation of spectra of brown dwarfs (Homeier, Hauschildt & Allard 2003), where the desperate resort of modelling them using methane spectra taken from Solar system gas giants and Titan has been used (Geballe et al. 1996). Methane is, of course, also an important greenhouse gas as well as being a constituent of many flames. There has been for some time, a clear and pressing need for a comprehensive data base of methane transitions. However, this is a seriously challenging problem involving the calculation of many billions of vibration–rotation transitions. Advances in computer power and nuclear motion treatments mean that it is becoming technically possible to contemplate a full and systematic computational solution to the methane opacity problem.

There has already been some work in this direction. Schwenke (2002) performed some preliminary studies with a view to computing a line list. More recently, Warmbier et al. (2009) did compute a line list using the code MULTIMODE (Carter & Bowman 1998). However, this line list has neither the number of transitions nor the accuracy required for models of exoplanet spectra, or indeed the other applications anticipated here. Currently, the main source of methane spectra is HITRAN (Rothman et al. 2009), which is only really appropriate for temperatures below 300 K and is still not

complete, or the low-resolution Pacific Northwest National Laboratory (PNNL) data base (Sharpe et al. 2004). There has recently been significant and coordinated experimental activity to try to understand methane spectra and create corresponding line lists (Albert et al. 2009; Wang et al. 2012), in particular to aid the interpretation of Titan spectra.

Methane is a 10-electron system like water (and ammonia): for water there are well-developed procedures for obtaining an ultra-high accuracy PES (Polyansky et al. 2003); application of these procedures should be easier for methane since it is possible to use the faster coupled-clusters approaches, such as CCSD(T), instead of MRCI because of the simpler topology of its PES. Methane has nine degrees of vibrational freedom compared to water which only has three and will therefore require the calculation of significantly more geometries. However, methane's symmetry reduces this number by a factor of 24 and use of modern computers should allow us to calculate upwards of 50 000 points in a few months using MOLPRO (Werner et al. 2010) even with no frozen core, a large (6Z level) or F12 basis set (Hill, Mazumder & Peterson 2010) while also including allowance for relativistic and adiabatic corrections. This potential can be improved using the extensive experimental data sets referenced above.

The much more difficult steps are the calculation of the 12D rotation–vibration wavefunctions and the subsequent calculation of all the associated transition intensities: it is to be anticipated that the final line list will comprise many billions of transitions. There are two possible strategies for solving this problem. In both cases the vibrational calculations will be performed with an upgraded and parallelized version of TROVE (Yurchenko et al. 2007). A strong point of TROVE is the automatic and general treatment of symmetries; this is important not only because maximizing the use of symmetry will help to keep the calculation tractable but also because symmetry is necessary to get nuclear spin effects correct when generating spectra.

The comprehensive solution is to use TROVE to simply compute all possible vibration–rotation transitions directly. The calculation of highly rotationally excited states (J up to 40) and, even more so, the calculation of huge lists of dipole transitions are computationally demanding in the extreme. It is unclear yet, both because the necessary benchmark calculations need to be performed and because of uncertainty about what computer power will be available, whether this approach will be completely feasible or only so in part.

A more pragmatic, but still reliable, approach is to follow that already used for the preliminary acetylene calculations (Urru et al. 2010). Well-converged wavefunctions from a $J = 0$ (i.e. vibration only) calculation will be used to compute (a) vibrational band intensities and (b) vibrational-state-dependent rotational constants. The rotational constants will be used to generate the required energy levels and transition frequencies. Vibrational band origins will be combined with so-called Hönl–London factors (well known for the high-symmetry methane molecule) to give the intensity of individual rotation–vibration transitions.

3.5 Larger molecules

A characteristic of hot molecules is that their spectra become very congested with many blended lines. For heavier molecules this limit can be reached at room temperature. Thus, for example, the HITRAN data base (Rothman et al. 2009) stores all data on species with four or more heavy atoms (about 30 species) as cross-sections rather than fully resolved line lists. However, cross-section data

are only applicable at the temperature of the measurement, usually room temperature. This is a severe disadvantage which makes the data inflexible. For example, it would be very difficult to use this cross-section data in atmospheric models of an earth-like planet even when there is only a relatively small temperature differential to earth, say for a super-earth at 350 K.

Conversely the use of variational procedures such as the one outlined above for these heavy systems would be both computationally very expensive and of much lower accuracy than would be required. We therefore propose a rather more empirical approach to address this problem.

The Watson (1968) Hamiltonian provides a general formulation for the nuclear motion of polyatomic systems which is particularly well suited for use with semirigid molecule. This Hamiltonian uses normal modes, and for well-behaved systems it is possible to simplify calculations by neglecting high-order coupling terms. This is the basis of the MULTIMODE approach of Carter & Bowman (1998) and DEWE (Mátyus et al. 2007); TROVE can also be adapted to work in this fashion. MULTIMODE has proved capable of giving reasonable results for the rotation–vibration spectra of relatively large molecules (Wang et al. 2008).

Calculations based on Watson's Hamiltonian will be used to model room temperature spectra of the species of interest, namely HNO_3, C_2H_4, C_2H_6 and C_3H_8. The calculations will use ab initio potentials largely represented by expansions about equilibrium in terms of force constants and higher order terms. These constants will be calculated ab initio as derivatives at equilibrium, empirically determined if available or a mixture of the two. For some large amplitude modes, such as the CH_3 rotations, full potentials will be used. The PES and, if necessary, the associated dipole moments will be systematically tuned to reproduce the measured room temperature cross-sections for each system. Initially this will have to be done essentially by trial and error. However, with several systems to work on it is anticipated that we should be able to develop systematic procedures for this tuning.

Having developed satisfactory room temperature models for each system, calculations will be repeated at a grid of temperatures to give temperature-dependent cross-sections. Experimental data such as those by Lorono Gonzalez et al. (2010) for C_2H_4 will be used to either confirm the model or to provide further input for an improved tuning procedure.

The final output of this model will be cross-sections, since at higher temperatures the number of individual lines will simply be vast and there is little prospect of high-resolution spectra of these species being fully resolved in astronomical observations in the near future.

3.6 Partition functions

Partition functions are important for models of hot molecules and not altogether straightforward to compute. Extensive compilations of partition functions of astrophysically important species have been made by Irwin (1981) and Sauval & Tatum (1984). These compilations are comprehensive but do not cover all the molecules to be considered in the ExoMol project; the partition function values themselves could also, undoubtedly, be improved at higher temperatures. Partition functions which can be considered reliable over an extended temperature range have been constructed for a number of polyatomic molecules including H_3^+ (Neale & Tennyson 1995), water (Vidler & Tennyson 2000), HCN/HNC (Barber et al. 2002) and recently acetylene (Amyay, Fayt & Herman 2011).

In general the partition function is given by

$$Z(T) = \sum_i g_i e^{-c_2 E_i / T}, \qquad (1)$$

where c_2 is the so-called second radiation constant and is appropriate when the energy, E_i, is given as a term value in cm^{-1}, T is the temperature and g_i is the statistical weight factor. The statistical weight deserves a special comment.

If the hyperfine structure is to be unresolved the statistical weight factor is given by

$$g_i = (2S + 1)\, g_{\mathrm{ns}}^{(i)}\, (2N_i + 1), \qquad (2)$$

where S is the total electronic spin angular momentum, $g_{\mathrm{ns}}^{(i)}$ is the state-dependent nuclear statistical weight and N_i is the rotational angular momentum of the nuclei of the ith state. If the spin-dependent states are resolved the statistical weight factor becomes

$$g_i = g_{\mathrm{ns}}^{(i)}\, (2J_i + 1), \qquad (3)$$

where J_i is total angular momentum of the ith state ($\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S}$). In equations (2) and (3) the hyperfine structure is assumed to be unresolved. We follow the HITRAN convention (Simeckova et al. 2006) and include the entire nuclear statistical weight $g_{\mathrm{ns}}^{(i)}$ of the molecule explicitly in g_i and hence the partition function $Z(T)$. For example, for BeH where ^{9}Be and H have nuclear spins 3/2 and 1/2, respectively, $g_{\mathrm{ns}}^{(i)} = 8$. If, as can be assumed for BeH (Yadin et al. 2012), the spin-rotation coupling for the ground electronic state $X\,^2\Sigma^+$ is unresolved, then each of rovibronic states i is assumed to be doubly $(2S + 1)$ degenerate. According to equation (2) the statistical weight factor of BeH is then given by $g_i = 2 \times 8 \times (2N_i + 1) = 16\,(2N_i + 1)$. If the spin-dependent states are resolved then according to equation (3) $g_i = 8\,(2J_i + 1)$. For the ^{12}C^{12}C molecule whose nuclear spin is 0, the statistical weights g_{ns} of the symmetric s and antisymmetric a rotational levels are 1 and 0, respectively. In the case of the $X\,^1\Sigma^+$ ground electronic state of this molecule $g_{\mathrm{e}} = 1$ and the statistical weight factors g_i are $(2J_i + 1)$ and 0 for the s and a states, respectively.

We note that the partition function Z can be used to estimate the completeness of a line list as a function of temperature. This can be done by comparing the ratio of the partition function computed by summing over all lower state energy levels used to compute the line list to the accurate partition function (Neale et al. 1996; Barber et al. 2006). Indeed this ratio can even be used to make corrections for the missing contribution to, for example, the cooling function (Neale et al. 1996).

3.7 The ExoMol data base

The backbone of the ExoMol data base will be line lists of transitions. However, the data base will include a variety of associated and ancillary data. These will include energy levels, partition functions, cooling functions and cross-sections.

The large amount of data produced in the above calculations, both completed and anticipated, require the development of strategies for data handling and distribution. For small line lists, which are likely to include most diatomics, a simple line list will be stored. However, for larger line lists we will employ a data structure which involves organizing our final line list into two files: an energy file and a transitions file. The energy file will contain energy levels for each state combined with a number for its position in the file and quantum number assignments, both rigorous and approximate. The transitions file will be arranged in ascending frequencies and will list only the number of the upper and lower states for each transition plus the associated Einstein A-coefficient. This provides a very compact means of representing the data which are essential for efficient use of storage. However, it is likely that the transition file will still need to be split into frequency bins for ease of distribution.

This data structure has other important advantages. It will also allow us to actively update the energy file with measured rotation–vibration energy, or indeed improved approximate quantum numbers, ensuring the best possible for each transition. Indeed Harris et al. (2008) turned an H^{12}CN/HN^{12}C line list into one for H^{13}CN/HN^{13}C by replacing the energy file with one appropriate for ^{13}C; this approach relied on the not unreasonable assumption that the Einstein A-coefficients do not change significantly between the two isotopologues.

The sheer volume of data contained in the line lists makes them fairly tricky to use. In practice most codes will use some sort of opacity or important sampling technique to identify key transitions and discard the rest. We have, however, constructed a set of zero-pressure, temperature-dependent cross-sections for the key species studied so far (Hill, Yurchenko & Tennyson 2012). The purpose of these is not to replace the underlying line lists, whose use will remain necessary for detailed studies and analysis of high-resolution spectra, but to allow the effects of adding a species to a model to be quickly and efficiently tested. The use of these cross-sections avoids the issues of handling huge line lists at the price of assuming local thermodynamic equilibrium and some loss of flexibility. The issue turning the line lists into cross-sections will be discussed elsewhere (Hill et al. 2012).

The results of the calculations outlined above will be a comprehensive data base of molecular transitions. The ExoMol data base, see www.exomol.com, will include not only the line lists, cross-sections cooling functions, partition functions and other data generated during the project, but will also provide access to those already available. The data base is web based and our aim will be to integrate it into the Virtual Atomic and Molecular Data Centre (VAMDC) project (Dubernet et al. 2010). VAMDC data storage is based on the use of XML Schema for Atoms, Molecules and Solids (XSAMS). XSAMS (Dubernet et al. 2011) is an XML-based data storage protocol which has been designed by the International Virtual Observatory Alliance to meet the needs of astronomers who wish to describe or access molecular (and other) data in distributed data sets worldwide.

XSAMS is both flexible and intuitive, making data manipulation and interpretation significantly easier and less error prone. However, the format is very verbose and in its current form it does not seem suitable for storing massive line lists such as individual lists with more than 10^{10} lines which are to be anticipated from the ExoMol project. This will require the development of new protocols and, presumably, adaptation of XSAMS.

Finally, we note that the recent test of models of water spectra in hot Jupiter exoplanet (Tinetti et al. 2012a) suggests that pressure broadening can have a significant influence, particularly at long wavelengths. This means that pressure broadening parameters, particularly those associated with collisions with H$_2$, should also be considered for inclusion in the ExoMol data base at some future date.

4 CONCLUSION

This paper lays out the scope and methodology for a new project, ExoMol, whose aim is to provide comprehensive line lists of molecular transition frequencies and probabilities. The major aim of this project is to provide the necessary data to model atmospheres

and interpret spectra for exoplanets and cool stars. However, it is recognized that the line lists will have many other applications within astrophysics and beyond. For example, it is our practice not to exclude transitions from our lists simply because they are too high in energy to be thermally occupied. This has already led to the identification of new class of very vibrationally hot water emissions in comets (Barber et al. 2009). It is to be anticipated that such data will be important for assigning and modelling maser emissions from high-lying or hot states. Similarly the data base will be available for modelling what may be observable in exoplanet characterization missions such as the proposed *Exoplanet Characterisation Observatory* (EChO) (Tinetti et al. 2012b) or *FINESSE* (Swain 2010) space-borne telescopes.

The ExoMol project will generate very extensive line lists. These will be documented in this journal and deposited in the linked Strasbourg data repository. The line lists, and other information about the project, will also be made available via the ExoMol website, www.exomol.com.

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