

# ExoMol molecular line lists – XXXV. A rotation-vibration line list for hot ammonia

Phillip A. Coles, Sergei N. Yurchenko and Jonathan Tennyson  

*Department of Physics and Astronomy, University College London, London WC1E 6BT, UK*

Accepted 2019 October 1. Received 2019 September 30; in original form 2019 August 8

## ABSTRACT

A new hot line list for  $^{14}\text{NH}_3$  is presented. The line list CoYuTe was constructed using an accurate, empirically refined potential energy surface and a CCSD(T)/aug-cc-pVQZ ab initio dipole moment surface of ammonia, previously reported. The line list is an improvement of the ammonia line list BYTe. The CoYuTe line list covers wavenumbers up to  $20\,000\text{ cm}^{-1}$ , i.e. wavelengths beyond  $0.5\ \mu\text{m}$  for temperatures up to 1500 K. Comparisons with the high temperature experimental data from the literature show excellent agreement for wavenumbers below  $6000\text{ cm}^{-1}$ . The CoYuTe line list contains 16.9 billion transitions and is available from the ExoMol website ([www.exomol.com](http://www.exomol.com)) and the CDS data base.

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

## 1 INTRODUCTION

Ammonia is the major nitrogen-containing molecule observable in a number of astrophysical environments. For example, its spectral signature has long been observed in the atmospheres of Jupiter, Saturn, and Titan (Woodman, Trafton & Owen 1977). Emissions from hot ammonia were observed following the collision of comet Shoemaker–Levy 9 with Jupiter (Orton et al. 1995) and recent analysis has shown ammonia absorption features in the visible spectrum of Jupiter (Irwin et al. 2018). These features were poorly represented by data available in standard data bases but could be modelled using a preliminary version of the line list presented here (Irwin et al. 2019).

Although attempts to detect ammonia in the atmosphere of an exoplanet have so far proved inconclusive (Beaulieu et al. 2011), it is thought to be an important component of the chemistry of hot Jupiter exoplanets (MacDonald & Madhusudhan 2017). On Earth, atmospheric ammonia is often associated with human activity such as biomass burning (Hegg et al. 1988). It has been proposed as a promising biosignature in  $\text{H}_2$ -dominated atmospheres on rocky exoplanets (Seager, Bains & Hu 2013). Line lists, such as the one presented here, are important for modelling spectra that might be observed in future space missions (Danielski et al. 2018; Tinetti et al. 2018).

Ammonia has recently been observed in a planet-forming disc (Salinas et al. 2016); circumstellar ammonia spectra can only be understood using a non-LTE multilevel radiative transfer model, which includes the effects of near-infrared (NIR) radiative pumping through vibrational transitions (Schmidt et al. 2016). Similarly,

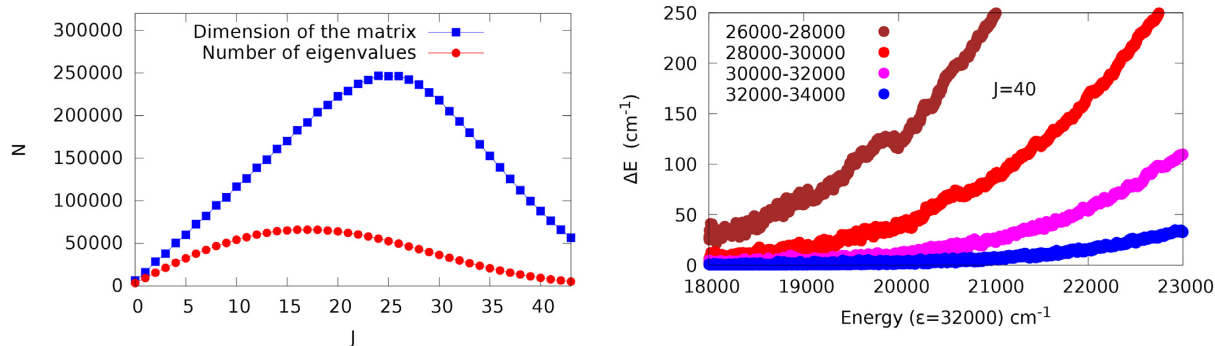
interstellar ammonia has long been observed to mase (Madden et al. 1986) and non-LTE spectra of ammonia have been observed in comets where its signature has been seen in fluorescence (Villanueva, Magee-Sauer & Mumma 2013).

Detailed ammonia spectra have been observed, and partially assigned, in the spectra of cool brown dwarfs (Bochanski et al. 2011; Carty et al. 2015); its presence has been used as a tracer of chemical equilibrium in T dwarfs (Saumon et al. 2006). The spectrum of ammonia is generally assumed to be a signature of Y dwarfs (Lucas et al. 2010; Saumon et al. 2012). However, recent observations of Y dwarfs suggest that the ammonia abundance may be lower than anticipated (Leggett et al. 2015; Morley et al. 2018).

Modelling or interpreting the spectrum of hot or non-LTE ammonia requires a substantial quantity of laboratory data. To this end a number studies of ammonia have been performed with the view of producing extensive line lists of spectroscopic transitions (Yurchenko et al. 2009; Huang, Schwenke & Lee 2011a,b; Yurchenko, Barber & Tennyson 2011; Hargreaves, Li & Bernath 2012; Yurchenko 2015; Coles et al. 2019). Notable amongst these are the BYTe line list of Yurchenko et al. (2011) and the HSL-pre3 line list (Huang & Lee 2013) of Sung et al. (2012). The transition frequencies predicted by HSL-pre3 are generally more accurate than those of BYTe but HSL-pre3 does not provide transition intensities. BYTe was the first, comprehensive line list capable of modelling the opacity and spectrum of hot ammonia. BYTe contains 1.1 billion transitions but becomes increasing less accurate in the NIR and is largely not useful at visible wavelengths. A preliminary, low-temperature version of the CoYuTe line list, called C2018, has been used to successfully model visible absorption by ammonia in Jupiter (Irwin et al. 2019).

This paper presents a new line list for hot ammonia called CoYuTe. CoYuTe is constructed as part of the ExoMol project

\* E-mail: [j.tennyson@ucl.ac.uk](mailto:j.tennyson@ucl.ac.uk)



**Figure 1.** Left – Dimensions of the  $E'$ -symmetry matrices (squares) and the corresponding number of eigenvalues below  $23\,000\text{ cm}^{-1}$  (circles). Right – Basis set convergence of  $J = 40$  ( $E'$  symmetry) energies as ( $J = 0$ )-contracted basis set threshold  $\epsilon$  is increased from 26 000 to 34 000. The difference  $E_{\epsilon=x} - E_{\epsilon=x+2000}$ , is displayed for  $x = 26\,000, 28\,000, 30\,000, 32\,000$  versus the energies computed using  $\epsilon = 32\,000\text{ cm}^{-1}$ .

(Tennyson & Yurchenko 2012), which aims to provide comprehensive line lists for studies of exoplanets and other hot or non-LTE atmospheres. CoYuTe can be seen as the logical successor to BYTe. It improves on the accuracy of BYTe by using a significantly improved potential energy surface (Coles et al. 2018), using empirical energy levels (Al Derzi et al. 2015; Coles et al. 2019), where available, to replace computed ones which is of particular importance for high resolution spectroscopic studies, and improvements in the variational nuclear motion code TROVE (Yurchenko, Thiel & Jensen 2007; Al-Refaie, Yurchenko & Tennyson 2017; Tennyson & Yurchenko 2017) made as part of the ExoMol project. The following sections detail the method used to compute the CoYuTe line list with particular emphasis on these improvements before discussing the final line list.

## 2 METHOD

Construction of a rotation-vibration line list requires three things: a potential energy surface (PES), dipole moment surface (DMS), and a nuclear motion program (Lodi & Tennyson 2010). In this work we use the newly created C2018 PES of Coles et al. (2018). Improvements in this potential were facilitated by recent significant progress in assigning ammonia spectra in the NIR (Xu et al. 2004; Li, Lees & Xu 2007; Lees, Li & Xu 2008; Sung et al. 2012; Barton et al. 2016, 2017a) and visible (Zobov et al. 2018) regions, as well as the availability of new hot ammonia spectra (Hargreaves, Li & Bernath 2011; Hargreaves et al. 2012; Barton et al. 2015, 2017b; Beale et al. 2017).

As part of this work we constructed a new multireference configuration interaction (MRCI; Werner & Knowles 1988; Knowles & Werner 1992) DMS using a large, aug-cc-pwCVQZ basis set (Dunning 1989; Kendall, Dunning & Harrison 1992; Peterson & Dunning 2002). However, detailed comparisons with a variety of observations (Coles 2019) showed that the DMS of Yurchenko et al. (2009) contracted using the CCSD(T)/aug-cc-pVQZ level of theory used to compute BYTe gave better agreement with observations. The issue here is not so much the level of theory used but the CCSD(T) DMS by Yurchenko et al. (2009) was generated on a substantially larger grid of points than we could afford for the more computationally expensive MRCI calculations. Choice of an extended grid is well known to be crucial in getting a good representation of a DMS (Tennyson 2012).

The program TROVE was used to perform the nuclear motion calculations (Yurchenko et al. 2007). TROVE has undergone a

number of updates since the construction of BYTe with a particular focus on the production of large line lists (Tennyson & Yurchenko 2017). Particularly important is the development of the program GAIN (Al-Refaie et al. 2017), which provides a highly efficient means of computing transition dipoles using GPUs; traditionally this step used to dominate the computer time requirement but GAIN speeds the process up by a factor of about 100. This meant that for CoYuTe construction and diagonalization of the Hamiltonian matrix became the computer-resource limiting step.

Nuclear motion calculations were performed on the Darwin and COSMOS high-performance computing (HPC) facilities in Cambridge, UK. At the time of performing these calculations, each of the computing nodes on the Darwin cluster provided 16 CPUs and a maximum of 64 Gb of RAM, with a wall clock limit of 36 h. COSMOS provided 7.3 Gb per CPU and 8 CPUs per node, with a maximum standard job size of 448 Gb and a wall clock limit of 12 h. Since multiple nodes can be accessed by a single user at any time, multiple computations could be carried out simultaneously. Our approach to constructing and diagonalizing the Hamiltonian matrix for  $\text{NH}_3$  in TROVE is the same as used by Underwood et al. (2016) for  $\text{SO}_3$ , which involves three steps. First the Hamiltonian is calculated and saved to disc. It is then diagonalized separately for each  $J$  and symmetry ( $\Gamma_{\text{tot}}$ ) using an MPI-optimized version of the eigensolver PDSYEVD (Blackford et al. 1997). Finally, TROVE reads the eigenvectors and eigenvalues and converts them into a human readable format.

TROVE uses a symmetry-adapted basis set (Yurchenko, Yachmenev & Ovsyannikov 2017). Construction of the Hamiltonian matrices for each  $J$  and  $\Gamma_{\text{tot}}$  was performed on the COSMOS HPC cluster. In total, for states with  $J = 1\text{--}43$  and symmetry blocks ( $A'_2, A''_2, E', E''$ ) this step took 725 h real time (11 737 CPU hours), and required a maximum of 223 Gb of RAM for the most expensive calculation, which corresponded to the  $E'$  symmetry block of the  $J = 25$  Hamiltonian. The process was then moved to Darwin for diagonalization, which took 272 h (real time), and for which the largest matrix to be diagonalized ( $J = 25, E'$  block) had 246 311 rows (see Fig. 1) and required the use of 24 parallel nodes.

Evaluation of the line strengths and corresponding Einstein-A coefficients was performed using the GAIN-MPI (Al-Refaie et al. 2017) program on the Wilkes2 GPU cluster at Cambridge. Each GPU node contains  $4 \times$  Nvidia P100 16 GB GPUs. With this program we were able to calculate approximately 22 000 transitions per second using up to 10 parallel nodes.

### 3 LINE LIST CONSTRUCTION

The CoYuTe line list was constructed to cover wavenumbers up to  $20\,000\text{ cm}^{-1}$ , i.e. wavelengths longer than  $0.5\ \mu\text{m}$  for temperatures up to  $1500\text{ K}$ . To this end transitions from all states with energies up to  $11\,000\text{ cm}^{-1}$  above the ground state were considered, which involved rotational states up to  $J = 43$ ; BYTe only includes states with  $J \leq 36$ . Comparison with the high temperature partition function of Sousa-Silva et al. (2014) suggests that these parameters are more than sufficient to cover temperatures up to  $1500\text{ K}$ .

An upper state energy threshold of  $23\,000\text{ cm}^{-1}$  was used. This means that a complete representation of the hot spectrum will be obtained for wavenumbers below  $12\,000\text{ cm}^{-1}$  but for wavenumbers above this value there will be some loss of opacity at higher temperatures. However, as the C2018 PES used in this work was predominantly tuned to experimental levels up to  $7254\text{ cm}^{-1}$  above the ground state, the precise location of the higher states included in the calculation is already highly uncertain and further extension to higher energies is hard to justify. The calculations truncate the  $J = 0$  contracted basis set at  $32\,000\text{ cm}^{-1}$ , this was necessary to keep within the compute limits available to us and the consequent reduction in Hamiltonian matrix dimension above  $J = 25$  is shown in Fig. 1. This truncation means that for high- $J$  states with energies close to  $23\,000\text{ cm}^{-1}$  the CoYuTe energies will not be fully converged. For  $J = 40$  levels of  $E'$  symmetry the resulting error, shown in Fig. 1, only becomes significant above approximately  $20\,000\text{ cm}^{-1}$ ; for  $J = 20$  levels the complete energy range is fully converged. It is important to note that this convergence error will affect only a minority of very weak lines that contribute to the continuum at wavelengths approaching, and into, the visible region. We therefore do not expect it to adversely affect the quality of the overall line list.

The number of lines computed is very large so it is desirable to prune the weakest lines. However, experience (Yurchenko et al. 2014) has shown that including weak lines is important for recovering the correct opacity. To balance these two issues we chose to retain all lines, which have an intensity greater than  $1 \times 10^{-36}\text{ cm}^{-1}/(\text{molec cm}^{-2})$  at  $1500\text{ K}$ . This results in  $16.9$  billion lines, which is an order of magnitude more transitions than BYTe, which contains  $1.1$  billion.

To ensure that the resulting CoYuTe line list provides transition frequencies that are as accurate as possible, we have substituted our computed energy levels with empirical ones where available. This procedure has been used for other polyatomic ExoMol line lists (Barber et al. 2014; Polyansky et al. 2018) and has been shown to give good results (Huang, Schwenke & Lee 2019). Empirical energy levels were taken from the MARVEL (measured active vibration-rotation energy levels) studies of  $^{14}\text{NH}_3$  due to Al Derzi et al. (2015) and Coles et al. (2019). At present  $4493$  out of  $5095\,730$  energy levels have been replaced, and we plan to update this as new experimental data becomes available. Transition wavenumbers between these levels should be highly accurate and, in particular, suitable for high-resolution studies of (exoplanetary) spectra. We note that at the moment the format used by the ExoMol data base (Tennyson, Hill & Yurchenko 2013; Tennyson et al. 2016) does not distinguish between those transitions that are reproduced with experimental accuracy and those that are the result of theoretical predictions. We are currently planning an update in the ExoMol data base and associated data structures to resolve this problem.

TROVE uses a local mode representation of the vibrational quantum numbers, compared to the more standard normal mode representation. Mapping between these forms is not entirely un-

ambiguous, and particular difficulties arise due to the doubly degenerate modes  $\nu_3$  and  $\nu_4$ . In order to facilitate the assignment of normal mode vibrational quantum labels to our energy levels using purely ab initio means, we apply the approach developed by Chubb, Jensen & Yurchenko (2018) in their treatment of the highly degenerate bending motion of  $\text{C}_2\text{H}_2$ . Namely, the two two-dimensional vibrational basis sets associated with  $\nu_3$  and  $\nu_4$  are transformed into eigenfunctions of the vibrational angular momentum operator squared  $\hat{L}_z^2$  using the variational method. Here,  $\hat{L}_z^2$  has been used rather than  $\hat{L}_z$  as TROVE currently only allows for the evaluation of matrix elements of the quadratic form. The operator  $\hat{L}_z^2$  commutes with the (reduced) two-dimensional Hamiltonian operator  $\hat{H}^{(2D)}$  for each of the degenerate normal modes  $\nu_3$  and  $\nu_4$ , which are treated as two-dimensional isotropic harmonic oscillators, and so eigenfunctions of  $\hat{L}_z^2$  are also eigenfunctions of  $\hat{H}^{(2D)}$ . The eigenfunctions of  $\hat{L}_z^2$  are labelled by their vibrational angular momentum quantum number  $L_i = |\ell_i| = \sqrt{\ell_i^2}$ , which does not distinguish between positive and negative components of  $\ell_i$ . For this reason we do not attempt to assign the total vibrational angular momentum  $L = |\ell_3 + \ell_4|$ , and provide only  $L_3 = |\ell_3|$  and  $L_4 = |\ell_4|$ . The vibrational angular momentum quantum numbers generated from this normal mode representation are mapped on to the local mode representation used by TROVE at the stage of solving the reduced 3D stretching, 2D bending, and 1D inversion Schrödinger equations (see Yurchenko et al. 2017), and are subsequently propagated through all full-dimensional vibrational and rotational-vibrational calculations.

### 4 RESULTS

The ExoMol data base uses a format that separates transitions into a states file (including quantum labels) and a transitions file (Tennyson et al. 2013). Extracts from these two files are given in Tables 1 and 2, respectively. These files themselves can be obtained from

<ftp://cdsarc.u-strasbg.fr/pub/cats/J/MNRAS/xxx/yy>, or <http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/MNRAS/xxx/yy> as well as the ExoMol website, [www.exomol.com](http://www.exomol.com). Updated states files will be made available at [www.exomol.com](http://www.exomol.com) as and when new empirical energy level data becomes available. In this sense users should consider this version of CoYuTe as living, whereas the CDS deposits capture the state of data base at the point of publication.

For the CoYuTe line list we follow BYTe and give vibrational quantum numbers both in the local mode form produced by TROVE ( $\nu_1, \nu_2, \nu_3, \nu_4, \nu_3, \nu_4$ ) and the more standard, for ammonia, normal mode form ( $n_1, n_2, n_3, n_4, l_3, l_4$ ). Due to the aforementioned additional step required to map from the local mode to the normal mode representation, the local mode quantum numbers should be regarded as the more reliable. To distinguish between those energies ( $\tilde{E}$ ) that have been derived from MARVEL and those that have been computed using the C2018 PES we have added an additional column ( $E_{\text{CYT}}$ ) to the states file. Where the energy  $\tilde{E}$  has been derived from MARVEL,  $E_{\text{CYT}}$  takes the theoretically determined energy value, otherwise it takes a value of  $-1.000000$ .

Partition functions can be used to determine the temperature range over which a line list is complete. Neale, Miller & Tennyson (1996) showed that completeness as a function of temperature can be quantified by the ratio of the partition sum given by the lower state energy levels to the true partition sum of the system. Sousa-Silva et al. (2014) provided converged partition sums for ammonia which extend to high temperature. Fig. 2 shows the ratio of the partition function,  $Q(T)$ , computed with the CoYuTe energy levels up to the low-energy cut-off, to the full partition function of

**Table 1.** Extracts from the final states file for the CoYuTe line list.

$i$	$\tilde{E}$	$g_{\text{tot}}$	$J$	$p$	$\Gamma$	$N_b$	$n_1$	$n_2$	$n_3$	$n_4$	$l_3$	$l_4$	$\tau_i$	$J$	$K$	$\tau_r$	$v_1$	$v_2$	$v_3$	$v_4$	$v_5$	$v_6$	$\Gamma_{\text{vib}}$	$E_{\text{CYT}}$
7779	0.793374	12	0	–	5	1	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	5	0.793374
7780	968.121906	12	0	–	5	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	3	5	968.121906
7781	1882.177407	12	0	–	5	3	0	2	0	0	0	0	1	0	0	0	0	0	0	0	0	5	5	1882.177426
7782	2895.521390	12	0	–	5	4	0	3	0	0	0	0	1	0	0	0	0	0	0	0	0	7	5	2895.521820
7783	3217.582251	12	0	–	5	5	0	0	0	2	0	0	1	0	0	0	0	0	0	0	2	1	5	3217.579464
7784	3337.097095	12	0	–	5	6	1	0	0	0	0	0	1	0	0	0	0	1	0	0	0	1	5	3337.097117
7785	4061.640928	12	0	–	5	7	0	4	0	0	0	0	1	0	0	0	0	0	0	0	0	9	5	–1.000000
7786	4173.090304	12	0	–	5	8	0	1	0	2	0	0	1	0	0	0	0	0	0	0	2	3	5	–1.000000
7787	4320.030627	12	0	–	5	9	1	1	0	0	0	0	1	0	0	0	0	1	0	0	0	3	5	4320.030627
7788	4843.355303	12	0	–	5	10	0	0	0	3	0	0	1	0	0	0	0	0	0	0	3	1	5	–1.000000

Notes:  $i$ : State counting number.

$\tilde{E}$ : State energy in  $\text{cm}^{-1}$ .

$g_{\text{tot}}$ : Total state degeneracy.

$J$ : Total angular momentum.

$p$ : Total parity of the state.

$\Gamma$ : Total symmetry index in  $D_{3h}(M)$ .

$N_b$ : Counting number in the  $(J, p, \Gamma)$  block.

$n_1$ : Symmetric stretch quantum number (normal mode).

$n_2$ : Symmetric bend quantum number (normal mode).

$n_3$ : Asymmetric stretch quantum number (normal mode).

$n_4$ : Asymmetric bend quantum number (normal mode).

$l_3$ : Asymmetric stretch vibrational angular momentum quantum number (normal mode).

$l_4$ : Asymmetric bend vibrational angular momentum quantum number (normal mode).

$\tau_i$ : Inversion parity (0 or 1).

$J$ : Total angular momentum.

$K$ : Projection of  $J$  on molecular symmetry axis.

$\tau_r$ : Rotational parity (0 or 1).

$v_1$ : Local mode vibrational quantum number.

$v_2$ : Local mode vibrational quantum number.

$v_3$ : Local mode vibrational quantum number.

$v_4$ : Local mode vibrational quantum number.

$v_5$ : Local mode vibrational quantum number.

$v_6$ : Local mode vibrational quantum number.

$\Gamma_v$ : Vibrational symmetry (local mode).

$E_{\text{CYT}}$ : Theoretical state energy in  $\text{cm}^{-1}$ .

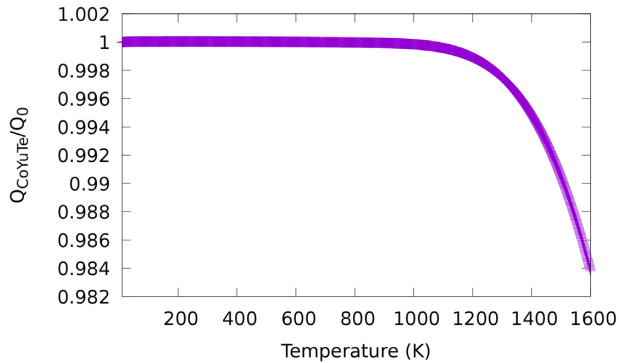
**Table 2.** Extract from the transitions file for the CoYuTe line list.

$f$	$i$	$A_{fi}$
2864780	2768903	2.69E-30
4664622	4624800	2.06E-25
4664622	4624800	2.06E-25
1785731	1883312	4.64E-25
1225073	1315315	1.86E-22
4595123	4550448	2.97E-21
1883390	1981447	2.24E-26
4751546	4716239	1.24E-20
4400507	4345966	1.33E-21
3866874	3635182	1.20E-23

Notes:  $f$ : Upper state counting number.

$i$ : Lower state counting number.

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



**Figure 2.** Ratio of CoYuTe effective partition function  $Q_{\text{CoYuTe}}$  to the full partition function of Sousa-Silva et al. (2014) ( $Q_0$ ) as a function of temperature.  $Q_{\text{CoYuTe}}$  is computed from the CoYuTe energies with  $E_{\text{max}} = 11\,000\text{ cm}^{-1}$  and  $J_{\text{max}} = 43$ .

Sousa-Silva et al. (2014). Below 1200 K this ratio remains close to unity but falls rapidly above this temperature. At 1500 K the ratio is about 0.99 and the CoYuTe line list can be regarded as effectively complete up to this temperature. It is still possible to use

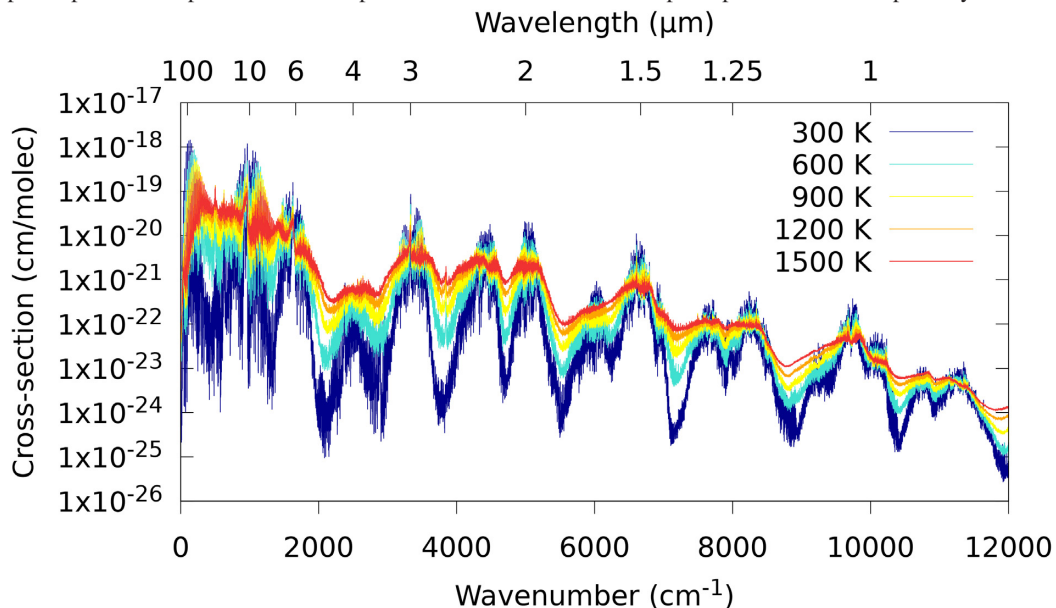
CoYuTe at higher temperatures but users should be aware that this will increasingly lead to missing opacity.

Figs 3 and 4 provide an overview of the CoYuTe line list, which has been split by wavenumber to reflect that below  $12\,000\text{ cm}^{-1}$  CoYuTe is expected to be effectively complete, but thereafter will increasingly suffer from missing opacity due to the energy thresholds employed. As is usual for such line lists, the total absorption decays approximately exponentially as wavenumber increases, and the effect of raising the temperature is to reduce the differences between the peaks and troughs in the overall absorption cross-sections.

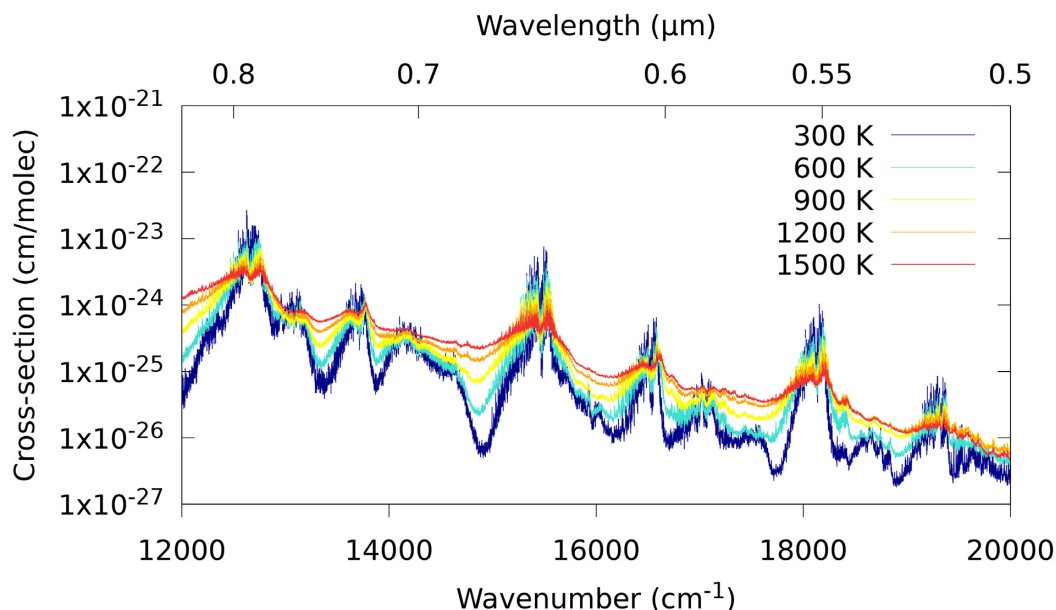
## 5 VALIDATION

Since the production of BYTe, there have been several experimental studies focusing on high temperature ammonia spectra in the NIR. To validate the application of CoYuTe to high temperature ammonia studies we performed a systematic comparison of the CoYuTe predictions with laboratory measurements from several of these sources.

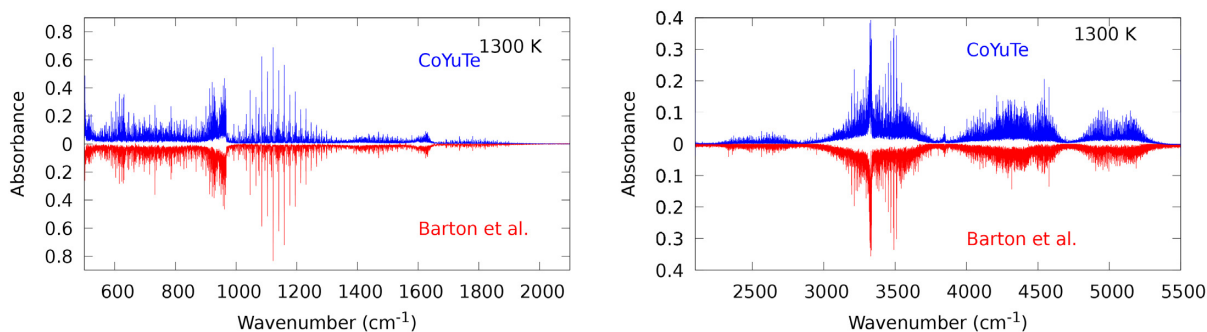
Barton et al. (2015) and Barton et al. (2017b) recorded moderate resolution ( $0.09\text{ cm}^{-1}$ ) ammonia spectra in the  $500\text{--}2100$  and  $2100\text{--}5500\text{ cm}^{-1}$  regions for temperatures up to 1300 K and atmospheric pressure using Fourier transform infrared (FTIR) spectroscopy. They provide their measured absorbance spectra, partially assigned peak lists measured at 1300 K, and accompanying experimentally derived upper state energies. Figs 5 and 6 compare synthetic absorbance spectra calculated using the CoYuTe line list to their measured spectra. For these comparisons, CoYuTe cross-sections were computed using the ExoCross program (Yurchenko, Al-Refaie & Tennyson 2018) and Voigt profiles with halfwidth at half-maximum (HWHM) of  $0.09\text{ cm}^{-1}$ . These were then converted into spectral absorbance using the procedure outlined by Barton et al. (2015). Overall agreement is very good, there are some discrepancies in magnitude for a number of strong absorbance peaks, which are predominantly due to small inaccuracies in CoYuTe transition frequencies which result in incorrect blending or separation of lines. Replacement of the CoYuTe energies computed from first principles with the empirically derived energies from



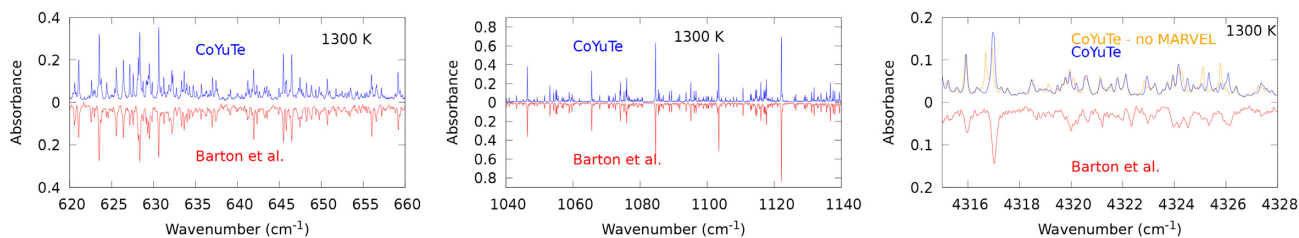
**Figure 3.** Overview of the CoYuTe line list in the  $0\text{--}12\,000\text{ cm}^{-1}$  region for temperatures up to 1500 K.



**Figure 4.** Overview of the CoYuTe line list in the 12000–20000  $\text{cm}^{-1}$  region for temperatures up to 1500 K.



**Figure 5.** Synthetic absorbance spectra computed using CoYuTe compared to the measurements by Barton et al. (2015) and Barton et al. (2017b) at a temperature of 1300 K.

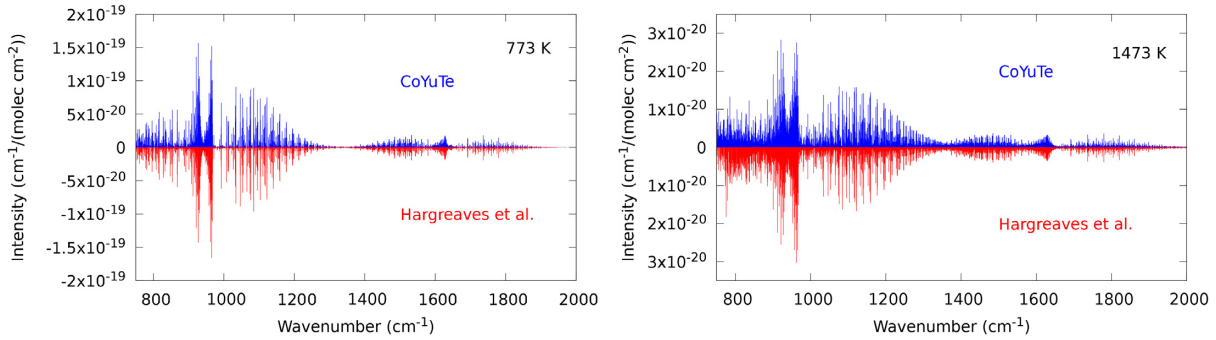


**Figure 6.** Close-up comparison of the synthetic absorbance spectra computed using CoYuTe, and the measurements by Barton et al. (2015) and Barton et al. (2017b) at a temperature of 1300 K.

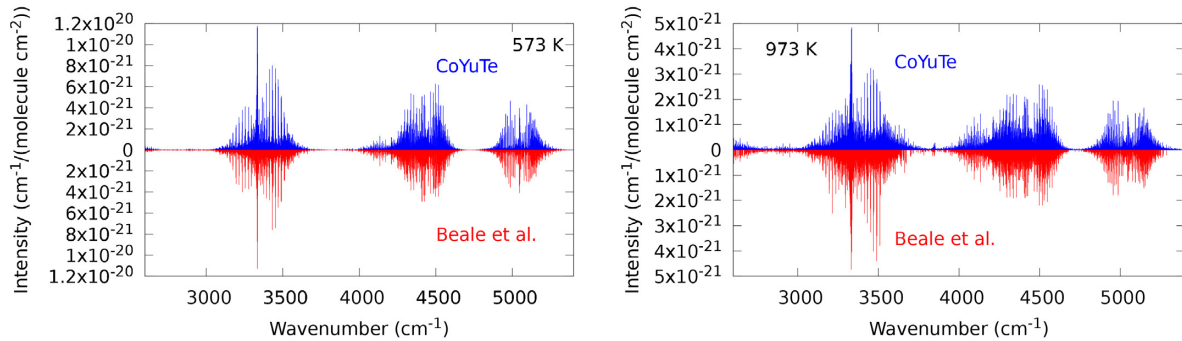
MARVEL resolve a number of these cases which would otherwise have been present in the line list, as is illustrated in the rightmost panel of Fig. 6.

Hargreaves et al. (2011), Hargreaves et al. (2012), and Beale et al. (2017) used high-resolution ( $0.01 \text{ cm}^{-1}$ ) Fourier transform infrared emission spectra to produce line lists for hot ammonia in the 740–2100, 1650–4000, and 2400–5500  $\text{cm}^{-1}$  regions, respectively. Fig. 7 makes a comparison between Hargreaves et al. (2011) and CoYuTe for temperatures of 773 and 1473 K. Fig. 8 shows a similar comparison for the work by Beale et al. (2017). There are a number of instances at 973 K where CoYuTe lines seemingly underestimate

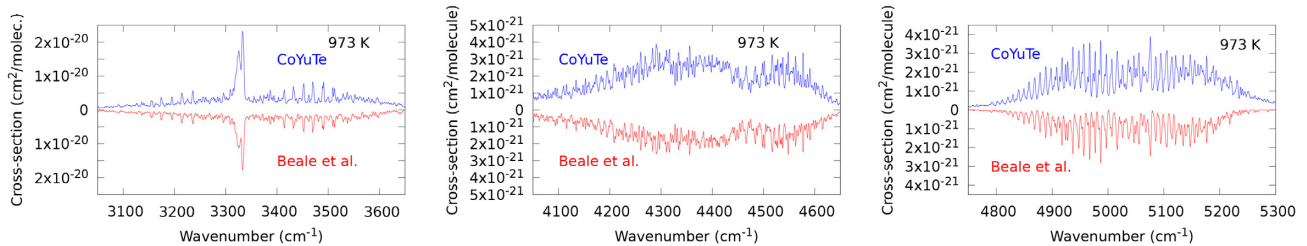
line intensities compared to those of Beale et al. This is because, despite the high-resolution nature of their spectra, a number of blended lines have gone unresolved in the experimental spectrum, resulting in two transitions in close proximity being perceived as one doubly strong transition. In this respect it is important to note the excellent agreement between absorption cross-sections (Gaussian profile, HWHM  $1.0 \text{ cm}^{-1}$ ) calculated using the CoYuTe line list and that by Beale et al. (2017), which is shown in Fig. 9. Referring back to the absorbance spectra measured by Barton et al. (2017b), shown in Figs 5 and 6, it is clear that Beale et al. (2017) are missing significant opacity.



**Figure 7.** Comparison of the ammonia line lists measured by Hargreaves et al. (2011) with the CoYuTe predictions for temperatures of 773 and 1473 K.



**Figure 8.** Comparison of the ammonia line lists measured by Beale et al. (2017) with the CoYuTe predictions for temperatures of 573 and 973 K.

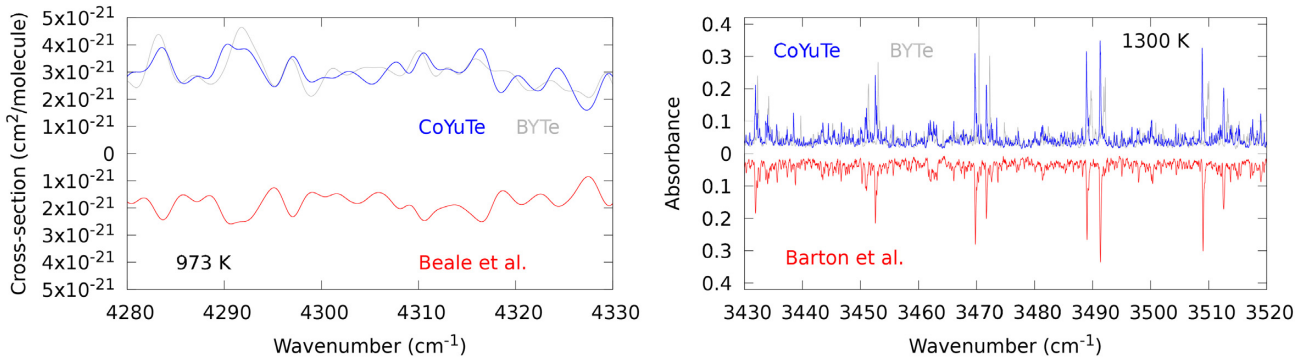


**Figure 9.** Close-up comparison of synthetic spectra generated using the experimental line list by Beale et al. (2017) and the CoYuTe line list for a temperature of 973 K. Both line lists have been convolved with Gaussian profiles with  $\text{HWHM} = 1.0 \text{ cm}^{-1}$ .

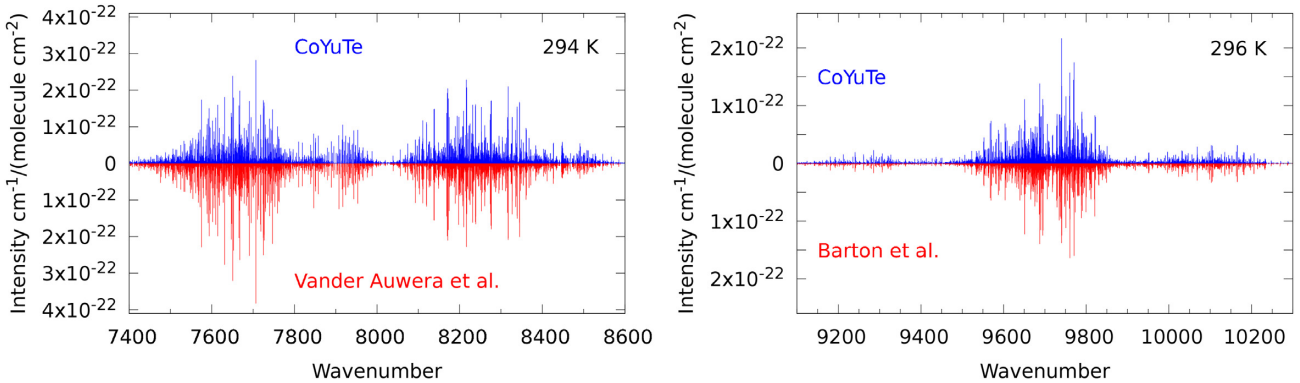
CoYuTe is the successor to BYTe, and aside from containing more opacity and extended coverage, the line positions and line intensities are significantly more accurate. Detailed analysis of the energy level predictions and room temperature spectra computed using the C2018 PES compared to that of BYTe has already been performed by Coles et al. (2018), with a further update by Coles (2019). In light of the astronomical applications intended for CoYuTe it is important to illustrate these improvements at high temperatures as well. Fig. 10 shows synthetic hot spectra generated using BYTe and CoYuTe compared to the absorbance spectra measured by Barton et al. (2017b) and cross-sections (Gaussian profile,  $\text{HWHM} 1 \text{ cm}^{-1}$ ) calculated using the experimental line lists by Beale et al. (2017). Clearly both experimental line positions and line intensities are substantially better represented by CoYuTe than they are BYTe. It is important to note that both BYTe and CoYuTe utilize the same DMS, and so the improvement in many line intensities is solely due to the improved PES which is inexorably linked to the line strength through the wavefunctions.

Above  $5300 \text{ cm}^{-1}$ , to our knowledge, no laboratory measurements of hot ammonia exist in the literature. Therefore our com-

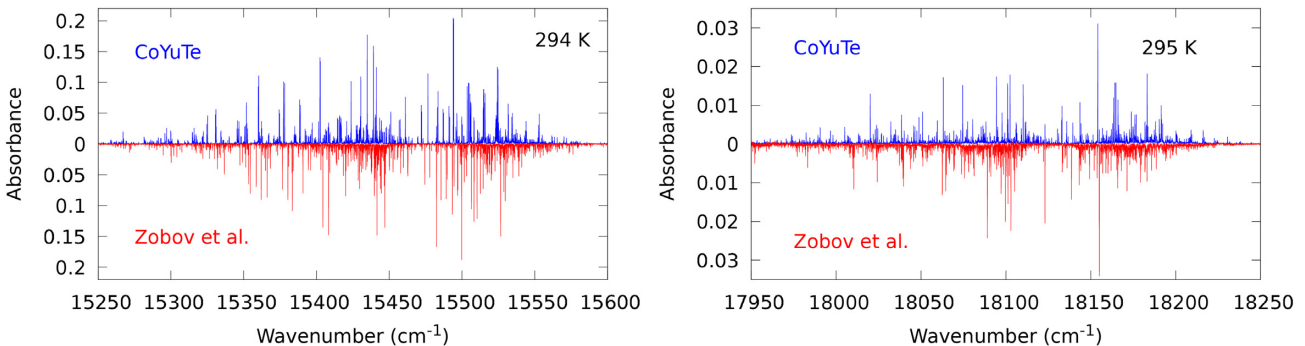
parisons with laboratory data at higher wavenumbers are restricted to room temperature only. Recently Barton et al. (2016) and Barton et al. (2017a) produced partially assigned line lists in the  $7400\text{--}8600$  and  $9000\text{--}10\,400 \text{ cm}^{-1}$  regions through analysis of FTIR spectra recorded in 1980 at the Kitt Peak National Observatory. Vander Auwera & Vanfleteren (2018) later reanalysed the same spectra between  $7400$  and  $8600 \text{ cm}^{-1}$  using an improved procedure, remeasured and reanalysed the region using an improved experimental set-up, and produced new line lists from their analyses. Fig. 11 (left-hand panel) compares simulated stick spectra calculated using the CoYuTe line list to the work by Vander Auwera & Vanfleteren (2018). Overall absorption features are represented well, however, there is a tendency to underestimate some bands by as much as 30 per cent. This underestimation is a feature of our chosen DMS, and has been discussed previously by Coles et al. (2018). Fig. 11 (right-hand panel) presents a similar comparison for the work by Barton et al. (2017a). Once again the overall band structure is represented well, and the reader is directed to Coles et al. (2018) for a more detailed analysis.



**Figure 10.** Synthetic absorption spectra generated using BYTe and CoYuTe compared to the measurements by Barton et al. (2017b) and the cross-sections (Gaussian profile, HWHM = 1.0 cm<sup>-1</sup>) calculated using the experimental line lists by Beale et al. (2017).



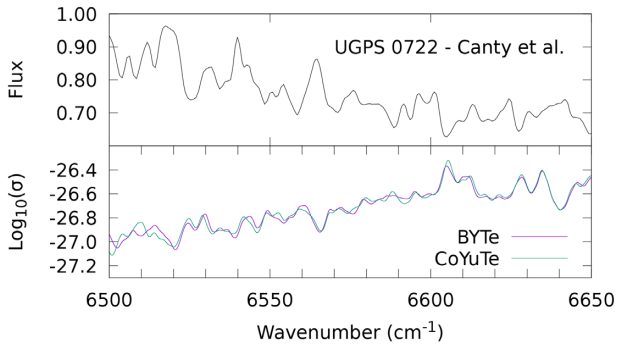
**Figure 11.** Comparison of the simulated CoYuTe and observed spectra of NH<sub>3</sub> at  $T = 294$  K for the 7400–8600 cm<sup>-1</sup> region (Vander Auwera & Vanfleteren 2018), and at  $T = 296$  K for 9100–10 300 cm<sup>-1</sup> region (Barton et al. 2017a).



**Figure 12.** Comparison of the simulated CoYuTe and observed (Zobov et al. 2018) spectra of NH<sub>3</sub> at  $T = 294/295$  K for the 15 250–15 600 and 17 950–18 250 cm<sup>-1</sup> regions.

Several studies have also focused on the measurement of ammonia spectra at visible wavelengths. The most recent and comprehensive of these is the analysis by Zobov et al. (2018) of a high-resolution Kitt Peak spectrum recorded in 1980. Their measured room temperature absorbance spectra is compared with synthetic spectra generated using CoYuTe at red (15 500 cm<sup>-1</sup>) and green (18 000 cm<sup>-1</sup>) visible frequencies in Fig. 12. For these comparisons, CoYuTe cross-sections were computed using the ExoCross program (Yurchenko et al. 2018) and Voigt profiles with HWHM of 0.01 cm<sup>-1</sup>. No information regarding the ammonia concentration in the Kitt Peak sample gas could be found, so we used concentration of 0.7 per cent (red spectrum) and 0.9 per cent (green spectrum) for our absorbance calculations, as these approximately

matched the peak heights of our calculated spectra to those of Zobov et al. (2018). In this regard the comparisons presented in Fig. 12 should not be taken as evidence of the accuracy of our absolute line intensities at visible wavelengths. However, some degree of reliability has already been confirmed in the work by Irwin et al. (2019). Regarding relative intensities the overall band profile of the red spectrum (Fig. 12, left) shows reasonable agreement between the calculated and measured spectra, although in most cases it is not possible to match individual lines by eye. In this region Zobov et al. (2018) noted discrepancies between the Kitt Peak measurements and the preliminary version of CoYuTe used in their analysis of up to 6 cm<sup>-1</sup> for  $J = 1-7$  lines, and we expect a similar level of error here. The green spectrum (Fig. 12, right) displays substantially worse



**Figure 13.** Comparison of the spectrum of late T dwarf UGPS 0722, which has an effective temperature of 500 K, due to Canty et al. (2015). Our models assume water, methane, ammonia atmosphere with the only difference being the line list used to represent ammonia. Results are presented as  $\log_{10}$  of the cross-sections,  $\sigma$  given in in  $\text{cm}^2/\text{molecule}$ ; see text for details.

agreement in overall structure, which is unsurprising seeing as only the  $6\nu_{\text{NH}}$  stretching band centres were included in the refinement of our potential (Coles et al. 2018). Inclusion of these band centres in the refinement procedure acts to offset the convergence error due to our vibrational stretching basis, but does not account for inaccuracies associated with rotational excitations within these bands. For this reason it is not recommended to use CoYuTe for high-resolution studies at short wavelengths in the visible region. Certainly additional assignments of the  $5\nu_{\text{NH}}$  and  $6\nu_{\text{NH}}$  stretching overtones would help rectify these errors in the next generation of theoretical line lists.

Finally there are a few high-resolution astronomical spectra of hot objects containing ammonia. One example are spectra of brown dwarf stars. Canty et al. (2015) analysed the spectra of late T dwarfs assigning a variety of features to ammonia and methane using the BYTe and 10to10 (Yurchenko & Tennyson 2014) line lists, respectively. They noted that while many of the general features in these spectra were reproduced by their models, a number of the absorption peaks were shifted. Fig. 13 shows a portion of one of the spectra analysed by Canty et al. (2015). In comparison we give results of a simple model constructed by us. The synthetic CoYuTe and BYTe spectra are based on composite  $\text{H}_2\text{O}+\text{CH}_4+\text{NH}_3$  cross-sections (Voigt profile, HWHM  $2.0\text{ cm}^{-1}$ ) which used the 10to10 and POKAZATEL (Polyansky et al. 2018) line lists for methane and water, respectively. Relative molecular abundances are taken from Saumon et al. (2006), which were also those used by Canty et al. Brown dwarf UGPS 0722 is assumed to have an effective temperature of 500 K. This is not a full stellar/radiative transport model so unsurprisingly we do not completely reproduce the observations. However, a number of observed absorption peaks which were not reproduced by BYTe are indeed present in our model, notably the peaks at  $6552$  and  $6588\text{ cm}^{-1}$ . We hope that future measurements of high temperature laboratory and astronomical spectra above  $6000\text{ cm}^{-1}$  will further demonstrate the superiority of CoYuTe at shorter wavelengths.

## 6 CONCLUSION

We present a new line for ammonia, CoYuTe, which replaces our previous line list, BYTe. Compared to BYTe, CoYuTe covers an increased temperature range, spectral range (extending to visible wavelengths), and is significantly more accurate. This improved accuracy is achieved by both starting from an improved potential

energy surface and by using empirical energy levels to improve the line positions for strong transitions.

Use of BYTe allowed the assignment of a number of laboratory ammonia spectra in the NIR. However, there remain outstanding issues with ammonia spectra at both NIR and visible wavelengths. Hopefully CoYuTe can be used to resolve some these issues and to assign currently unassigned spectra. Such data would naturally feed through into further improvements in line lists.

## SUPPORTING INFORMATION

Supplementary data are available at <ftp://cdsarc.u-strasbg.fr/pub/cats/VI/157>

Please note: Oxford University Press is not responsible for the content or functionality of any supporting materials supplied by the authors. Any queries (other than missing material) should be directed to the corresponding author for the article.

## ACKNOWLEDGEMENTS

This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) grant EP/M506448/1 and Servomex Ltd. We acknowledge support from the UK Science and Technology Research Council (STFC) No. ST/R000476/1 and COST Action CM1405 MOLIM. A substantial part of the calculations were performed using high performance computing facilities provided by DiRAC for particle physics, astrophysics, and cosmology and supported by BIS National E-infrastructure capital grant ST/J005673/1 and STFC grants ST/H008586/1, ST/K00333X/1. The authors also acknowledge the use of the UCL Legion High Performance Computing Facility (Legion@UCL), and associated support services, in the completion of this work.

## REFERENCES

- Al Derzi A. R., Furtenbacher T., Tennyson J., Yurchenko S. N., Császár A. G., 2015, *J. Quant. Spectrosc. Radiat. Transfer*, 161, 117
- Al-Refaie A. F., Yurchenko S. N., Tennyson J., 2017, *Comput. Phys. Commun.*, 214, 216
- Barber R. J., Strange J. K., Hill C., Polyansky O. L., Mellau G. C., Yurchenko S. N., Tennyson J., 2014, *MNRAS*, 437, 1828
- Barton E. J., Yurchenko S. N., Tennyson J., Clausen S., Fateev A., 2015, *J. Quant. Spectrosc. Radiat. Transfer*, 167, 126
- Barton E. J., Yurchenko S. N., Tennyson J., Béguier S., Campargue A., 2016, *J. Mol. Spectrosc.*, 325, 7
- Barton E. J. et al., 2017a, *J. Quant. Spectrosc. Radiat. Transfer*, 203, 392
- Barton E. J., Yurchenko S. N., Tennyson J., Clausen S., Fateev A., 2017b, *J. Quant. Spectrosc. Radiat. Transfer*, 189, 60
- Beale C. A., Hargreaves R. J., Coles P., Tennyson J., Bernath P. F., 2017, *J. Quant. Spectrosc. Radiat. Transfer*, 203, 410
- Beaulieu J.-P. et al., 2011, *ApJ*, 731, 16
- Blackford L. S. et al., 1997, *ScaLAPACK Users' Guide*. Society for Industrial and Applied Mathematics, Philadelphia
- Bochanski J. J., Burgasser A. J., Simcoe R. A., West A. A., 2011, *AJ*, 142, 169
- Canty J. I. et al., 2015, *MNRAS*, 450, 454
- Chubb K. L., Jensen P., Yurchenko S. N., 2018, *Symmetry*, 10
- Coles P. A., 2019, PhD thesis, University College
- Coles P. A., Ovsyannikov R. I., Polyansky O. L., Yurchenko S. N., Tennyson J., 2018, *J. Quant. Spectrosc. Radiat. Transfer*, 219, 199
- Coles P. A., Owens A., Kuepper J., Yachmenev A., 2019, *ApJ*, 870, 24
- Danielski C., Baudino J.-L., Lagage P.-O., Boccaletti A., Gastaud R., Coulais A., Bezdard B., 2018, *AJ*, 156, 276
- Dunning T. H., 1989, *J. Chem. Phys.*, 90, 1007

- Hargreaves R. J., Li G., Bernath P. F., 2011, *ApJ*, 735, 111
- Hargreaves R. J., Li G., Bernath P. F., 2012, *J. Quant. Spectrosc. Radiat. Transfer*, 113, 670
- Hegg D. A., Radke L. F., Hobbs P. V., Riggan P. J., 1988, *Geophys. Res. Lett.*, 15, 335
- Huang X., Lee T. J., 2013, HSL-pre3 Energies List. Available at: <http://huang.seti.org/NH3/nh3.html>
- Huang X., Schwenke D. W., Lee T. J., 2011a, *J. Chem. Phys.*, 134, 044320
- Huang X., Schwenke D. W., Lee T. J., 2011b, *J. Chem. Phys.*, 134, 044321
- Huang X., Schwenke D. W., Lee T. J., 2019, *J. Quant. Spectrosc. Radiat. Transfer*, 225, 327
- Irwin P. G. J., Bowles N., Braude A. S., Garland R., Calcutt S., 2018, *Icarus*, 302, 426
- Irwin P. G. J., Bowles N., Braude A. S., Garland R., Calcutt S., Coles P. A., Yurchenko S. N., Tennyson J., 2019, *Icarus*, 321, 572
- Kendall R. A., Dunning T. H., Harrison R. J., 1992, *J. Chem. Phys.*, 96, 6796
- Knowles P. J., Werner H.-J., 1992, *Theor. Chem. Acc.*, 84, 95
- Lees R. M., Li L., Xu L.-H., 2008, *J. Mol. Spectrosc.*, 251, 241
- Leggett S. K., Morley C. V., Marley M. S., Saumon D., 2015, *ApJ*, 799, 37
- Li L., Lees R. M., Xu L.-H., 2007, *J. Mol. Spectrosc.*, 243, 219
- Lodi L., Tennyson J., 2010, *J. Phys. B: At. Mol. Opt. Phys.*, 43, 133001
- Lucas P. W. et al., 2010, *MNRAS*, 408, L56
- MacDonald R. J., Madhusudhan N., 2017, *MNRAS*, 469, 1979
- Madden S. C., Irvine W. M., Matthews H. E., Brown R. D., Godfrey P. D., 1986, *ApJ*, 300, L79
- Morley C. V. et al., 2018, *ApJ*, 858, 97
- Neale L., Miller S., Tennyson J., 1996, *ApJ*, 464, 516
- Orton G. et al., 1995, *Science*, 267, 1277
- Peterson K. A., Dunning T. H., 2002, *J. Chem. Phys.*, 117, 10548
- Polyansky O. L., Kyuberis A. A., Zobov N. F., Tennyson J., Yurchenko S. N., Lodi L., 2018, *MNRAS*, 480, 2597
- Salinas V. N. et al., 2016, *A&A*, 591, A122
- Saumon D., Marley M. S., Cushing M. C., Leggett S. K., Roellig T. L., Lodders K., Freedman R. S., 2006, *ApJ*, 647, 552
- Saumon D., Marley M. S., Abel M., Frommhold L., Freedman R. S., 2012, *ApJ*, 750, 74
- Schmidt M. R. et al., 2016, *A&A*, 592, A131
- Seager S., Bains W., Hu R., 2013, *ApJ*, 777, 95
- Sousa-Silva C., Hesketh N., Yurchenko S. N., Hill C., Tennyson J., 2014, *J. Quant. Spectrosc. Radiat. Transfer*, 142, 66
- Sung K., Brown L. R., Huang X., Schwenke D. W., Lee T. J., Coy S. L., Lehmann K. K., 2012, *J. Quant. Spectrosc. Radiat. Transfer*, 113, 1066
- Tennyson J., 2012, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2, 698
- Tennyson J., Yurchenko S. N., 2012, *MNRAS*, 425, 21
- Tennyson J., Yurchenko S. N., 2017, *Int. J. Quantum Chem.*, 117, 92
- Tennyson J., Hill C., Yurchenko S. N., 2013, eds, *AIP Conf. Proc. Vol. 1545*, Data structures for ExoMol: Molecular line lists for exoplanet and other atmospheres. Am. Inst. Phys., New York, p. 186
- Tennyson J. et al., 2016, *J. Mol. Spectrosc.*, 327, 73
- Tinetti G. et al., 2018, *Exp. Astron.*, 46, 135
- Underwood D. S., Yurchenko S. N., Tennyson J., Al-Refaie A. F., Clausen S., Fateev A., 2016, *MNRAS*, 462, 4300
- Vander Auwera J., Vanfleteren T., 2018, *Mol. Phys.*, 116, 3621
- Villanueva G. L., Magee-Sauer K., Mumma M. J., 2013, *J. Quant. Spectrosc. Radiat. Transfer*, 129, 158
- Werner H.-J., Knowles P. J., 1988, *J. Chem. Phys.*, 89, 5803
- Woodman J. H., Trafton L., Owen T., 1977, *Icarus*, 32, 314
- Xu L.-H., Liu Z., Yakovlev I., Tretyakov M. Y., Lees R. M., 2004, *Infrared Phys. Technol.*, 45, 31
- Yurchenko S. N., 2015, *J. Quant. Spectrosc. Radiat. Transfer*, 152, 28
- Yurchenko S. N., Tennyson J., 2014, *MNRAS*, 440, 1649
- Yurchenko S. N., Thiel W., Jensen P., 2007, *J. Mol. Spectrosc.*, 245, 126
- Yurchenko S. N., Barber R. J., Yachmenev A., Thiel W., Jensen P., Tennyson J., 2009, *J. Phys. Chem. A*, 113, 11845
- Yurchenko S. N., Barber R. J., Tennyson J., 2011, *MNRAS*, 413, 1828
- Yurchenko S. N., Tennyson J., Bailey J., Hollis M. D. J., Tinetti G., 2014, *Proc. Natl. Acad. Sci.*, 111, 9379
- Yurchenko S. N., Yachmenev A., Ovsyannikov R. I., 2017, *J. Chem. Theory Comput.*, 13, 4368
- Yurchenko S. N., Al-Refaie A. F., Tennyson J., 2018, *A&A*, 614, A131
- Zobov N. F. et al., 2018, *J. Quant. Spectrosc. Radiat. Transfer*, 209, 224

This paper has been typeset from a  $\text{\TeX/L\AA}^{\text{A}}\text{\TeX}$  file prepared by the author.