# Molecular Line Lists and Absorption Cross-Sections Based on Laboratory Measurements

Peter Bernath<sup>1</sup>

<sup>1</sup> Old Dominion University, Norfolk, Virginia, USA; pbernath@odu.edu

<sup>2</sup> Also, University of Waterloo, Waterloo, Ontario, Canada

**Abstract.** Our experimental observations of hot water, ammonia and methane are summarized. Line lists were prepared from infrared absorption and emission spectra recorded with a high resolution Fourier transform spectrometer and a tube furnace to heat the samples. Infrared absorption cross-sections were also measured for hot ethane, propane and propene in the 3.3  $\mu$ m region.

## Introduction

The spectral energy distributions (SEDs) of "cool" (i.e., temperatures less than about 3000 K) astronomical objects such as M-stars, brown dwarfs and exoplanets are dominated by molecular absorption features (Bernath 2009). Modeling of these SEDs (Sharp & Burrows 2007) requires an atmospheric model with temperature, pressure and composition as a function of altitude and a scheme for carrying out radiative transfer to obtain the SED emitted at the top of the atmosphere. Crucial model inputs are molecular line lists (line positions, line strengths and lower state energies) with a line shape function or absorption cross-sections as a function of wavelength. These line lists and cross-sections can be derived from experiment as discussed here or be calculated or be some combination of experiment and theory.

For T-type brown dwarfs with surface temperatures of about 600-1400 K (Bailey 2014), the molecules that provide the most infrared opacity are water, methane and ammonia (Cushing et al. 2006). As these objects cool, ammonia is expected to become more abundant and is particulary important for Y dwarfs (Cushing et al. 2011) which have temperatures less than 600 K. Hot Jupiter exoplanets are also expected to have a similar atmospheric composition (Venot et al. 2012). Ammonia has not yet been detected in exoplanets although methane and water have been observed (Swain, Vasisht, & Tinetti 2008). Our experimental observations of hot water, methane and ammonia are summarized below.

### Hot Water Vapor

Our work began in 1995 with the identification of hot water vapor in the spectrum of a sunspot (Wallace et al. 1995). The late L. Wallace (Kitt Peak National Observatory) showed me a high resolution infrared spectrum (Wallace et al. 1996) of a large sunspot with an effective temperature of about 3200 K recorded with J. Brault's Fourier trans-

form spectrometer at the McMath-Pierce Solar Observatory. The spectrum contained a large number of unassigned absorption lines with no discernable pattern near  $20 \,\mu$ m and I suggested that they were pure rotational lines of hot water. No hot water line lists were available at the time and the spectrum of hot water cannot be predicted from cold water because the molecule distorts too much as rotation increases. We therefore recorded a high resolution emission spectrum with our Fourier transform spectrometer by heating water vapor to 1800 K in a tube furnace (Wallace et al. 1995). Although the laboratory sample was substantially cooler than the sunspot, thousands of lines matched so there was no doubt we had identified "Water on the Sun".

The main problem was we had no quantum number assignments for the observed lines so we began an extensive collaboration with J. Tennyson (University College London) and co-workers. Assignments could be made (Polyansky et al. 1997) by comparison with a new line list calculated by solving the vibration-rotation Schrödinger equation with *ab initio* potential energy and dipole surfaces. We continued to record new hot water and water isotopologue emission spectra including that of an oxyacetylene torch to obtain a sample temperature of 3000 K (Zobov et al. 2008). Several hot water line lists are available such as the BT2 list (Barber et al. 2006) which is widely used in astronomy and the HITEMP list (Rothman et al. 2010) which combines experimental lines and BT2 predictions. An overview of water vapor spectroscopy is available (Bernath 2002).

### **Hot Ammonia Emission**

A line list such as HITRAN (Rothman et al. 2013) is typically compiled at a reference temperature (e.g., 296 K) but the line intensities S' (Hargreaves, Li, & Bernath 2011) need to be adjusted to the actual temperature of the sample using the equation,

$$\frac{S'}{S'_{0}} = \frac{Q_{0}}{Q} \exp\left(\frac{E_{Low}}{kT_{0}} - \frac{E_{Low}}{kT}\right) \left[\frac{1 - \exp\left(-\frac{h\nu_{10}}{kT}\right)}{1 - \exp\left(-\frac{h\nu_{10}}{kT_{0}}\right)}\right]$$
(1)

with Q the internal partition function and  $E_{Low}$  the lower state energy of the transition;  $S'_0$  and  $Q_0$  refer to the reference temperature  $T_0$ , and Q is at the new temperature T. Partition functions are readily available (Gamache et al. 2017) and are best calculated by direct summation of energy levels  $E_i$  with degeneracy  $g_i$  as  $Q = \Sigma g_i \exp(-E_i/kT)$ . Lower state energies, however, are not available without quantum number assignments for the energy levels involved in the line. It is possible to estimate lower state energies purely from experiment by recording spectra at a number of sample temperatures and then using the temperature dependence of the line intensities as given by equation (1) to derive an empirical  $E_{Low}$ . Ammonia was our test case to derive line lists with empirical lower state energies from spectra recorded at high temperatures (Hargreaves, Li, & Bernath 2011).

We recorded high resolution Fourier transform infrared emission spectra from NH<sub>3</sub> heated in a tube furnace for 12 temperatures (300°C - 1300°C in 100°C intervals and 1370°C). The 12 line lists generated were calibrated for position and intensity using HITRAN and cover the 740 - 2100 cm<sup>-1</sup> range, which includes the majority of the  $v_2$  umbrella bending mode region (11  $\mu$ m) and the  $v_4$  antisymmetric bending mode region (6.2  $\mu$ m). We were able to derive empirical lower state energies from the set of spectra. A similar experiment was carried out to shorter wavelengths to cover the 1650 - 4000

cm<sup>-1</sup> range, which includes the  $v_1$  and  $v_3$  fundamentals plus a number of overtones and hot bands (Hargreaves, Li, & Bernath 2012). These line lists can be used directly in the modeling of exoplanetary atmospheres and brown dwarfs.

# **Hot Methane Emission**

Our work on hot methane emission began with the Fourier transform emission recorded at just three sample temperatures (800, 1000 and 1273 K) in two spectral ranges (2000 - 5000 cm<sup>-1</sup> and 5000 - 6400 cm<sup>-1</sup>) by Nassar & Bernath (2003). These line lists were used to identify hot methane in the transit spectrum of the exoplanet HD 189733b (Swain, Vasisht, & Tinetti 2008). A more complete set of spectra were recorded by Hargreaves et al. (2012). Calibrated line lists were derived temperatures in the 300 - 1400°C range at twelve 100°C intervals spanning the 960 - 5000 cm<sup>-1</sup> (2.0 - 10.4  $\mu$ m) region of the infrared. This range covers the dyad, pentad, and octad regions. The line lists for each temperature include line positions and calibrated line intensities and empirical lower state energies.

### Absorption Spectroscopy of Hot Methane and Ammonia

Emission spectroscopy of hot samples is not without drawbacks; intensity calibration is difficult and not very accurate. Moreover, in order to prevent damage to the windows and window seals, only the center of the alumina sample tube was heated and the ends were water-cooled. The emission from the hot sample therefore suffers from self-absorption by the cool molecules at the end of the tube. The self-absorbed lines are missing or distorted and cannot be used to make the line list. Our solution was to replace the lines above a certain intensity threshold with lines taken from the HITRAN database (Rothman et al. 2013).

A better experimental approach is to work with absorption spectra recorded with a sample at a uniform temperature. We therefore designed a method to directly measure transmission spectra of hot samples using methane to demonstrate proof-of-principle (Hargreaves et al. 2015a). A new sample cell was made entirely of quartz with the windows hard-sealed onto the 50-cm long sample tube. The cell was placed entirely inside our tube furnace and heated uniformly for nine temperatures: room temperature (i.e., 23°C) and 200°C - 900°C in 100°C intervals. To record sample transmittance at high temperature, four individual spectra are required to correct for the emission of CH<sub>4</sub> and the cell. At each temperature *T*, the four spectra are:

- 1. A-CH<sub>4</sub> absorption with lamp;
- 2. A-Background with lamp off;
- 3. B-CH<sub>4</sub> thermal emission with lamp off;
- 4. B-Background thermal emission of the cell.

The true transmission  $\tau$  of the cell is then  $\tau = (A_{CH_4} - B_{CH_4})/(A_{Background} - B_{Background})$ . The 2600 - 5000 cm<sup>-1</sup> (2.0 - 3.8  $\mu$ m) spectral range was covered and includes pentad and octad regions. As before, empirical lower state energies were derived and included in the line lists. Similar spectra have been recorded in the 5000 - 9000 cm<sup>-1</sup> (1.1 - 2.0  $\mu$ m) range but not published yet.

The hot methane absorption work of Hargreaves et al. (2015a) has some important conclusions obtained by comparison with state-of-the-art line lists calculated *ab initio* 

4

and with HITRAN. The line list called 10to10 by Yurchenko & Tennyson (2014) has been used by astronomers (Yurchenko et al. 2014). It has about 10 billion lines and is aimed at simulating CH<sub>4</sub> observations up to 1500 K. A similar line list for temperatures up to 2000 K with even more lines was prepared by Rey, Nikitin, & Tyuterev (2014). On a compressed scale or at low resolution both of these calculated line lists agree well with our experimental observations: they are complete and reproduce the line intensities well. However at higher resolution it is clear that most of the calculated lines are shifted from the observed positions. Both calculations use vibrational band origins determined from experiment if they are available because the vibrational part of the calculation is less accurate than the rotational part. As expected HITRAN (Rothman et al. 2013) is missing many high J rotational transitions and many hot bands, because it is designed for low temperature applications.

For applications for example in astronomy, line lists with billions of lines are difficult to use. Hargreaves et al. (2015a) demonstrated that the huge number of lines generate a "quasi-continuum" of unresolved vibration-rotation lines that can be observed experimentally. Our analysis of each spectrum therefore consisted of an empirical continuum at each temperature along with some 10's of thousands of lines (not millions or billions). Our experimental continuum agrees very well with the continuum that appears from the overlap of the unresolved weak lines in the calculated line lists. This CH<sub>4</sub> quasi-continuum is necessary to reproduce the observed molecular opacity in T-type brown dwarfs such as 2MASS 0559-14 (Hargreaves et al. 2015a). Our experimental line lists and continua reproduce astronomical observations at both high and low spectral resolutions. They can be used directly to simulate the atmospheric spectra of hot Jupiter exoplanets and brown dwarfs.

A similar experiment was carried out to record absorption spectra of hot  $NH_3$  at 7 temperatures from 296 K to 973 K in the 2400 - 5500 cm<sup>-1</sup> spectral range (Beale et al. 2017). (As for hot  $CH_4$ , spectra have also been recorded in the 5000 - 9000 cm<sup>-1</sup> range but not published yet.) Empirical lower state energies were derived and included in the line lists. In addition, some quantum number assignments were made with the help of the calculated BYTe line list (Yurchenko, Barber, & Tennyson 2011) and the Down et al. (2013) line list predicted from experimental energy levels.

### Absorption Spectroscopy of Hot Hydrocarbons

Although only hot  $CH_4$  has been detected to date in exoplanets (and brown dwarfs), photochemical models predict that larger hydrocarbons such as ethane ( $C_2H_6$ ) are present (Line et al. 2011). For larger molecules, line lists are not very useful because even at room temperature, the lines are mainly overlapped and unresolved at high resolution. In this case, laboratory observations need to be analyzed in terms of absorption crosssections, rather than as line lists. (For practical applications by astronomers, line lists are often converted to cross-sections anyway.)

The technique that we used to record hot CH<sub>4</sub> absorption spectra (Hargreaves et al. 2015a) was used for larger hydrocarbons and so far we have recorded spectra of hot ethane, propane (C<sub>3</sub>H<sub>8</sub>) and propene (C<sub>3</sub>H<sub>6</sub>) in the 3.3  $\mu$ m region. For hydrocarbons the strongest infrared bands are typically the in the C-H stretching region around 3000 cm<sup>-1</sup> (3.3  $\mu$ m). Infrared absorption cross-sections were determined by Hargreaves et al. (2015b) from high resolution spectra (0.005 cm<sup>-1</sup>) from 2200 - 5600 cm<sup>-1</sup> at 5 temperatures covering the 296 - 773 K range. Similar cross-sections were measured by Beale,

Hargreaves, & Bernath (2016) for propane and by Buzan, Hargreaves, & Bernath (2016) for propene. These hot hydrocarbon spectra have strong quasi-continua even at room temperature and their strength relative to the resolved lines increases markedly with temperature.

Acknowledgments. Research funding was provided mainly by NASA.

### References

- Bailey, J. 2014, PASA, 31, e043
- Barber, R. J., Tennyson, J., Harris, G. J., & Tolchenov, R. N. 2006, MNRAS, 368, 1087
- Beale, C. A., Hargreaves, R. J., & Bernath. P. F. 2016, JQSRT, 182, 219
- Beale, C. A., Hargreaves, R. J., Coles, P., Tennyson, J., & Bernath, P. F. 2017, JQSRT, doi:10.1016/j.jqsrt.2017.02.012
- Bernath, P. F. 2002, PCCP, 4, 1501
- Bernath, P. 2009, Int Rev Phys Chem, 28, 681
- Buzan, E., Hargreaves, R. J., & Bernath, P. F. 2016, Mol Astro, 3-4, 16
- Cushing, M. C., Roellig, T. L., Marley, M. S., et al. 2006, ApJ, 648, 614
- Cushing, M.C., Kirkpatrick, J.D., Gelino, C.R., et al. 2011, ApJ, 743, 50
- Down, M. J., Hill, C., Yurchenko, S. N., et al. 2013, JQSRT, 130, 260
- Gamache, R. R., Roller, C., Lopes, E., et al. 2017, JQSRT, doi:10.1016/j.jqsrt.2017.03.045
- Hargreaves, R. J., Li, G., & Bernath, P. F. 2011, ApJ, 735, 111
- Hargreaves, R. J., Li, G., & Bernath, P. F. 2012, JQSRT, 113, 670
- Hargreaves, R. J., Beale, C. A., Michaux, L., Irfan, M., & Bernath, P. F. 2012, ApJ, 757, 46
- Hargreaves, R. J., Bernath, P. F., Bailey, J., & Dulick, M. 2015, ApJ, 813, 12
- Hargreaves, R. J., Buzan, E., Dulick, M., & Bernath, P. F. 2015, Mol Astro, 1, 20
- Line, M. R., Vasisht, G., Chen, P., et al. 2011, ApJ, 738, 32
- Nassar, R., & Bernath, P. 2003, JQSRT, 82, 279
- Polyansky, O., Zobov, N. F., Viti, S., et al. 1997, Science, 277, 346
- Rey, M., Nikitin, A. V., & Tyuterev, V. G. 2014, ApJ, 789, 2
- Rothman, L. S., Gordon, I. E., Barber, R. J., et al. 2010, JQSRT, 111, 2139
- Rothman, L. S., Gordon, I. E., Babikov, Y., et al. 2013, JQSRT, 130, 4
- Sharp, C. M., & Burrows, A. 2007, ApJS, 168, 140
- Swain, M. R., Vasisht, G. V., & Tinetti, G. 2008, Nature, 452, 329
- Venot O, Hébrard, E., Agúndez, M., et al. 2012, AA, 546, A43
- Wallace, L., Bernath, P., Livingston, W., et al. 1995, Science, 268, 1155
- Wallace, L., Livingston, W., Hinkle, K., & Bernath, P. 1996, ApJS, 106, 165
- Yurchenko, S. N., Barber, R. J., & Tennyson, J. 2011, MNRAS, 413, 1828
- Yurchenko, S. N., & Tennyson, J. 2014, MNRAS, 440, 1649
- Yurchenko, S. N., Tennyson, J., Bailey, J., Hollis, M. D. J., & Tinetti, G. 2014, PNAS, 111, 9379
- Zobov, N. F., Shirin, S. V., Ovsyannikov, R. I., et al. 2008, MNRAS, 387, 1093