An Overview of Molecular Opacities

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Abstract. Molecular opacities are based on extensive line lists or absorption crosssections that apply to a particular composition, temperature and pressure. Line lists need to include line positions, line intensities and lower state energies at a minimum. Modern methods to generate these line lists are reviewed.

Introduction

Molecules are ubiquitous in the Universe and are found in diverse sources including diffuse clouds, dark clouds, giant molecular clouds, planetary nebulae, circumstellar envelopes, stellar and brown dwarf atmospheres, protoplanetary disks, comets, supernovas, planetary and exoplanetary atmospheres, and galaxies (Bernath 2009). Except for objects in our Solar System that can be sampled directly, all observations are via remote sensing; that is by applied spectroscopy. I have written a textbook, "Spectra of Atoms and Molecules" (Bernath 2016) that introduces the subject to new graduate students, senior undergraduates and to researchers from different fields such as astrophysics. The book has a particularly useful treatment of the confusing topic of line intensities needed for remote sensing in astronomy.

Molecules are generally found in "cool" (i.e., temperatures less than about 6000 K) astronomical sources because at higher temperatures they are dissociated into atoms and atomic ions. Modeling of these astronomical spectra (Sharp & Burrows 2007) requires a physical model with temperature, pressure and composition, and a scheme for carrying out radiative transfer to obtain the emitted spectrum. Crucial model inputs are molecular line lists with a line shape function or absorption cross-sections as a function of wavelength. These line lists and cross-sections (commonly called "molecular opacities") can be derived from experiment or be calculated or more typically be some combination of experiment and theory.

The requirements for molecular opacities can be derived by consideration of the Beer–Lambert law (or its differential from) for the transmission $\tau = I/I_0$ through a homogeneous sample of length *l* with a molecular concentration *N* molecules/m³ for a single line,

$$\tau = e^{-S'g(\nu - \nu_{10})Nl}.$$
(1)

In this equation, $g(v - v_{10})$ is the normalized line shape function which depends on the frequency v, and v_{10} is line center of the transition between energy levels E_1 and E_0 ($v_{10} = (E_1 - E_0)/h$). In SI units, the line intensity or strength S' is defined as (Bernath

2016),

$$S' = \frac{2\pi^2 v_{10} S_{J'J''}}{3\varepsilon_0 h c Q} e^{-E_0/kT} (1 - e^{-hv_{10}/kT}),$$
(2)

with Q the internal partition function, E_0 the lower state energy and $S_{J'J''}$ the square of the quantum mechanical transition dipole moment (Bernath 2016) for an allowed transition.

The first conclusion from equation (1) is that the line shape function g is a crucial ingredient for any practical application. Traditionally a Voigt line shape (convolution of a Lorentzian for pressure broadening and a Gaussian for Doppler broadening) is used (Bernath 2016), but it is increasingly clear that for high precision work for example with planetary atmospheres requires non-Voigt line shapes (Tennyson et al. 2014). The pressure-broadening parameters in the Voigt line shape are also a problem because reliable values are rarely available over the full temperature and pressure range needed for typical astrophysical broadeners such as H₂, He and CO₂.

Equation (2) indicates that a practical line list such as HITRAN (Rothman et al. 2013) or HITEMP (Rothman et al. 2010) is valid for a reference temperature (assuming thermodynamic equilibrium). Line intensities then have to be adjusted to the actual temperature of the sample using the equation,

$$\frac{S'}{S'_{0}} = \frac{Q_{0}}{Q} \exp\left(\frac{E_{Low}}{kT_{0}} - \frac{E_{Low}}{kT}\right) \left[\frac{1 - \exp\left(-\frac{h\nu_{10}}{kT}\right)}{1 - \exp\left(-\frac{h\nu_{10}}{kT_{0}}\right)}\right]$$
(3)

obtained by taking the ratio of equation (2) for temperature T relative to the reference temperature T_0 . A partition function is required, but fortunately they are readily available even for relatively high temperatures (Gamache et al. 2017). A lower state energy E_{Low} is also needed and is known if the quantum number assignment of the level is known. This is not always the case but empirical lower state energies can be determined from experiment by measuring the temperature dependence of line intensities and applying equation (3), as has been demonstrated for hot methane (Hargreaves et al. 2012) and hot ammonia (Hargreaves, Li, & Bernath 2011). In summary, the minimum requirements for a line list are line positions, line intensities and lower state energies; or for a specific temperature, only line positions and intensities are needed.

The task is thus to create extensive line lists for all relevant molecules that are typically converted by users into opacity tables (absorption cross-section as a function of wavelength) suitable for a range of temperatures, pressures and compositions. For larger molecules that have blended lines, absorption cross-sections are obtained directly (e.g., from experiment) without a line list. Line lists (v_{10} , S', E_{Low}) can be created from experimental measurements by recording and analyzing spectra. The also can be calculated *ab initio* by solving the electronic Schrödinger equation to obtain potential energy functions and (transition) dipole surfaces, then solving the vibration-rotation Schrödinger equation for each electronic state to obtain energy levels (for transitions) and wavefunctions (for intensities). *Ab initio* calculations provide the large number of transitions needed at high temperature, but line position accuracy is too low. Experimental measurement has the required accuracy, but not the millions (or billions) of lines needed. Very often calculated line positions are improved by, for example, empirical adjustment of the potential energy surfaces to agree better with experiment.

Considering main sequence stars and brown dwarfs, the list of molecules is extensive; for G-type stars (5200-6000 K) like the Sun, CO, CN, C₂, MgH, OH, NH, CH and H_2 are significant (Bernath 2009). As the surface temperature drops, electronic transitions of diatomic metal oxides such as VO and TiO appear for M-type stars (2000-3700 K) and dominate the visible and near infrared spectra; H_2O vibrational overtone bands are present in the infrared (Kirkpatrick 2005). For L-type dwarfs (1300-2000 K), the metal oxide bands weaken and the spectra are dominated by metal hydride electronic transitions from FeH and CrH in the near infrared (Bailey 2014). For T-type brown dwarfs (700-1300 K) the vibration-rotation bands of CH₄ and H₂O are strong in the infrared and near infrared regions. For the late T dwarfs NH₃ appears (Cushing et al. 2006) and is important for Y dwarfs, which have temperatures less than 700 K (Cushing et al. 2011).

Diatomic Molecules

The spectrum of the photosphere of the Sun (5800 K, G2 V) is dominated by atomic transitions but molecular features are clearly present. For example, the Atmospheric Chemistry Experiment (ACE) satellite mission (Bernath 2016) has published a high resolution infrared atlas of the Sun (Hase et al. 2010) free from telluric absorption. Line assignments were made for atomic features as well as vibration-rotation lines of CO, OH, NH and CH, and pure-rotation lines of OH and NH. The solar absorption lines for OH (Bernath & Colin 2009), NH (Ram & Bernath 2010) and CH (Colin & Bernath 2010) were combined with laboratory measurements to improve the spectroscopic analysis. These three free radicals also serve as examples for the calculation line lists that include reliable line intensities.

Masseron et al. (2014) have calculated extensive line lists for CH and ¹³CH for infrared ($X^2\Pi - X^2\Pi$), $A^2\Delta - X^2\Pi$, $B^2\Sigma^- - X^2\Pi$ and $C^2\Sigma^+ - X^2\Pi$ transitions from all existing laboratory and solar data plus unique observations of carbon-enhanced metalpoor stars (CEMPs). CEMPs show the electronic spectra of CH very strongly in the near UV with relatively few overlapping atomic lines. They also had many strong unassigned broad absorption features that could be attributed to CH and were included in the analysis. These lines are not seen in laboratory emission spectra because the upper levels are predissociated and the molecule falls apart before a photon can be emitted. Once again the value of including both astronomical and laboratory data in the analysis is illustrated. The CEMP data allowed the "Bond-Neff feature" in the spectra of barium stars to be assigned to CH.

The analysis method consists of:

1. Collect all measured line positions from both laboratory and astronomical spectra.

2. Fit the lines with an effective Hamiltonian using, for example, Western's PGOPHER program (Western 2017) and find new lines (e.g., predissociated lines seen in CEMP stars but not in the laboratory emission spectra). Iterate refitting and finding new lines until all data is satisfactorily accounted for.

3. Calculate (e.g., using MOLPRO) ab initio dipole and transition dipole moment functions. In the case of CH, calculations by Hettema & Yarkony (2005) were taken from the literature and used.

4. Determine the mechanical vibrational G(v) and rotational B(v) polynomial energy level expressions from the PGOPHER fit for use with LeRoy's RKR program (Le Roy

2017a) to obtain the potential energy function for each electronic state. The RKR potential energy functions and the (transition) dipole moment functions are used with LeRoy's LEVEL program (Le Roy 2017b) to solve the radial vibrational Schrödinger

equation to obtain energy levels and vibrational wavefunctions to calculate (transition) dipole matrix elements. RKR and LEVEL ignore electron spin but the rotational dependence of the dipole matrix elements is included from the centrifugal term present in the effective potential function, which makes the vibrational wavefunctions depend on rotation.

5. Use PGOPHER to calculate line lists using transition dipole matrix elements from LEVEL that include vibrational and rotational dependence.

This semi-empirical method works well although neglect of electron spin is a problem in converting the output of LEVEL into the input of PGOPHER. It is possible to derive a transformation Brooke et al. (2016) from the Hund's case (b) matrix element from LEVEL in terms of the quantum number N to the Hund's case (a) matrix elements needed as input by PGOPHER in terms of J ($\mathbf{J} = \mathbf{N} + \mathbf{S}$). As demonstrated by Brooke et al. (2016) for the vibration-rotation bands of OH in the ground X²II state (Meinel bands), the transformation gives results that agree with experiment and with an analysis that explicitly includes electron spin. Using similar methods line lists have been generated for the vibration-rotation bands of NH (X³Σ⁻) (Brooke, Bernath, & Western 2015); the Swan system of C₂ (Brooke et al. 2013) and C¹³C (Ram et al. 2014a); A²II - X²Σ⁺ transition of CP (Ram et al. 2014b); B²Σ⁺ - X²Σ⁺ and A²II - X²Σ⁺ transitions of CN (Brooke et al. 2014), ¹³CN and C¹⁵N (Sneden et al. 2014); and B' ²Σ⁺ - X²Σ⁺ and A²II - X²Σ⁺ transitions of MgH (GharibNezhad, Shayesteh, & Bernath 2013) and isotopologues (Hinkle et al. 2013). These line lists are collected on the MOLLIST web site (http://bernath.uwaterloo.ca/molecularlists.php).

Recently a new computer program called DUO has become available that is able to calculate directly line lists for non-singlet diatomic molecules (Yurchenko et al. 2016a). As input, DUO needs potential energy functions, dipole moment functions and any coupling functions such as spin-orbit coupling that are generally provided by high level *ab initio* calculations. These input functions can be refined by comparison with experimental observations of line positions and other reference data. DUO makes fewer approximations than the semi-empirical approach and is more reliable for extrapolation when there is no experimental data. It has difficulty, however, reproducing experimental line positions within experimental error so experimentally derived data are often used in the final line list. DUO has been used to make line lists for AlO (Patrascu, Yurchenko, & Tennyson 2015), CaO (Yurchenko et al. 2017); see the ExoMol web site, http://exomol.com/.

Polyatomic Molecules

There are two general approaches to creating line lists needed for polyatomic molecules such as H_2O , NH_3 and CH_4 . The traditional method (e.g., for HITRAN) uses an effective Hamiltonian matrix with adjustable parameters that is diagonalized numerically to provide ro-vibronic energy levels and wavefunctions. The parameters are adjusted until experimental and calculated line positions agree to within experimental error. Line intensities are measured individually for each line or calculated using the wavefunctions and (transition) dipole moments based on experiment. The main advantage of this traditional approach is that the line positions and intensities are incomplete because of missing overtones, combination bands and hot bands that are needed but not

measured. Moreover, the fitting of experimental data is usually based on polynomials which extrapolate poorly for missing vibrational and rotational data. In order to reproduce observations, numerous fitting parameters are often needed and they can be poorly determined with little physical meaning.

The variational method starts with solution of the electronic Schrödinger equation to obtain potential energy and dipole surfaces. The rovibrational energy levels and wavefunctions are obtained from variational solution of the vibration-rotation Schrödinger equation in a second step. The main advantage of this approach is that the line lists can be very complete with all important bands and isotopologues. The main disadvantage is that the line positions are usually rather far from experimental values, although the calculated line intensities can be as good as experiment for small molecules. Another problem is that the calculations take a large amount of computer time, which becomes prohibitive for larger molecules.

An example of the traditional approach is absorption spectra of hot NH₃ recorded with a Fourier transform spectrometer at 7 temperatures from 296 K to 973 K in the 2400 - 5500 cm⁻¹ spectral range (Beale et al. 2017). Empirical lower state energies were derived from the temperature dependence of the line intensities and included in the line lists. 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 derived from HITRAN. Another example is the derivation of infrared absorption cross-sections for hot propane (C₃H₈) by Beale, Hargreaves, & Bernath (2016) based on high resolution (0.005 cm⁻¹) absorption spectra in the 2550 - 3500 cm⁻¹ region at five temperatures (from 296 to 700 K).

There are several line lists for hot water vapor calculated by the variational method: the popular BT2 list with 0.5 billion lines from Barber et al. (2006), the HITEMP water line list that is BT2 plus experimental line positions (Rothman et al. 2010) and a line list from Partridge & Schwenke (1997). They all work well at low spectral resolution and reproduce observations, e.g., by Stephens et al. (2009) for L dwarfs. At high resolution HITEMP works best because the stronger line positions are experimental values, which therefore match observations, but the weaker lines calculated by BT2 are still shifted from the measured values.

For NH₃ there are three extensive variational line lists that are readily available; the original BYTe list (Yurchenko, Barber, & Tennyson 2011) that aimed to predict the NH₃ vibration-rotation spectra up to 1500 K and a more recent update by Polyansky et al. (2016); the NASA-Ames group Huang, Schwenke, & Lee (2011) has a line list for lower temperatures but with higher accuracy for the calculated line positions. Comparison of the BYTe line list predictions with hot NH₃ absorption spectra (Beale et al. 2017) shows good agreement from 2500 to 5500 cm⁻¹ at low resolution but at high resolution the differences in line positions are substantial (typically 1-2 cm⁻¹). A similar comparison with between CH₄ absorption spectra (Hargreaves et al. 2015a) and the predictions of the variational line list of Yurchenko & Tennyson (2014) and of Rey, Nikitin, & Tyuterev (2014) lead to similar conclusions. The 10to10 line list (Yurchenko & Tennyson 2014) does a good job of reproducing the spectra of T-type brown dwarfs (Yurchenko et al. 2014). The spectra of hot CH₄ are also needed to interpret the transit spectra of hot Jupiter exoplanets, which show evidence of CH₄ absorption (Swain, Vasisht, & Tinetti 2008).

6 Peter Bernath

The near infrared spectra of CH_4 are largely unassigned even at room temperature. There is a high quality experimental WKLMC line list (Campargue et al. 2013) for CH_4 (296 K and 80 K) and remarkable progress is being made in predicting the observed spectra with a new variational line list (Rey et al. 2016). This work will soon lead to much improved predictions of hot CH_4 spectra for astronomy.

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