



MoLLIST: Molecular Line Lists, Intensities and Spectra

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ABSTRACT

The simulation of astronomical spectra of cool stars, brown dwarfs and exoplanets requires high resolution line lists and absorption cross sections of many molecules. Similar data sets are needed for the Earth's atmosphere and other planets in our solar system. The requirements for line lists are reviewed and methods used to create them are discussed. Equations to convert between different units are provided. The MoLLIST (Molecular Line Lists, Intensities and Spectra) data compilation is presented and used as an example.

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1. Introduction

Modern astronomy is particularly focused on “cool” sources that are full of molecules. The range of temperatures starts at about 10 K for cores of dark interstellar clouds where stars are born and includes diffuse interstellar clouds, planetary and exoplanetary atmospheres, comets, brown dwarfs, circumstellar envelopes and the atmospheres of cool stars with surface temperatures of several 1000 K. Even spectra of the solar photosphere at 5800 K [1] and especially sunspots (as cool as 3000 K) show prominent molecular features [2]. Fig. 1 shows lines of the C₂ Swan System (d³Π_g–a³Π_u) and CH A²Δ–X²Π electronic transition in solar spectra [3].

Traditionally astronomers have used atomic lines to obtain elemental abundances but cool sources often have no suitable atomic

features. In order to extract properties such as temperature and elemental abundances from spectra of cool astronomical objects, a radiative transfer model is needed that makes use of suitable spectroscopic data. For example, the MOOG model [4] used in Fig. 1 takes a molecular line list as input and the resulting carbon abundances depend strongly on the quality of this line list. A typical astronomical line list (e.g., for MOOG, <http://www.as.utexas.edu/~chris/lab.html>) includes a line position (in air wavelength units, Å), a lower state energy (in eV) and a line intensity given as a log(*gf*) value (log is base 10 and ln is base e). In the infrared, vacuum wavelengths are used instead of air wavelengths.

Radio astronomers typically replace wavelength units with frequency units (MHz) and line intensities are quoted in the JPL (Jet Propulsion Laboratory) database (<https://spec.jpl.nasa.gov/>) in units of nm² MHz at 300 K [5]. The popular HITRAN database [6] aimed primarily at the simulation of spectra of the Earth's atmosphere (but widely used in astronomy) provides line positions and lower

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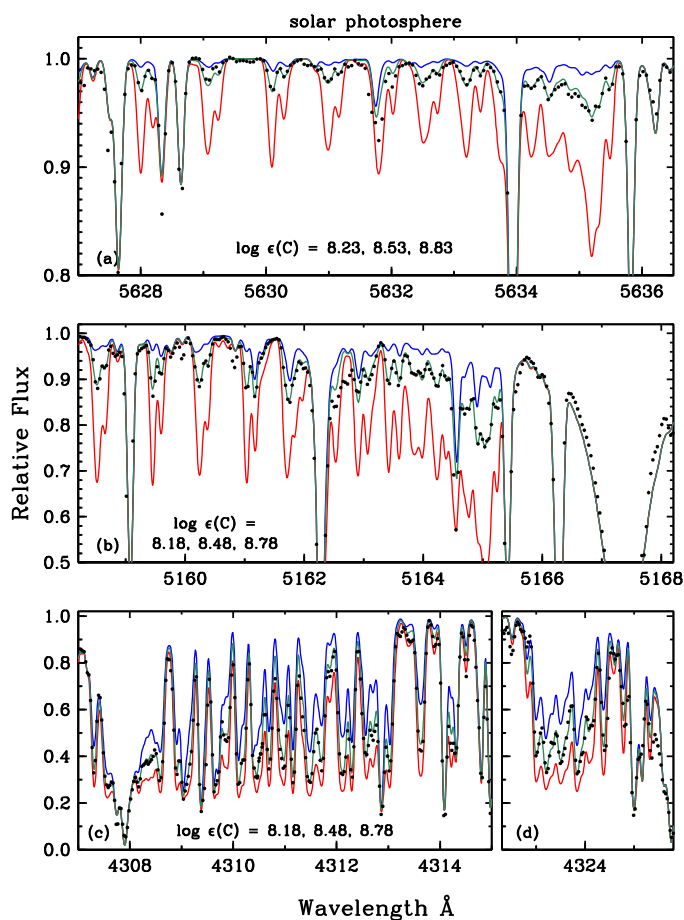


Fig. 1. Calculated (colored lines) and observed (black points) solar spectra for three wavelength regions [3]. The top two panels show absorption lines of the C₂ Swan system and the bottom panel has CH A²Δ-X²Π lines. In each panel, the smallest, best fit, and largest C abundances are indicated with blue, dark green and red lines, and their values are written in the panel legend. Carbon abundances are relative to hydrogen on a log₁₀ scale with hydrogen having an abundance of 12.

state energies in units of cm⁻¹ and line intensities in units of cm/molecule units at 296 K.

In addition to a line position and a line intensity, the simulation of a spectrum such as in Fig. 1 also requires a line shape function that depends on temperature, pressure and chemical composition. For larger molecules, absorption cross sections at a specified temperature, pressure and composition are used because individual lines are no longer resolved. For the very useful Pacific Northwest National Laboratory (PNNL) infrared cross section database [7], the x-axis is in cm⁻¹ and the y-axis is -log₁₀(I/I₀) for 1 ppm-m of sample diluted in 1 atm of N₂. Most of the PNNL cross sections now included in the HITRAN database (<https://hitran.org/>) have the y-axis converted to units of cm²/molecule. Given the diversity of units for closely-related quantities, it is not surprising that there is considerable confusion especially for new students and others just starting in the field. The goal of this review is to clarify the relationship between the various quantities and discuss how to use data from various sources with the MoLLIST database (<http://bernath.uwaterloo.ca/molecularists.php>) as an example.

2. Beer-Lambert law and absorption cross sections

A conveniently simple starting point is the Beer-Lambert law [8] for the transmission ($\tau = I/I_0$) of radiation at a particular fre-

quency ν through a uniform system with a path length l (m),

$$\tau = \frac{I}{I_0} = e^{-\sigma(N_0-N_1)l} = e^{-\alpha l} = e^{-\sigma x}. \quad (1)$$

In Eq. (1) the left side is dimensionless; σ is the absorption cross section (m² in SI units) for a non-degenerate two-level system (E_1 , E_0) with a population density (molecules/m³) of N_1 in the upper state and N_0 in the lower state. N_1 appears in Eq. (1) to account for stimulated emission from the upper state. The cross section σ can be combined with the population difference $N_0 - N_1$ to give the absorption coefficient α (m⁻¹). The population difference can also be combined with the path length l to give the column density x (molecules/m²). Notice that the Beer-Lambert law can also be written using base 10 logarithms, e.g., in analytical chemistry and some engineering disciplines, which affects the value of the absorption cross section. Population densities, i.e. concentrations, are also measured in a wide variety of units.

For today's students, SI units are best and the basic equations in this article are in SI units unless otherwise indicated. The safest way to carry out a calculation is to work with SI units and convert from (to) "practical" or customary units at the beginning (end). In some cases the conversion is easy (e.g., the customary units for cross sections are cm² and for path lengths are cm). However, more care is required if concentrations are in mole fractions, for example.

It is often convenient to convert line lists into cross section tables, as discussed below. Each table has absorption cross sections (usually in cm² per molecule) at a specified temperature, pressure and composition as a function of wavelength (usually Å) or wavenumber (usually cm⁻¹). For example, a table might be for the hydrocarbon propane at 296 K with 1 atm of nitrogen gas, and tables can be combined to provide total cross sections for a system at a particular temperature, pressure and composition. Such "opacity" tables are convenient in astrophysics as well as useful for rapid calculations of transmission through the Earth's atmosphere.

There are potential pitfalls in using cross section tables provided, for example by the HITRAN database (as cm²/molecule on a linear cm⁻¹ grid). Optical and infrared astronomers often prefer to work on a linear wavelength (λ) grid typically Å in air or in the infrared are typically in μm in vacuum. It is a spectroscopic custom to use air wavelengths for $\lambda > 2000$ Å, at the end of the vacuum UV spectral region. The use of air wavelengths is a problem because the refractive index of air, n , is needed, $\lambda_{\text{air}} = \lambda_{\text{vac}}/n$ for the conversion of frequency units or cm⁻¹ (by definition cm⁻¹ is in vacuum) to wavelength units. This can be seen by considering dry air at 15 °C and 760 Torr for which $n = 1.0002790$ at 5 000 Å. Thus $\lambda = 5\,000.000$ Å in air corresponds to $\lambda_0 = 5\,001.395$ Å in vacuum and $\tilde{\nu} = 19994.42$ cm⁻¹ rather than 20 000 cm⁻¹.

Conversion from wavenumbers to air wavelengths requires an accurate refractive index for air as given, for example, by Edlén's updated formula as corrected by Birch and Downs [9] for "standard dry air" (15 °C, 760 Torr, 450 ppm CO₂),

$$(n-1) \times 10^8 = 8342.44 + \frac{2406147}{130 - (\sigma/\mu\text{m}^{-1})^2} + \frac{15998}{38.9 - (\sigma/\mu\text{m}^{-1})^2} \quad (2)$$

with σ being vacuum wavenumbers in reciprocal microns not cm⁻¹ (1 μm⁻¹ = 10⁴ cm⁻¹). The refractive index also varies with temperature, pressure, humidity and carbon dioxide concentration [10]. Although there are more recent conversion formulas, Eq. (2) is recommended by the International Astronomical Union (IAU) and is widely used. Edlén's updated formula is valid in the range 2000 Å - 2 μm [10]. The conversion of cross section tables from cm⁻¹ to Å proceeds by conversion to air wavelength and then

interpolation onto a linear wavelength grid conveniently carried out with a computer program such as IDL or MATLAB.

The conversion from air wavelength to cm^{-1} is more difficult because Eq.(2) is a function of wavenumber (in vacuum by definition). However, Eq.(2) can be inverted so that it is a function of the “air” wavenumber s as

$$(n-1) \times 10^8 = 8336.624 + \frac{2408926.87}{130.11 - (s/\mu\text{m}^{-1})^2} + \frac{15997.41}{38.926 - (s/\mu\text{m}^{-1})^2} \quad (3)$$

in which $s = 10^4/\lambda_{\text{air}}$ (λ_{air} in cm) and $\lambda_{\text{vac}} = \lambda_{\text{air}}n$. Eq.(3) is attributed to N. Piskunov and can be found in the Vienna Atomic Line Database (VALD, <http://vald.astro.uu.se/>, Ryabchikova et al. [11]), which now includes some molecular line data.

3. Spectroscopic data

Spectroscopic data is published in a variety of primary journals including the *Journal of Molecular Spectroscopy* and the *Journal of Quantitative Spectroscopy and Radiative Transfer*, plus a wide variety of more general publications including the *Journal of Chemical Physics*, *Journal of Physical Chemistry A*, *Physical Review A*, *Chemical Physics Letters* and *Molecular Astrophysics*. Some spectroscopy relevant to astronomy is published in the *Astrophysical Journal* and *Astronomy and Astrophysics*, some relative to planetary science in *Icarus* and some relevant to atmospheric science in the *Journal of Geophysical Research*, but data compilations are widely used.

For pure rotational transitions in the microwave, millimeter wave and submillimeter wave spectral regions the standard compilations are the Cologne Database for Molecular Spectroscopy, CDMS (<https://cdms.astro.uni-koeln.de/>), [12] and the Jet Propulsion Laboratory, JPL (<https://spec.jpl.nasa.gov/>), catalog [5]. CDMS also maintains a current list of interstellar and circumstellar molecules; McGuire [13] has recently reviewed this topic. The VAMDC (Virtual Atomic and Molecular Data Centre) is a portal (<https://portal.vamdc.eu/>) that provides access to more than 30 databases including CDMS.

In the infrared, covering mainly vibration-rotation transitions, the standard critically-evaluated database is HITRAN [6], now available online at <https://hitran.org/>. HITRAN includes lines, infrared absorption cross sections [14], collision-induced absorption parameters [15] and some complex refractive indexes for aerosols. The GEISA database [16] covers similar topics.

In the ultraviolet and visible there are more limited data compilations that typically provide absorption cross sections for the electronic transitions of larger molecules. The Mainz UV/Visible database (MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest, http://satellite.mpic.de/spectral_atlas) has an extensive collection of absorption cross sections of over 1000 molecules [17]. The JPL kinetics evaluation [18] has a more limited set of critically-evaluated UV/Visible cross sections for molecules relevant to atmospheric science.

Other collections of data are located at various web sites and only a few examples are cited. MoLLIST (Molecular Line Lists, Intensities and Spectra, <http://bernath.uwaterloo.ca/molecularlists.php>) collects the line lists and absorption cross sections generated by the Bernath group. A few spectra are also included such as the solar atlas [1] and atmospheric atlases [19] created from the ACE (Atmospheric Chemistry Experiment) Fourier transform spectrometer in Earth orbit [20]. MoLLIST is organized alphabetically by molecular formula and under each formula are the literature citations and a link to the data. The data are zip files of ascii data such as line lists and cross sections corresponding to the literature citations.

The ExoMol site (High temperature molecular line lists for modelling exoplanet atmospheres, <http://exomol.com/>) has the line lists calculated by the Tennyson group and has collected some additional line lists from the literature [21]. The TheoReTS site (Theoretical Reims–Tomsk Spectral data, <http://theorets.tsu.ru/>) has collected the calculated line lists from the Tyuterev, Rey and Nikitin collaboration [22].

4. Data and units

The values of the fundamental physical constants underlie the units and conversions between units in line lists. The current 2018 CODATA revision of the fundamental physical constants <https://physics.nist.gov/cuu/Constants/> has a number of significant changes. These 2018 values incorporate an important revision of the SI system and, in addition to the speed of light (c), the Planck constant (h), the elementary charge (e), the Boltzmann constant (k), and the Avogadro constant (N_A) all have fixed values.

The lines in line lists are typically reported in customary units of MHz, cm^{-1} or \AA and conversions between them are not a problem except for the possible use of air wavelengths and the refractive index of air, as discussed above. In spite of spectroscopic custom, the use of air wavelengths should be avoided as much as possible because of the ambiguity associated with the selection of a particular refractive index of air. In the SI system, line positions are generally given in frequency ν in units of Hz (s^{-1}).

The customary units for cross sections are $\text{cm}^2/\text{molecule}$ and the conversion to SI units, $\text{m}^2/\text{molecule}$, is simple. The conversion of PNNL cross section units to $\text{cm}^2/\text{molecule}$ involves multiplication by 9.28697×10^{-16} . However, the conversion of line lists to cross sections is more difficult because lineshape functions are needed. In astronomy and atmospheric science, line-by-line calculations of radiative transfer are the most accurate, but slow. The use of absorption cross sections at a particular temperature, pressure and composition greatly speeds up the calculation of spectra. Some databases such as HITRAN include lineshape parameters and even provide tools to calculate cross sections and spectra [23]; however, most line lists do not and lineshape parameters need to be estimated.

The standard lineshape function is the Voigt function, which is a convolution of a Gaussian function for Doppler broadening and a Lorentzian function for pressure broadening [8]. The Doppler broadening part is easy to calculate because the FWHM (Full Width at Half Maximum), $\Delta\nu_D$, of the Gaussian is

$$\Delta\nu_D = 2\nu_0 \sqrt{\frac{2kT \ln(2)}{mc^2}} = 7.2 \times 10^{-7} \nu_0 \sqrt{\frac{T}{M}}, \quad (4)$$

in which T is in K, M in atomic mass units u , ν_0 and $\Delta\nu_D$ are in the same frequency units (e.g., cm^{-1}). The FWHM of the Lorentzian function $\Delta\nu_{1/2} = bp$ (p is pressure and b is the pressure broadening coefficient) depends on temperature and composition, and is often not known from experiment. Values can be estimated from similar systems or from a crude “rule-of-thumb” such as $b = 10 \text{ MHz/Torr}$, although calculated values are becoming available, e.g., [24]. Perhaps the most useful computer program for generating cross sections and spectra from line lists is ExoCross, which takes input line lists in HITRAN or ExoMol format [25].

Voigt lineshapes are no longer satisfactory for high accuracy work, for example, in atmospheric remote sensing. Deviations from the Voigt profile are measured in laboratory experiments and in atmospheric spectra [26] and need to be taken into account. The Hartmann–Tran lineshape function is the most common non-Voigt lineshape used [27] and with the inclusion of line mixing [28] appears to be capable of accurate representation of line profiles.

The diverse units used for line strengths are a source of confusion. To start at the beginning [8], it is necessary to define a line:

a line is a transition between two J values of an atom or molecule. (Lines can split, for example, into hyperfine components.) For this two-level system, the upper energy state J' has a degeneracy $g = 2J' + 1$ and the lower energy state degeneracy is $2J'' + 1$ associated with the M_J quantum number, in the absence of electric and magnetic fields. The key quantum mechanical quantity that determines line strengths for electric dipole transitions is the square of the transition dipole matrix element $S_{J'J''}$, i.e.,

$$S_{J'J''} \equiv \sum_{M'} \sum_{M''} |\langle J'M' | \boldsymbol{\mu} | J''M'' \rangle|^2, \quad (5)$$

in which $\boldsymbol{\mu} = -e\Sigma\mathbf{r}_i$ is the dipole operator. $S_{J'J''}$ is defined for both atoms and molecules, and has SI units of $\text{C}^2 \text{m}^2$. The customary unit for dipole and transition dipole moments is debye (D) and conversions from D to C m and atomic units are $1 \text{ D} = 3.335\,640\,952 \times 10^{-30} \text{ C m} = 0.393\,430\,2695 \text{ at. units} (ea_0) = 10^{-18} \text{ esu cm}$.

In a two-level system, the rate of radiative decay of the excited state is the Einstein A coefficient (reciprocal of the radiative lifetime) is given in SI units by

$$A_{J' \rightarrow J''} = \frac{16\pi^3 \nu^3 S_{J'J''}}{3\epsilon_0 \hbar c^3 (2J' + 1)}. \quad (6)$$

The $A_{J' \rightarrow J''}$ value is the best and simplest measure of line strength because it is unambiguous, has a simple interpretation and always has units of s^{-1} . Our line lists in MoLLIST include Einstein A values as does ExoMol and now HITRAN also. However, optical astronomers have traditionally liked absorption oscillator strengths, f , which are easily calculated from Einstein A values

$$f_{J' \leftarrow J''} = \frac{\epsilon_0 m_e c^3}{2\pi e^2 \nu^2} \frac{2J' + 1}{2J'' + 1} A_{J' \rightarrow J''}. \quad (7)$$

In fact, astronomers typically quote “ gf ” values, i.e., $gf = (2J'' + 1)f_{J' \leftarrow J''}$.

The drawback to A and f values in line lists is their lack of direct connection with the Beer–Lambert law, Eq. (1), i.e., they need to be converted to absorption cross sections σ before they can be used in radiative transfer calculations. With degeneracy included, Eq. (1) becomes

$$\frac{I}{I_0} = e^{-\sigma(N_0 - N_1 \frac{g''}{g'})l} = e^{-\alpha l}. \quad (8)$$

The conversion of A and f to a cross section σ in Eq. (8) for a single line requires a lineshape function $g(\nu - \nu_{10})$,

$$\sigma = \frac{A_{J' \rightarrow J''} \lambda^2 g(\nu - \nu_{10})}{8\pi} \frac{2J' + 1}{2J'' + 1} \quad (9)$$

and

$$\sigma(\nu) = \frac{e^2}{4\epsilon_0 m_e c} f_{J' \leftarrow J''} g(\nu - \nu_{10}). \quad (10)$$

Eqs. (1) and (8) or their differential forms make no assumption about thermodynamic equilibrium and involve only the populations of the two levels connected by the transition. This is a disadvantage in the usual case of thermodynamic equilibrium because the total population of a given species $N = \Sigma N_i$ is of interest and the populations of the individual levels are given by the usual Eq. from statistical thermodynamics,

$$N_i = N \frac{g_i e^{-\frac{E_i}{kT}}}{Q} \quad (11)$$

with the partition function Q defined as

$$Q = \Sigma g_i e^{-\frac{E_i}{kT}}. \quad (12)$$

It is therefore convenient to assume thermodynamic equilibrium at a temperature T , and to replace N_0 and N_1 by N in Eq. (8).

HITRAN makes this transformation at 296 K [6] and therefore provides line strengths S' (confusingly also called S) in the surprising units of $\text{cm}/\text{molecule}$ (or $\text{cm}^{-1}/(\text{molecule cm}^{-2})$) defined by another form of the Beer–Lambert law that also includes a lineshape function $g(\nu - \nu_{10})$

$$\tau = \frac{I}{I_0} = e^{-S'g(\nu - \nu_{10})Nl}. \quad (13)$$

Clearly the line intensity, S' , is an integrated effective cross section that can be determined by solving Eq. (13) as

$$S' = \frac{1}{Nl} \int \ln(I_0/I) d\nu \quad (14)$$

with the integration covering a single line to eliminate the lineshape function, $g(\nu - \nu_{10})$. The integration could also be over an entire band, in which case S' is interpreted as a band strength. From Eq. (14), the SI units for S' are thus $\text{m}^2 \text{s}^{-1}$ (or $\text{m}^2 \text{s}^{-1}/\text{molecule}$) but these are unfortunately almost never encountered.

If ν in Eq. (14) is replaced by $\tilde{\nu}$ in cm^{-1} , l in cm and N in $\text{molecules}/\text{cm}^3$, then S' has the “HITRAN units” of $\text{cm}^{-1}/(\text{molecule cm}^{-2})$ or $\text{cm}/\text{molecule}$. If the integral in Eq. (14) is taken over an entire infrared band, and the cm of the HITRAN unit is converted to km and moles are used instead of molecules in concentration, then the units km/mole favored by quantum chemists are obtained for S' . The conversion from $\text{cm}/\text{molecule}$ to km/mole requires multiplication by the numerical factor of $10^{-5} N_A = 6.022\,140\,76 \times 10^{18}$. Another possible choice is to measure concentration N in pressure units such as atmospheres, leading to S' in $\text{cm}^{-2}/\text{atm}$ (with $\tilde{\nu}$ in cm^{-1} , l in cm). The conversion from $\text{cm}^{-2}/\text{atm}$ to HITRAN units thus requires the use of the ideal gas law. To convert from $\text{cm}^{-2}/\text{atm}$ to $\text{cm}/\text{molecule}$, divide by the factor $0.101\,325/kT = 7.338\,940 \times 10^{21}/T$. Finally the conversion from HITRAN units ($\text{cm}/\text{molecule}$) to SI units ($\text{m}^2 \text{s}^{-1}/\text{molecule}$) requires multiplication by $10^{-2} c = 2\,997\,924.58$.

Conversion from Einstein A values to S' in SI units is accomplished by the equation

$$S' = \frac{c^2 (2J' + 1)}{8\pi \nu^2 Q} e^{-E_0/kT} (1 - e^{-h\nu_{10}/kT}) A_{J' \rightarrow J''}. \quad (15)$$

The analogous equation for S' in terms of S is

$$S' = \frac{2\pi^2 \nu}{3\epsilon_0 \hbar c Q} e^{-E_0/kT} (1 - e^{-h\nu_{10}/kT}) S_{J'J''} \quad (16)$$

and from f

$$S' = \frac{e^2 (2J'' + 1)}{4\epsilon_0 m_e Q} e^{-E_0/kT} (1 - e^{-h\nu_{10}/kT}) f_{J' \leftarrow J''}. \quad (17)$$

HITRAN tabulates S' for each line in HITRAN units at 296 K and to shift the line strength from the reference temperature T_0 to T , the ratio of Eq. (16) for two temperatures gives

$$\frac{S'}{S'_0} = \frac{Q_0}{Q} \exp\left(\frac{E_0}{kT_0} - \frac{E_0}{kT}\right) \left[\frac{1 - \exp\left(-\frac{h\nu_{10}}{kT}\right)}{1 - \exp\left(-\frac{h\nu_{10}}{kT_0}\right)} \right]. \quad (18)$$

Bernath’s textbook [8] provides many additional relations between line strength parameters, including numerical relationships in common units.

For quantitative spectroscopy, partition functions are essential and can be quickly estimated using the equations for the harmonic oscillator, rigid rotor approximation given in thermodynamics textbooks. However, for accurate work more reliable values are needed and are usually calculated by applying Eq. (12) to a large line list. As usual, the degeneracy factor g_i requires care because often nuclear spin is included. Several collections of partition functions are available including TIPS (Total Internal Partition Sums) associated partly with HITRAN [29] <https://hitran.org/docs/iso-meta/>

and from ExoMol calculations <http://exomol.com/data/data-types/partitionfunction/>. The JPL and CDMS rotational databases also provide values, but they are often just rotational partition functions. Barklem and Collet [30] have calculated partition functions for 291 diatomic molecules of astrophysical interest and all atoms in the periodic table.

JPL and CDMS also tabulate S' values in "JPL" intensity units to be used in Eq. (13) but the reference temperature is 300 K. JPL units are derived from Eq. (14) using ν in MHz and converting $1/Nl$ from $\text{m}^2/\text{molecule}$ to $\text{nm}^2/\text{molecule}$ by multiplying by 10^{18} . For numerical convenience, \log_{10} of these values are tabulated.

The conversion from JPL units to HITRAN units starts by dividing by $2.997\,924\,58 \times 10^{18}$. But as usual for line intensities, there are complications. HITRAN divides each line strength by a standard natural isotopic abundance <https://hitran.org/docs/iso-meta/> so that if an isotopologue line is used to measure an abundance, the total concentration of the molecule is obtained, not just the concentration of that isotopologue. JPL/CDMS assume all isotopologues are 100% abundant. The JPL/CDMS partition functions may be different because of nuclear spin factors and HITRAN always uses the total internal partition function. Finally the reference temperatures are different so the values need to be adjusted using Eq. (18).

5. Methods

The obvious method of obtaining line lists is to use the Beer-Lambert law, Eq. (13), and measure absorption spectra at a known temperature, concentration (N) and path length (l). Fitting the lines of the absorbance spectrum ($-\ln(I/I_0)$) with a suitable line shape function ($g(\nu - \nu_{10})$) yields a set of line positions (ν_{10}) and strengths (S'). Measurements at several temperatures and the application of Eq. (18) yields empirical lower state energies (E_0) for the lines, e.g., for NH_3 and CH_4 as provided on MoLLIST. Using spectra with different pressures of a broadening gas yields pressure-broadening coefficients (b) and their temperature dependence. In this way, a completely experimental line list can be obtained with Voigt line shape parameters.

In fact, "experimental" line lists such as HITRAN make considerable use of theory. Line positions and lower state energies are typically obtained by fitting the experimental data with a set of spectroscopic constants using, for example, the PGOPHER program [31]. This traditional model provides line positions to spectroscopic accuracy and interpolates to predict missing lines, but does not extrapolate very well because it is based on perturbation theory. An *ab initio* model is now possible by first solving the electronic Schrödinger equation to obtain a potential energy function and then solving the vibration-rotation Schrödinger equation to obtain energy levels. Experimental data are often used to adjust the potential energy function to improve agreement with experiment. The *ab initio* model does not reach experimental accuracy, but extrapolates more reliably because it is a more realistic and less empirical model. However, experimental line positions are usually used to replace calculated values to improve agreement with experiment. MoLLIST line lists use the traditional model for line positions, ExoMol and TheoReTS use the *ab initio* method, and HITRAN now uses both methods.

Line lists with experimental accuracy can also be generated by the MARVEL (Measured Active Rotational/Vibrational Energy Levels) procedure [32]. MARVEL takes as input the observed line positions from all sources with estimated errors and carries out a weighted least squares fit to obtain a set of energy levels with errors. By applying appropriate selection rules, a line list of all possible transitions among these levels can be generated with experimental accuracy and without recourse to any spectroscopic model. Many

molecules have now been analyzed by the MARVEL procedure, notably water vapor [33].

For line strengths, there are two cases: small molecules which have individual lines and large molecules for which lines are blended under typical conditions and cross sections are more appropriate. Intermediate sized molecules such as ethane, C_2H_6 , have both line-by-line analyses and cross sections available. In these cases, cross sections are often the better choice for real systems because in a given spectral region, line lists for hot bands and isotopologues may not be available. Cross sections are obtained by experimental measurements (calculations are also possible, e.g., [34]) under suitable conditions to match the target system, e.g., 1 atm of air and 296 K for atmospheric measurements near the surface of the Earth. These measurements make use of another version of the Beer-Lambert law,

$$\tau = \frac{I}{I_0} = e^{-\sigma Nl}, \quad (19)$$

in which σ is an effective cross section. MoLLIST provides a collection of high resolution infrared absorption cross sections for hot hydrocarbons (ethane, propane and propene) and cold organic molecules (ethane, propane, acetone, acetaldehyde, acetonitrile, methanol and isobutane). NIST (National Institute of Standards and Technology) has reference infrared cross sections for 40 organic molecules <https://webbook.nist.gov/chemistry/quant-ir/> at 296 K, 1 atm of nitrogen at 0.125 cm^{-1} maximum resolution [35]. The PNNL database has cross sections for several hundred molecules recorded under similar conditions and units are as in NIST, but at 5, 25 and 50°C . HITRAN includes most of the PNNL cross sections and many more collected at high spectral resolution, but mostly using air as the broadening gas.

For high temperature applications (e.g., for stellar atmospheres or combustion), line lists for small molecules become so large that they are unusable for practical applications. For example, Rey et al. [36] calculated more than 150 billion lines for CH_4 to simulate infrared spectra for sample temperatures up to 3000 K. These billions of lines are needed because although they are not resolved they contribute opacity. In the laboratory, high temperature absorption spectra of CH_4 consist of resolved lines and an underlying "quasicontinuum" of overlapped and blended lines [37]. Hargreaves et al. [37] analyzed these spectra in the pentad and octad regions ($2500\text{--}5000\text{ cm}^{-1}$) by fitting about 25 000 lines at each temperature and defining the remaining absorption after the lines are removed from the spectrum as an empirical continuum cross section. The huge *ab initio* line lists can be compressed in a similar way by explicitly including a few million strong and medium strength lines and combining the billions of weak lines into "superlines" [36] or continua [38]. These "hybrid" line lists therefore include corresponding continua and allow for much fast calculation of spectra.

The traditional method of handling line strengths in spectroscopy fits the experimental observations to simple models that assume the separation of electronic, vibrational and rotational motion, possibly with the inclusion of a correction function. A rovibronic line has an S value of $|\mathbf{R}_e|^2 q_{\nu\nu'} S_J^{\Delta J}$, the product of an electronic transition moment \mathbf{R}_e squared, a vibrational Franck-Condon factor q (or factors for polyatomic molecules) and a rotational Hönl-London factor $S_J^{\Delta J}$. Rovibrational lines have $S_{J,J'} = |\mathbf{M}_{\nu\nu'}|^2 S_J^{\Delta J}$, with the \mathbf{M} proportional to the square of a dipole moment derivative. Rotational lines have S given by $|\mu_i|^2 S_J^{\Delta J}$, in which μ_i is a dipole component.

This approximate separation does not generally reach experimental precision without inclusion of corrections such as Herman-Wallis factors [8] to account for vibration-rotation interaction. The *ab initio* method (e.g., ExoMol) makes the Born-Oppenheimer ap-

proximation in the separation of electronic and nuclear motion, but the solution of the vibration-rotation Schrödinger equation does not assume the separation of vibrational and rotational motion. For diatomic molecules with electron spin and orbital angular momentum, Yurchenko et al. [39] have written the program DUO to calculate line lists and spectra using the *ab initio* method.

We have developed an alternate method [40–42] to calculate high resolution line lists for diatomic molecules that has a number of advantages over the *ab initio* method. This semi-empirical method was developed as part of the Ph.D. thesis of J. Brooke, in collaboration with C. Western (University of Bristol).

The analysis method consists of:

1. Collect all measured line positions from both laboratory and astronomical spectra, recording new spectra as needed.
2. Fit the lines with an effective Hamiltonian using, for example, the PGOPHER program [31] and find new lines, e.g., predissociated lines of CH seen in Carbon-Enhanced Metal Poor (CEMP) stars but not in the laboratory emission spectra [43]. Measure new laboratory spectra, if needed. Iterate refitting and finding new lines until all data are satisfactorily accounted for.
3. Calculate (e.g., using MOLPRO program) *ab initio* dipole and transition dipole moment functions. In the case of CH [43], transition dipole moment calculations in the literature were used.
4. Determine the mechanical vibrational $G(v)$ and rotational $B(v)$ polynomial energy level expressions from the PGOPHER fit for use with Le Roy's RKR1 program [44] to obtain the potential energy function for each electronic state. The RKR potential energy functions and the (transition) dipole moment functions are used with Le Roy's LEVEL program [45] to solve the radial vibrational Schrödinger equation to obtain energy levels and vi-

brational 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 (for the Herman–Wallis effect).

5. Transform the dipole matrix element output from LEVEL without electron spin (Hund's case (b)) to matrix elements that include electron spin (Hund's case (a)) needed for input into PGOPHER [40,41].
6. Use PGOPHER to calculate line lists using transformed transition dipole matrix elements from LEVEL that include vibrational and rotational dependence.

In the semi-empirical approach the line positions and lower state energies have experimental accuracy. The line strengths, however, are based on a high level, *ab initio* dipole or transition moment functions. For small molecules, these *ab initio* line strengths can be as good as or even better than those derived from experiment [46].

The semi-empirical method was applied to the vibration-rotation bands of the $X^3\Sigma^-$ ground state of the NH free radical [40,41]. These infrared lines have been used to determine the N abundance in cool stars [47]. Often the CN radical is used for this purpose, but using NH gives a value that is independent of the C abundance. The line positions including data from a new exoatmospheric solar spectrum [1] were fitted to experimental accuracy using an effective Hamiltonian. This contrasts with *ab initio* methods, even with the DUO fitting program, that are unable to reproduce observations. High accuracy line positions are crucial, for example, in providing cross correlation templates for the characterization of exoplanet atmospheres [48].

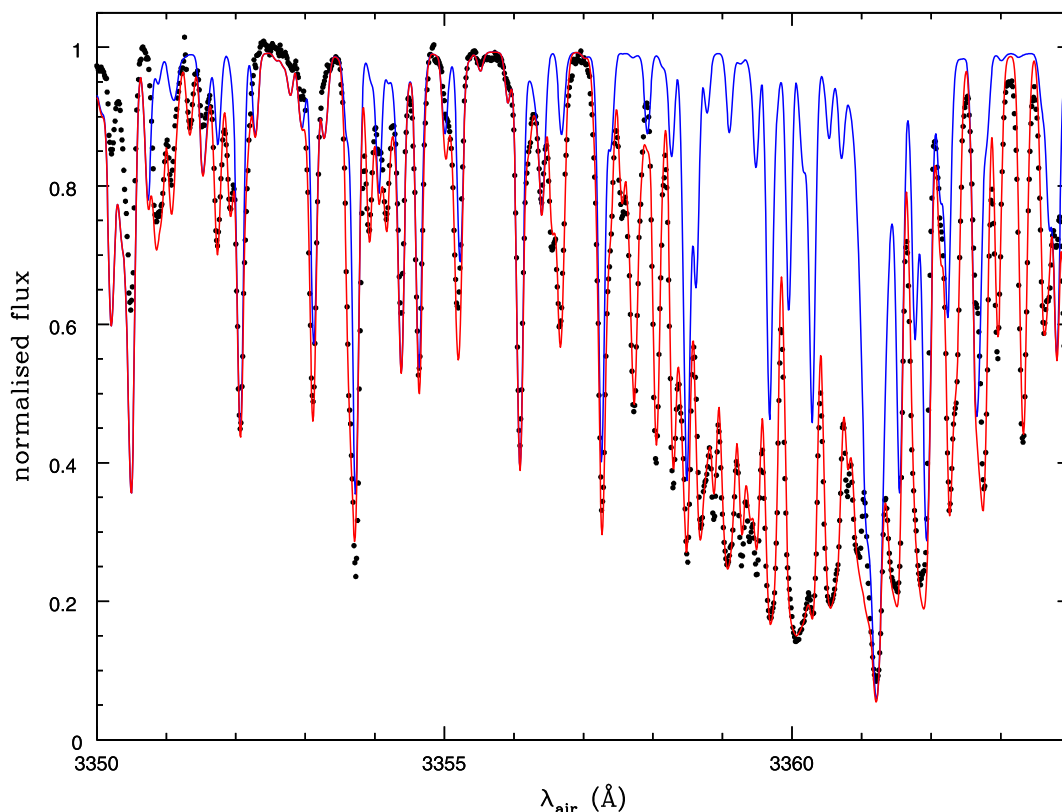


Fig. 2. Spectrum of the nitrogen-rich metal-poor star HD196944 (black dots), simulation without A-X NH lines, simulation with the best previous NH line list (green curve) and the simulation with our new A-X line list [49].

The semi-empirical method works equally well for electronic transitions as illustrated for the $A^3\Pi-X^3\Sigma^-$ transition of NH [49]. The A-X transition is observed in the photosphere of the Sun, in comets, in diffuse interstellar clouds and is prominent in CEMP stars [50]. Spite et al. [50] noticed a systematic discrepancy in the N abundance derived from the NH A-X lines compared to the value derived from CN. They suggested that the NH A-X line list needed revision, which we carried out [49]. The results are illustrated in Fig. 2, for a spectrum of the nitrogen-rich metal-poor star HD 196944. The dots are the observed spectrum [51], the blue simulation is without NH, the green simulation is with the previous standard line list and the red simulation is with our new A-X line list. The N abundance was obtained by Masseron et al. [51] by using CN transitions. Fig. 2 demonstrates that there is now very good agreement with the N abundance obtained from the CN lines in contrast to the value obtained with the previous NH line list.

The semi-empirical method has been applied to several important astronomical molecules including vibration-rotation bands [40,41] and $A^3\Pi-X^3\Sigma^-$ electronic transition [49] of NH, the vibration-rotation bands [52] and $A^2\Sigma^+-X^2\Pi$ transition of OH [53], $B^2\Sigma^+-X^2\Sigma^+$ and $A^2\Pi-X^2\Sigma^+$ transitions of CN plus isotopologues [3,54], $A^2\Pi-X^2\Sigma^+$ transition of CP [55], vibration-rotation bands and $A^3\Pi-X^3\Sigma^-$ transition of OH⁺ [56] and the Swan System of C₂ [57] and C¹³C [58]. These line lists are all available on the MoLLIST site.

For diatomic molecules in singlet states, a variation on the semi-empirical can be used. In this case, RKR potentials are not used, but in step 4 the experimental data are fitted to a parameterized potential energy function that can include corrections to the Born-Oppenheimer approximation. For this purpose, Le Roy's dPot-Fit [59] is the standard computer program. Step 5 is not needed and the output of LEVEL directly gives the final line list. This method was used to create line lists for the ground $X^1\Sigma^+$ states of LiF, LiCl [60], NaF, KF [61], AlF and AlCl [62], as well as the ground $X^2\Sigma^+$ states of MgF [63] and CaF [64] available on MoLLIST. For MgF and CaF ground $X^2\Sigma^+$ states, the small spin splitting was ignored.

The semi-empirical method also works for larger molecules. For example, a tensorial Hamiltonian was used to fit the strongest lines and features in the pentad bands of CF₄ in the 1600–1800 cm⁻¹ region [65]. The spectrum was dense because of numerous hot bands and individual line intensities were difficult to determine so they were obtained using a dipole moment function from a high level *ab initio* calculation.

6. Conclusion

Line lists are essential for the interpretation of astronomical and atmospheric spectra. Modern methods create large line lists with accurate line positions and line strengths that can be converted to absorption cross sections for more rapid calculation of spectra. For larger molecules, cross sections are measured in the laboratory with suitable conditions to match the temperature, pressure and composition of the target source. Data compilations of line lists and cross sections such as MoLLIST, HITRAN and ExoMol are very useful tools for spectral simulation.

Declaration of Competing Interest

None.

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