

REALISTIC NUMERICAL SYNTHESIS OF MOLECULAR SPECTRA

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INTRODUCTION

Spectroscopy is the classical diagnostic tool of astrophysics. Intensities and line shapes of well identified emission and/or absorption atomic and molecular features are used to provide information on species concentrations, and degree of excitation, from which gas kinetic, rotational, vibrational, electronic and excitation "temperatures" can be inferred when LTE conditions exist. Departures from LTE can also be determined spectroscopically. Diagnostic interpretation of spectra in optically thin circumstances is fairly straightforward. However, in optically thick conditions when the photon mean free path is very much less than the geometrical path, the emission spectrum is controlled by the absorption coefficient (Armstrong and Nicholls, 1972), (see equation 4a).

In high temperature and high pressure circumstances, thermal and collision broadening effects often cause strong overlap between neighbouring lines. In such cases it is very useful to be able to compare an observed spectrum profile with a realistically calculated synthetic profile whose form is controlled by relevant input data on species concentrations, temperature and pressure conditions, and basic atomic and molecular structure and transition probability constants. Over the past three decades, spectral synthesis methods of increasing power and flexibility have been developed for the diagnostic interpretation of molecular spectra which occur in astrophysics, atmospheric physics and laboratory circumstances. It is the purpose of this paper to provide a brief review of the methods and to give an example of one of them.

THE PRINCIPLE OF SPECTRAL SYNTHESIS

Spectrum synthesis is based on the well known equations (1a and 3a) for emission and absorption intensities. The integrated power of an emission spectral feature arising from transitions between an U(pper) and a L(ower) level is:

$$I_{UL} = K N_U A_{UL} E_{UL} \quad (1a)$$

where k is a constant which takes account of units, optical collection geometry and instrumental response, N_U is the species number density in the upper state, A_{UL} is the Einstein coefficient or transition probability per particle per second, and E_{UL} is the energy quantum involved.

For diatomic molecular spectra, the terms of equation (1a) are:

$$E_{UL} = hc/\lambda_{UL} = hc\nu_{UL} \quad (1b)$$

$$A_{UL} = (64\pi^4/3hc^3) \nu_{UL}^3 R_e^2 (\bar{r}_{v'v''}) q_{v'v''} S_{J'J''} \quad (1c)$$

$$N_U = (N/Q) \exp(-E_U/kT) \quad (1d)$$

$$\text{where } \nu_{UL} = \nu_{00} + \Delta G_v + \Delta F_J \quad (1e)$$

is the wavenumber of the spectral feature. It is determined by spectral structure constants of the vibrational ($G(v)$) and rotational ($F(J)$) eigenvalues (Herzberg, 1950). R_e is the electronic transition moment of the transition, $\bar{r}_{v',v''}$ is the r -centroid and $q_{v',v''}$ is the Franck-Condon factor of the band in question, and $S_{J',J''}$ is the Hönl-London factor of the line (Nicholls, 1969). When LTE conditions obtain, the Boltzman equation (1d) (in which Q is the partition function, N is the total species number density, and E_U is the upper level energy) can be used to predict species population and also to determine an appropriate temperature T . If the species of interest are formed in chemical reactions, chemical kinetics are used to estimate species concentration N and its variation with T .

Equation (1a) is recast in equation (2) as a function of ν to show how the contributions from the profiles of a number of lines contribute to the emission intensity at wavenumber ν .

$$I(\nu) = K \sum N_U R_e^2 (\bar{r}_{v',v''})^4 \nu_{v',J',v'',J''}^4 q_{v',v''} S_{J',J''} b(\nu) \tag{2}$$

Here $b(\nu)$ is the line profile function and \sum is the summation over every feature which contributes to the profile at wavenumber ν . Numerical spectral synthesis methods use this equation to calculate $I(\nu)$ at each of a number of closely spaced grid points.

Similarly, under optically thin conditions, the spectral transmission of an absorbing slab is given by:

$$I/I_0 = \exp(-\tau) \tag{3a}$$

where I_0 is the incident flux and I is the emergent flux. τ is the optical depth, which when integrated over a spectral feature is:

$$\tau = N \sigma X \tag{3b}$$

where N is the number density of absorbers, τ is the cross section per absorber, and X is the path length. When N_i absorbers of type i contribute to the extinction at wavenumber ν , equation (3b) becomes:

$$\tau = X \sum N_i \sigma_i(\nu) \tag{3c}$$

$$\text{and } \sigma_i(\nu) = (8\pi^3/3hc) \nu R_e^2 (\bar{r}_{v',v''})^4 q_{v',v''} E_{v',v'',J',J''} S_{J',J''} b(\nu) \tag{3d}$$

Numerical synthesis methods for absorption spectra are based on these equations.

In optically thick gases the absorption cross section $\sigma(\nu)$ controls the emission spectrum through equations (4a,b,c). Spectrum synthesis of $\sigma(\nu)$ is thus of great importance in both emission and absorption applications.

$$I(\nu) = B(\nu,T) (1-\exp(-k'(\nu,T) X)) \tag{4a}$$

where $B(\nu,T)$ is the Planck-Function and $k'(\nu)$ is the absorption coefficient with stimulated emission taken into account.

$$k'(\nu,T) = k(\nu) (1-\exp(-h\nu/kT)) \tag{4b}$$

and

$$k(\nu) = \sum N_i \sigma_i(\nu) \tag{4c}$$

These equations have also been used to predict radiation flux through radiometer pass bands in shock tube radiometry (Arnold and Nicholls, 1973; Cooper and Nicholls, 1975).

To use equations (2), (3) and (4) for spectrum synthesis it is necessary to:

- i) Determine all spectral feature line centres.
- ii) Place a line profile function $b(\nu)$ appropriate to each line at its centre.

- iii) Adjust the amplitude of the profile function to take account of transition probability and population factors.
- iv) Select a closely spaced grid of ν -values, and at each grid point add the contributions from each line whose profile has a significant value at the point.

Use of these procedures enables one to plot a realistic high resolution synthetic spectrum. The line profile function $b(\nu)$ derives from combined effects of collision (Lorentz) and thermal (Gaussian) line shapes. It is a Voigt function, algorithms for which exists (Armstrong, 1967; Whiting, 1968). To produce a synthetic spectrum plot for comparison with observed spectra it is also necessary to degrade the high resolution spectrum by convolution with an instrumental resolution profile. A normalized triangle function with suitable half-width can often be used for this purpose.

To perform the above procedures the following information is needed:

a) Line centre locations: They can either be determined from "look-up" tables of line centres, or from equation (1e) using molecular structure constants. Molecular structure data are not always known accurately enough, particularly for transitions between high quantum states, to locate line centres with sufficient precision for very high resolution spectra. The important compilation and assessment of Huber and Herzberg (1979) provides authoritative information on the reliability of available molecular data. Many of these data were derived from low temperature excitation sources, or in absorption.

b) The transition probability constants: Electronic transition moment $R_e(r)$, Franck-Condon factors $q_{v',v''}$, and r-centroids $r_{v',v''}$, Hönl-London factors $S_{J',J''}$. Many measurements of electronic transition moments and band strengths $S_{v',v''} = R_e^2 q^2$ have been reported in the literature for numerous band systems of astrophysical importance (Nicholls, 1977). Tables of Franck-Condon factors and r-centroids have been published for many band systems, based on a number of models of molecular potentials, including realistic potentials (Jarman, 1971; Jarman and McCallum, 1970). Approximate formulae for Franck-Condon factors are available for cases where insufficient molecular data, required for more complete calculations, exist (Nicholls, 1981, 1982). Extensive information on Hönl-London factors is available (Tatum, 1967; Kovacs, 1969; Whiting and Nicholls, 1974; Whiting, Paterson, Nicholls and Kovacs, 1973). None of these data should be accepted uncritically.

c) Effective half-widths of the Gaussian and Lorentzian line profiles for evaluation of the effective Voigt profile: These depend upon temperature, pressure and molecular constants (see equations (5a), (5b) below).

MOLECULAR SPECTRAL SYNTHESIS METHODS

The concept of Band Models was the earliest method of spectral synthesis to be developed. It often adopts a statistical approach to the distribution of lines in a band and their profiles (Goody, 1974; Penner, 1959; Plass, 1958; Kidd and King, 1971). This method is widely used to model intensity distributions of polyatomic molecular spectral features.

In the 1960's a number of laboratories developed dedicated spectral synthesis codes to calculate low resolution spectral absorption coefficient data of heated air (1000 to 200,000°) from soft X-ray to IR spectral regions. The SACHA (spectral absorption coefficient of heated air) code developed at the Lockheed Palo Alto laboratories is an example of such work (Armstrong and Nicholls, 1972; Churchill and Meyerott, 1965; Landhoff and Magee, 1969).

The Atmospheric Optics Laboratory of the Air Force Geophysics Laboratory has developed a most useful set of synthetic spectrum programmes for calculation of the spectral transmittance of and radiance through the earth's atmosphere. AFGL has also developed a massive compilation of line parameters; locations: strengths, and widths for 120,000 absorption lines of atmospheric molecules (Rothman et al., 1983). The best known of these programmes is LOWTRAN (Kneizys et al., 1983) for low spectral resolution calculations based on a band model method. For the synthesis of high resolution spectra FASCOD1 which calls on the AFGL line data set has been developed (Clough et al., 1981). HITRAN is referred to in various AFGL

reports for precision line-by-line calculations in small spectral regions, for example around laser frequencies (McClatchey et al., 1978). All of these programmes are for applications to the terrestrial atmosphere.

One of the first truly flexible programmes for calculation of intensity distributions of molecular spectra on a line-by-line basis was developed at the NASA Ames Laboratory by Arnold, Whiting and Lyle (1969). It treats emission and absorption spectra from electronic transitions from diatomic molecules, and some atoms, on a line-by-line basis in the spirit of equations (3,4,5). The capability of this programme has been extended in our laboratories over the past decade and several new programmes have been written for application to shock tube spectra (Shin and Nicholls, 1978) discharge spectra (Danylewych and Nicholls, 1978), astrophysical spectra (Danylewych et al., 1978), atmospheric absorption studies in the UV (Cann et al., 1979), Red (Cann et al., 1982), IR (Cann et al., 1985a) and microwave regions of the spectrum (Cann and Nicholls, 1985).

HIGH PRESSURE HIGH TEMPERATURE ABSORPTION SPECTRUM OF OXYGEN BETWEEN 180 AND 300 NM

To illustrate the numerical synthesis of molecular spectra, a brief description is given here of the results of a recent study made in our laboratories of the absorption coefficient of O₂ between 180 and 300 nm for temperatures between 300 and 3000°K, and for pressures between 1 and 50 atm. (Cann et al., 1984). While the work was done for applications to combustion and explosions, it does illustrate how the detailed character of molecular spectra are very sensitive to the molecular environment. High pressures and high temperatures are found in numerous astrophysical situations. A brief review of the principal trends is given below. Full details are given in Cann et al. (1984).

The principal contributors to the absorption coefficient of O₂ in the waveband are the O₂ Herzberg I (X³Σ - A³Σ) and Schumann-Runge (X³Σ - B³Σ) band systems and associated photodissociation continua.

Input data for the calculations were as follows:

a) Molecular Structure Constants: The constants from which line locations were calculated were taken from the literature (Creech and Nicholls, 1975; Cann et al., 1979).

b) Transition Probability Data: These were adopted from the recommendations of a critical review of the literature (Cann et al., 1979). Franck-Condon factors for the bands, and Franck-Condon Densities for the photodissociation continua were determined by use of the TRAPB programme of Jarman and McCallum, 1970 for realistic potentials. Hönl-London factors for effective singlet states were used, (Herzberg, 1950).

c) Line Profiles: The Voigt function profile $b(\nu)$ was generated by Whiting's (1968) approximation. The profile is specified by effective Gaussian and Lorentzian half widths W_G and W_L given by:

$$W_G = 2\nu(2kT \ln 2/mc^2)^{1/2} \text{ cm}^{-1} \quad (5a)$$

$$W_L = aP(273.2/T)^s \text{ cm}^{-1} \quad (5b)$$

and their ratio. P is the pressure in atmospheres, T is the temperature in degrees Kelvin, a is 0.3 and s is 0.7. Predissociation broadening was added to W_L as appropriate.

d) Thermodynamic Constants: Total number densities N of O₂ molecules were interpolated from thermochemical tables (Gray, 1972) and the relative populations in thermally excited vibration levels of X³Σ were evaluated from equation (1d).

To minimise computing, before making calculations of high resolution spectra, quantitative assessments were made in each case of which bands make major contributions to the absorption coefficient. Lines of these bands were incorporated in the calculations. High resolution spectra included about 7000 lines (at 300°) and 32,000 lines (at 3000°). The computation increment is typically 5×10^{-5} nm and a total number of points computed for each spectrum was about 5×10^5 . For

comparison with typical observational spectra the high resolution spectra were degraded numerically by convolution with a triangular "slit" function of full width at half maximum of 0.05nm which as stepped across the spectrum in 0.0125nm increments.

Examples of the many spectra which were calculated are displayed in Figures 1 and 2. They respectively display spectra at 300°K (1 and 50 atm) and at 3000°K (1 and 50 atm). In each case the lower plot is 1 atm and the upper is 50 atm. As temperature and pressure increase, spectral detail is quickly lost. At lower temperatures, the absorption coefficient decreases by many decades with increase in wavelength across the spectrum. The similar decrease at high temperatures is only a few decades. This is due to the effects of thermal and pressure broadening.

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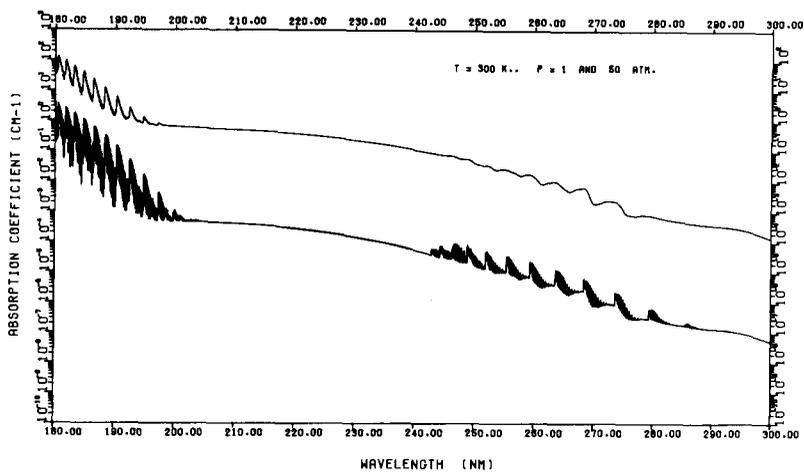


Figure 1: Synthetic 300°K O₂ Absorption Spectra at 1 (lower curve) and 50 (upper curve) Atmospheres.

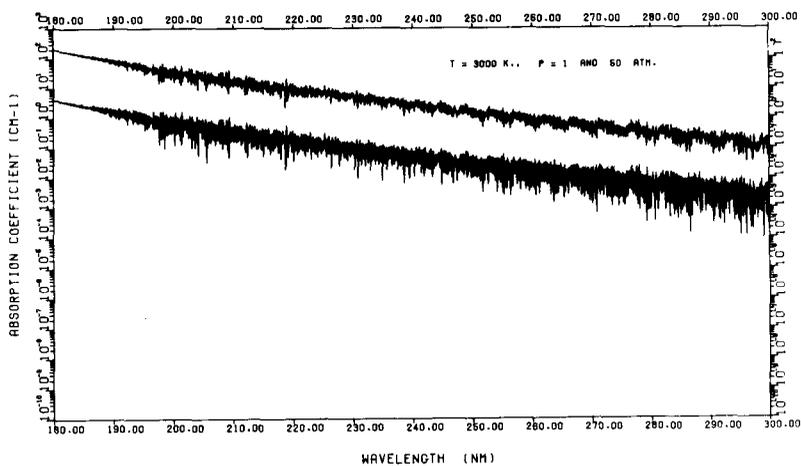


Figure 2: Synthetic 3000°K O₂ Absorption Spectra at 1 (lower curve) and 50 (upper curve) Atmospheres.