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Pressure broadening calculations for OH in collisions with argon: Rotational, vibrational, and electronic transitions

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ABSTRACT

Collisional parameters describing both the pressure-induced broadening and shifting of isolated lines in the spectrum of the hydroxyl radical in collisions with argon have been determined through quantum scattering calculations using accurate potential energy surfaces describing the OH($X^2\Pi$, $A^2\Sigma^+$)–Ar interactions. These calculations have been carried for pure rotational, vibrational, and electronic transitions. The calculated pressure broadening coefficients are in good agreement with the available measurements in the microwave, infrared, and ultraviolet spectral regions. Computed pressure broadening coefficients as a function of temperature are reported for these three types of transitions.

1. Introduction

The measurement of molecular concentrations invariably involves spectroscopic observation of the intensities of molecular spectral features. However, conversion of line intensities to level concentrations in finite-pressure environments requires taking account the effects of collisions, which can broaden or cause overlap of the molecular transitions. Hartmann et al. [1] have written a monograph that presents an extensive discussion of pressure broadening and other collisional effects on molecular spectra. Collisional line broadening parameters have been determined experimentally or theoretically through both semi-classical and quantum scattering calculations.

The hydroxyl (OH) radical is an important free radical in many environments, including combustion media and the earth's atmosphere. This species can be detected in the microwave, infrared, and ultraviolet spectral regions. Because of the importance of this radical, there have been a number of measurements of pressure broadening parameters in all three spectral regions. In view of the availability of state-of-the-art PES's for the interaction of OH with inert gases and small molecular partners [2–5], whose reliability has been calibrated by comparison of computed state-to-state cross sections with experimental measurements, it is useful to carry out quantum scattering calculations of pressure broadening parameters for OH spectroscopic transitions. We focus here on the effect on OH transitions of collisions with Ar. Comparison of these calculations will provide an additional check on the accuracy of the PES's. Moreover, calculations can then be performed on transitions and temperatures of interest, for which there are no experimental measurements.

We review here laser-based measurements of pressure broadening of OH transitions. Burrows et al. [6] measured in a laser magnetic resonance experiment line broadening parameters at room temperature for the OH lines at 118.6 cm^{-1} in the far infrared in collisions with He, Ar, and O_2. Chance et al. [7] employed tunable far-infrared spectroscopy to measure broadening parameters for the same line at two different temperatures with a variety of collision partners. These two experiments were in good agreement for the one collider (He) studied in both investigations. Park et al. [8] have carried out similar measurements of OH lines at 83.868 cm^{-1} at two different temperatures.

To our knowledge, there has been only one experimental investigation of collisional effects in the infrared spectrum of OH. Schiffman and Nesbitt [9] determined room-temperature pressure broadening coefficients for lines in the *P* branches of the $v = 1 \leftarrow v = 0$ vibrational transition in collisions with He, O_2, and N_2. In the case of Ar as a collision partner, evidence for Dicke narrowing was found, and the line shapes were analyzed in terms of a “hard collision” model to extract pressure broadening coefficients and Dicke narrowing parameters.

There have been several published reports of measurements of pressure broadening in the OH *A*–*X* electronic transition near 308 nm. Kessler et al. [10] measured line broadening and shifting of a number of lines in the *A*–*X* (1,0) in atmospheric-pressure hydrogen-air combustion gases. Shirinzadeh et al. [11] employed a narrow-band tunable uv laser to measure the pressure broadening width and shift at room temperature of one line in the *A*–*X* (0,0) band in collisions with a variety of collision partners, including Ar. Rea et al. [12] employed a rapidly scanned narrow-band laser and

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carried out a shock tube study of collisional broadening of lines in this band by Ar and N_2 at 2000 K. Kasyutich [13] has employed sum-frequency generation of two diode lasers (one frequency doubled) to measure room-temperature pressure broadening widths and shifts for several lines near the band origin of the A–X (0,0) band in collisions with a number of collision partners, including Ar.

Several theoretical calculations of OH pressure broadening parameters for pure rotational transitions have been reported. Buffa et al. [14] have employed Anderson theory to compute line shapes in collisions with N_2. Benećh et al. [15] used a semiclassical formalism with PES's composed of long- and short-range contributions to calculate temperature-dependent linewidths for Λ-doublet and pure rotational transitions in collisions with N_2, O_2, and Ar.

Because of the importance of pressure broadening in the interpretation of spectra of atmospheric species, the HITRAN spectroscopic database [16,17] includes collisional line parameters for OH transitions. This database covers only rotational and vibrational transitions of OH. The line broadening parameters in this database are based [18] on the data from Chance et al. [7], Park et al. [8], and Schiffman and Nesbitt [9].

In the present study, we have performed time-independent quantum scattering calculations of pressure broadening cross sections as a function of energy for pure rotational transitions and lines in the $v = 1 \leftarrow v = 0$ vibrational transition and the (0,0) band of the A–X electronic transition. We have averaged over the collision energy to determine coefficients for the broadening and shifting of the lines.

It should be mentioned that other recent theoretical work has explicitly included treatment of speed-dependent collision rates and velocity changing collisions, along with broadening and shifting of the lines [19–21].

This paper is organized as follows: Section 2.1 presents a brief review of time-independent quantum scattering calculation of pressure broadening cross sections, while Section 2.2 describes the sources of the employed PES's. Section 3 presents the details of the scattering calculations. Pressure broadening cross sections and coefficients for OH pure rotational, rovibrational, and electronic transitions are presented in Section 4. A discussion in Section 5 concludes the paper.

2. Theory

2.1. Pressure broadening cross sections

The fundamental theory of broadening of spectral lines through molecular collisions in terms of the S matrix, obtained from time-indepemdent quantum scattering calculations, has been known for some time [22,23]. From Shafer and Gordon [24], the cross section for pressure broadening of an isolated line, from an initial level with total angular momentum j_i to a final level j_f, can be written as

$$\sigma^K_{f\leftarrow i} = (\pi/k^2) \sum_{JJ'LL'} [J][J'](-1)^{L-L'} \begin{Bmatrix} j_i & K & j_f \\ J' & L & J \end{Bmatrix} \times \begin{Bmatrix} j_i & K & j_f \\ J' & L' & J \end{Bmatrix} \left[\delta_{LL'} - S^{J'*}_{fL',iL} S^{J}_{fL,iL} \right] \tag{1}$$

In Eq. (1), K is the tensor order and equals 1 for dipole transitions and 0 or 2 for Raman transitions, $\{:::\}$ is a 6j symbol [25], and $[x] = 2x + 1$. The first and second set of S matrix elements in Eq. (1) are computed for the initial and final levels, respectively, in close-coupling scattering calculations at total energies corresponding to the same collision energy. The J and L, and J' and L', are the total and orbital angular momenta, respectively, of the collision complex. The real and imaginary parts of the pressure broadening cross section in Eq. (1) contribute to the broadening and shifting of the line, respectively.

Pressure broadening coefficients can be obtained by taking a Boltzmann average of pressure broadening cross sections over the collision energy E_c:

$$k^{\mathrm{PB}}_{f\leftarrow i}(T) = \left[\frac{8}{\pi\mu (k_B T)^3} \right]^{1/2} \int_0^\infty E_c \sigma^{\mathrm{PB}}_{f\leftarrow i}(E_c) e^{-E_c/k_B T} dE_c \tag{2}$$

where μ is the collision reduced mass and k_B is the Boltzmann constant. Pressure broadening parameters are usually reported in units of $\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$. In these units, the broadening (FWHM) γ and shift η of a spectral line are

$$\gamma = 2\,\mathrm{Re}(k^{\mathrm{PB}}) N/2\pi c \tag{3}$$

$$\eta = -\,\mathrm{Im}(k^{\mathrm{PB}}) N/2\pi c \tag{4}$$

where N is the collider density at 1 atm, and c is the speed of light.

Baranger [22] showed that for a pair of nondegenerate levels the real part of the pressure broadening cross sections for an isolated line can be resolved with the help of the optical theorem into inelastic and elastic contributions. We have

$$\mathrm{Re}[\sigma^{\mathrm{PB}}_{f\leftarrow i}(E)] = \frac{1}{2} \left[\sum_{f'} \sigma^{\mathrm{inel}}_{f'\leftarrow i}(E) + \sum_{i'} \sigma^{\mathrm{inel}}_{f\leftarrow i'}(E) \right] + \int |f_i(\Omega, E) - f_f(\Omega, E)|^2 d\Omega \tag{5}$$

where $\sigma^{\mathrm{inel}}_{f'\leftarrow i}$ and $\sigma^{\mathrm{inel}}_{f\leftarrow i'}$ are state-to-state inelastic integral cross sections out of the initial level and into the final level, respectively, and $f_i(\Omega, E)$ and $f_f(\Omega, E)$ are differential elastic scattering amplitudes. Strekalov [26] derived this relationship in general within the centrifugal decoupling, coupled states approximation. We have been unable to prove this relationship in the full, close coupled treatment of the scattering. It will nevertheless be interesting to compare the real part of the pressure broadening cross section with the inelastic contribution in Eq. (5). The dependence of the pressure-broadening linewidth upon the cross sections for removal of population by inelastic collisional processes is understandable since inelastic collisions have the effect of shortening the time spent in a given level and hence increasing the energy uncertainty (width) through the time-energy uncertainty principle.

2.2. Potential energy surfaces

Since the OH($X^2\Pi$) electronic state is orbitally degenerate, the interaction of this species with a structureless collision partner (e.g. argon) must be described by two PES's, of A' and A'' symmetry [27]. These PES's were taken from the work of Scharfenberg et al. [3]. Here, the spin-unrestricted coupled-cluster method [UCCSD (T) method with an aug-cc-pvqz basis was employed]. Calculations of the A' and A'' interaction energies as a function of the atom-molecule separation R (35 values) and Jacobi angle θ (10 values) were carried out for 4 values of the OH internuclear separation r. The interaction potentials for OH in its v=0 and 1 vibrational levels were obtained by averaging over the r probability distributions for these levels.

For the scattering calculations, the angular dependence of the sum V_{sum} and difference V_{dif} of the A' and A'' PES's were fit to the following expressions [27] in terms of reduced rotation matrix elements: