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 $\text{OH}(X^2\Pi, A^2\Sigma^+)$ –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.

Keywords: pressure broadening, hydroxyl, quantum scattering calculations

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 semiclassical and quantum scattering calculations.

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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, 3, 4, 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 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 . Beneč 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, 20, 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 Sec. 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 Sec. 4. A discussion in Sec. 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-independent 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

$$\sigma_{f \leftarrow i}^K = (\pi/k^2) \sum_{JJ'LL'} [J][J'] (-1)^{L-L'} \left\{ \begin{matrix} j_i & K & j_f \\ J' & L & J \end{matrix} \right\} \times \left\{ \begin{matrix} j_i & K & j_f \\ J' & L' & J \end{matrix} \right\} [\delta_{LL'} - S_{fL',iL}^{J'*} S_{fL',iL}^J] \quad (1)$$

In eq 1, K is the tensor order and equals 1 for dipole transitions and 0 or 2 for Raman transitions, $\{ \begin{smallmatrix} :: \end{smallmatrix} \}$ 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 :

$$k_{f \leftarrow i}^{\text{PB}}(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_0^\infty E_c \sigma_{f \leftarrow i}^{\text{PB}}(E_c) e^{-E_c/k_B T} dE_c \quad (2)$$

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

$$\gamma = 2\text{Re}(k^{\text{PB}})N/2\pi c \quad (3)$$

$$\eta = -\text{Im}(k^{\text{PB}})N/2\pi c \quad (4)$$

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

$$\begin{aligned} \text{Re}[\sigma_{f \leftarrow i}^{\text{PB}}(E)] = & \frac{1}{2} \left[\sum_{f'} \sigma_{f' \leftarrow i}^{\text{inel}}(E) + \sum_{i'} \sigma_{f \leftarrow i'}^{\text{inel}}(E) \right] \\ & + \int |f_i(\Omega, E) - f_f(\Omega, E)|^2 d\Omega \end{aligned} \quad (5)$$

where $\sigma_{f' \leftarrow i}^{\text{inel}}$ and $\sigma_{f \leftarrow i'}^{\text{inel}}$ 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 $\text{OH}(X^2\Pi)$ 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:

$$V_{\text{sum}} = \sum_{\lambda=0}^{10} V_{\lambda 0}(R) d_{00}^{\lambda}(\theta) \quad (6)$$

$$V_{\text{dif}} = \sum_{\lambda=2}^{10} V_{\lambda 2}(R) d_{20}^{\lambda}(\theta) \quad (7)$$

The angular expansion coefficients were determined for a given value of R by a linear least squares fit of the angle-dependent energies. The isotropic term V_{00} was morphed at long range to the functional form $-C_6R^{-6} - C_8R^{-8}$ with a hyperbolic tangent function, with the values of C_6 and C_8 determined by fitting the values of V_{00} at $R = 10a_0$ and $15a_0$. The anisotropic $V_{\lambda 0}$ terms and the $V_{\lambda 2}$ terms were damped to zero with the same hyperbolic tangent function. Contour plots of the PES's and the angular expansion coefficients of a slightly earlier calculation of the OH($X^2\Pi$)–Ar potential can be found in the work of Paterson et al. [28, 29].

The PES's describing the OH($A^2\Sigma^+$)–Ar interaction was taken from Kłos et al. [2]. In this work, CASSCF calculation with 5 electrons in 3 active orbitals was first carried out, with an aug-cc-pvqz basis. Canonical orbitals were obtained from the CASSCF orbitals and then used in RHF calculations. Finally, RCCSD(T) calculations with the RHF orbitals were carried out. The angular dependence of the PES was fit to eq 6. The angular expansion terms were morphed at long range in the manner as was done for the OH($X^2\Pi$)–Ar V_{sum} PES. Specifically, the isotropic term V_{00} was morphed at long range to $-C_6R^{-6} - C_8R^{-8}$ radial dependence, and the anisotropic $V_{\lambda 0}$ terms were damped to zero at large R . A contour plot of this PES is available in Ref. [2].

3. Scattering calculations

Full close-coupling time-independent calculations of pressure broadening cross sections for pure rotational, vibrational, and electronic transitions were performed with the HIBRIDON suite of programs [30], extended to include the calculation of pressure broadening cross sections. Care was taken to include a sufficient number of partial waves and OH rotational/fine-structure levels in the scattering basis to converge the cross sections. For the X state, the OH rotational basis included levels up to $j = 16$ and partial waves up to $J = 408$ at the highest total energies. For the A state, the OH rotational basis included levels up to $j = 17$ and partial waves up to $J = 397$. Integral and pressure broadening cross sections were computed on a grid of 30 collision energies, up to a maximum collision energy of 1500 cm^{-1} .

Figure 1: The real and imaginary parts of the pressure broadening cross section for the OH $j = 4.5 F_1e \leftarrow j = 3.5 F_1e$ pure rotational transition as a function of the collision energy. Also plotted are the total inelastic cross sections for transitions out of the $j = 4.5 F_1e$ and $j = 3.5 F_1e$ levels.

4. Results

4.1. Pure rotational transitions

Figure 1 presents the energy dependence of the real and imaginary parts of the pressure broadening cross section for one pure rotational transition and the total integral inelastic cross section for transitions out of the lower level and into the upper level of this transition. The energy dependence displayed by these cross sections is typical for the transitions and levels we have investigated. It is seen that the cross sections are large at low energies and decrease with increasing collision energy. We see that the total inelastic cross sections go through a shallow minimum and then increase modestly at higher collision energy. The real part of the pressure broadening cross section is only slightly larger than the average of the summed inelastic cross sections for the initial and final levels.

To explore the role of the various contributions to the pressure broadening cross sections, it is of interest to investigate their dependence upon the impact parameter. Since the rotational angular momentum j is generally much smaller than the orbital angular momentum L , we can investigate the impact parameter dependence by examining partial cross sections, i.e. the cross sections for the individual total angular momenta J .

Figure 2: Partial cross sections as a function of the total angular momentum J of the real and imaginary parts of the pressure broadening cross section for the OH $j = 4.5$ $F_1e \leftarrow j = 3.5$ F_1e transition at a collision energy of 300 cm^{-1} . Also plotted are the total inelastic partial cross sections for transitions out of the $j = 4.5$ F_1e and $j = 3.5$ F_1e levels.

Figure 2 compares the partial cross sections for the processes plotted in Fig. 1 for a collision energy of 300 cm^{-1} . We see that the range of total angular momenta J , and hence impact parameter, is essentially identical for the real part of the pressure broadening cross section and the total inelastic cross sections out of the lower level and into the upper level of this transition. By contrast, the range of total angular momenta that contribute to the imaginary part of the pressure broadening cross section is much narrower.

We have computed room-temperature (296 K) coefficients for collisional broadening and shifting of OH pure rotational transitions due to collisions with Ar. Figure 3 presents the results of such calculations at a temperature of 296 K. The broadening coefficients for the f levels are smaller than those for the e levels at the lowest values of j , but these coefficients are essentially equal at $j = 3.5$. The pressure broadening coefficients are seen to decrease monotonically with increasing j . As we show in Sec. 4.2 for both pure rotational and vibrational transitions, the j dependence and the magnitude of the coefficients mirror quite closely the j dependence of the total inelastic rate coefficients for the initial and final levels. If eq 5 can be applied to these close-coupling calculations, this suggests that the elastic contribution to the pressure broadening is small.

Figure 3: Computed 296 K coefficients for collisional broadening and shifting by Ar for OH pure rotational $j' = j + 1$ $F_1e/f \leftarrow j$ F_1e/f transitions (R_{1ee} and R_{1ff} branches). Also plotted is the pressure broadening coefficient measured by Burrows et al. [6] for one transition.

We have also included in Fig. 3 the pressure broadening coefficient from the only measurement involving the Ar collision partner, by Burrows et al. [6]. This measurement was carried out in a laser magnetic resonance experiment, and the e/f symmetry was not specified. We see that the agreement between experiment and theory is quite good. The coefficient for the pressure-induced shift is approximately constant for the e levels as a function of j , while those for the f levels are smaller than for the e levels and change sign above $j = 3.5$. It should be noted that the shift coefficient is positive for most transitions, while the imaginary part of the pressure broadening cross section is negative (see Fig. 1), since the imaginary part of the cross section and pressure shift coefficient have opposite signs from eq 4.

We have extended our calculations of pressure broadening parameters to a range of temperatures. Table 1 presents the broadening coefficients for the OH pure rotational $j' = j + 1$ $F_1e \leftarrow j$ F_1e transitions. We see that for all the transitions the magnitude of the broadening coefficient decreases as a function of temperature. This follows from the fact that the pressure broadening cross sections have a monotonically decreasing dependence upon the collision energy (see Fig 1).

Table 1: Pressure broadening coefficients γ as a function of temperature for the OH $j' = j + 1 \ F_1e \leftarrow j \ F_1e$ pure rotational transitions

T (K)	$\gamma / 10^{-2} \text{ cm}^{-1} \text{ atm}^{-1}$					
	$j = 1.5$	$j = 2.5$	$j = 3.5$	$j = 4.5$	$j = 5.5$	$j = 6.5$
200	13.20	9.77	8.28	7.10	6.06	5.16
220	12.28	9.14	7.75	6.68	5.73	4.90
250	11.15	8.36	7.12	6.16	5.33	4.59
273	10.43	7.87	6.72	5.84	5.07	4.39
296	9.81	7.45	6.38	5.56	4.85	4.21
320	9.25	7.07	6.07	5.30	4.65	4.05
350	8.64	6.65	5.73	5.03	4.43	3.88
400	7.80	6.08	5.27	4.64	4.12	3.63
500	6.54	5.21	4.55	4.05	3.63	3.23

4.2. Vibrational transitions

It is interesting to compare the pressure broadening coefficients for pure rotational transitions and transitions within a vibrational band with the rate coefficients for removal of population from the lower level and population of the upper level of the transition. This will allow us to gauge the importance of the elastic contribution to pressure broadening, assuming that eq 5 can be applied to close-coupling calculations. Figure 4 presents these coefficients for pure rotational transitions and transitions within the (1,0) vibrational band. It can be seen that in Fig. 4(a), except for the transition out of the $j = 1.5$ level, the pressure-broadening coefficients are only slightly larger than the average of the total rate coefficients for transitions out of the lower level and into the upper levels. This suggests that the elastic contribution to pressure broadening of pure rotational transitions is small. Comparing Figs. 4(a) and 4(b), the pressure broadening coefficients for the vibrational transition are seen to be slightly larger than those for the corresponding pure rotational transitions. This reflects the slight differences in the PES's for the interaction of OH($X, v=0$) and OH($X, v=1$) with Ar.

Figure 5 presents computed room-temperature coefficients for collisional broadening and shifting of OH transitions for P -branch transitions within the (1,0) vibrational band. The P -branch transitions have greater intensity than lines in the R branches in a vibrational transition, and lines in these branches were chosen for experimental measurement [9]. As found for pure rotational transitions and mirroring the j dependence of the total removal coefficients

Figure 4: Computed 296 K rate coefficients for collision-induced broadening and total inelastic removal from the lower and population of the upper level for OH (a) $j' = j + 1$ $F_{1e} \leftarrow j F_{1e}$ pure rotational transitions and (b) $j' = j + 1$ $F_{1e} \leftarrow j F_{1e}$ within the (1,0) vibrational band.

(see Fig. 4), the pressure broadening coefficients are seen to decrease with increasing j . For low OH rotational angular momentum j , the pressure broadening coefficients for P_{1ee} transitions are slightly larger than those in the P_{1ff} branch, but at higher j the coefficients are essentially identical for these two branches. The computed coefficients for the R_{2ee} branch are found to be somewhat smaller than those in the P_{1ee} and P_{1ff} branches.

We have also plotted in Fig. 5 the measured pressure-broadening coefficients reported by Schiffman and Nesbitt [9]. There is reasonable agreement between the measured and computed pressure-broadening coefficients for low j . However, at higher j the experimental values are somewhat lower than those computed here. As Schiffman and Nesbitt note, they found that the OH line shapes in collisions with Ar, in contrast to the other perturbers investigated, were affected by line narrowing. They extracted the pressure-broadening coefficients within a "hard collision" model. It is possible that this approach could lead to an underestimate of the width of the Lorentzian pressure-broadening coefficient.

Table 2 presents pressure broadening coefficients for the transitions within the P_{1ee} branch of the OH (1,0) vibrational band. We see that these coef-

Figure 5: Computed 296 K coefficients for collision-induced broadening and shifting by Ar for OH transitions within the (1,0) vibrational band: $j' = j - 1$ $F_{1,2e}/f \leftarrow j$ $F_{1,2e}/f$ transitions (P_{1ee} , P_{2ee} , and P_{1ff} branches). Also plotted (solid points) are experimental pressure-broadening measurements by Schiffman and Nesbitt [9].

ficients decrease with increasing temperature, similar to what we found for the pure rotational transitions (see Table 1).

4.3. Electronic transitions

Figure 6 presents computed room-temperature coefficients for collisional broadening and shifting of OH transitions in the Q_1 and P_1 branches of the $A - X$ (0,0) electronic band. Comparison of the coefficients for these lines in the $A - X$ electronic transition with those for pure rotational (see Fig. 3) and transitions within the (1,0) vibrational band (see Fig. 5) shows that the coefficients for the electronic transition are significantly larger. Moreover, the coefficients for the electronic transitions show almost no dependence upon the OH rotational angular momentum j , in contrast to the strong dependence upon j for the pure rotational and vibrational transitions. We found a similar weak dependence of the pressure broadening coefficient for other branches, viz. the R_1 branch.

We compare in Fig. 6 these computed coefficients with the experimental measurements of Shirinzadeh et al. [11] and Kasyutich [13]. We see that there is quite good agreement for the three lines for which experimental measurements have been made. The agreement between experiment and

Table 2: Pressure broadening coefficient γ as a function of temperature for the OH $j' = j - 1 F_1 e \leftarrow j F_1 e$ transitions (P_{1ee} branch) of the (1,0) vibrational band

T (K)	$\gamma / 10^{-2} \text{ cm}^{-1} \text{ atm}^{-1}$					
	$j = 2.5$	$j = 3.5$	$j = 4.5$	$j = 5.5$	$j = 6.5$	$j = 7.5$
200	14.11	10.54	9.14	7.93	6.83	5.87
220	13.10	9.84	8.53	7.43	6.43	5.54
250	11.85	8.98	7.80	6.82	5.94	5.15
273	11.07	8.44	7.34	6.43	5.63	4.90
296	10.39	7.98	6.95	6.10	5.37	4.69
320	9.78	7.55	6.59	5.81	5.13	4.50
350	9.12	7.10	6.21	5.49	4.86	4.28
400	8.21	6.47	5.68	5.04	4.50	3.98
500	6.86	5.52	4.87	4.36	3.92	3.51

Figure 6: Computed 296 K coefficients for collision-induced broadening and shifting by Ar for OH transitions in the (a) Q_1 and (b) P_1 branches of the (0,0) band of the $A - X$ electronic transition. The OH angular momentum j is the value for the lower level. Also plotted (solid points) are experimental measurements of the broadening and shifting of transitions by Kasyutich [13] (Q_1 transitions) and Shirinzadeh et al. [11] ($P_1(1.5)$ transition).

Figure 7: Computed 296 K coefficients for collision-induced broadening and inelastic rate coefficients for removal of the lower levels and population of upper levels for OH Q_1 transitions in the $A - X$ (0,0) band.

theory is not generally quite as good for the line shift. This measurement depends upon accurate determination of the absolute laser wavenumber.

To explore the differences in the j dependence of the pressure broadening coefficient for the three types transitions, we compare in Fig. 7 pressure broadening coefficients and inelastic rate coefficients for removal of the lower levels and population of the upper levels of lines in the $A - X$ electronic transition. We see that the rate coefficients for removal of population of the lower and into the upper levels of these transitions display a general decrease in magnitude with increasing j , as expected for the rotational dependence of cross sections for collision-induced rotational transitions (see Fig. 4). Unlike pure rotational and vibrational transitions, the pressure broadening coefficients for the electronic transition are much larger than the average of the rate coefficients for collisional removal of the lower levels and population of the upper levels of the transition. Indeed, the increase of the elastic contribution to the pressure broadening coefficient with increasing j roughly compensates for the decrease in the population transfer rate coefficients so that the pressure broadening coefficient has a very weak dependence upon j .

It is understandable that the elastic contribution to the pressure broadening coefficient for the electronic transition should be so much larger than the

Table 3: Pressure broadening coefficients γ as a function of temperature for lines in the Q_1 branch of the OH $A - X$ (0,0) band

T (K)	$\gamma / 10^{-2} \text{ cm}^{-1} \text{ atm}^{-1}$						
	$j = 1.5$	$j = 2.5$	$j = 3.5$	$j = 4.5$	$j = 5.5$	$j = 6.5$	$J = 7.5$
200	18.12	19.34	19.42	19.21	19.77	20.13	19.40
220	16.89	17.97	18.04	17.79	18.31	18.68	18.02
250	15.38	16.27	16.35	16.07	16.53	16.90	16.33
273	14.44	15.20	15.28	14.99	15.41	15.77	15.25
296	13.62	14.28	14.36	14.07	14.45	14.80	14.33
320	12.88	13.44	13.52	13.24	13.59	13.92	13.49
350	12.09	12.53	12.62	12.34	12.66	12.96	12.58
400	10.98	11.28	11.37	11.11	11.38	11.66	11.33
500	9.31	9.40	9.49	9.28	9.49	9.70	9.46

elastic contributions for rotational and vibrational transitions. The interaction of OH($X^2\Pi$) with Ar is quite different than that for the excited $A^2\Sigma^+$ state. For the $X^2\Pi$ state, the well depth D_e of the V_{sum} PES is 142 cm^{-1} , at an Ar–HO linear geometry, with a shallow secondary Ar–OH minimum with a well depth of 92 cm^{-1} [3]. By contrast, the well depths for the excited $A^2\Sigma^+$ state, at the two linear geometries, are much greater (1219 and 1720 cm^{-1} for the Ar–HO and Ar–OH geometries, respectively) [2].

As with the other types of transitions discussed in Secs. 4.1 and 4.2, we present computed pressure broadening coefficients of the OH electronic transition. Table 3 presents parameters for lines in the Q_1 branch of the $A - X$ (0,0) band. These coefficients show a similar dependence upon temperature as the pressure broadening coefficients as for pure rotational and vibrational transitions.

5. Discussion and Conclusion

In this paper, we have reported quantum scattering calculations of coefficients for pressure broadening and shifting of pure rotational, rovibrational, and electronic transitions of the OH radical in collisions with argon. These calculations were carried out with recently calculated high-quality PES’s for the interaction of OH($X^2\Pi, v = 0, 1$) and OH($A^2\Sigma^+$) with Ar [2, 28, 29]. The computed room-temperature pressure broadening coefficients were compared with experimental measurements where available. Agreement between

experiment and theory was generally quite good.

Within the centrifugal decoupling, coupled states approximation, the real part of the pressure broadening cross section, and hence coefficient, equals the sum of the average of the corresponding quantities for removal of the lower level and population of the upper level of the transition and an elastic contribution (eq 5). While this relationship does not hold rigorously for full, close-coupling calculations, it is nevertheless interesting to compare the magnitudes of the pressure broadening and population removal rates. We find that the OH pressure broadening rate is only slightly larger than the average of population removal rate for pure rotational and rovibrational transitions. Since the population removal rate coefficients decreases with increasing rotational excitation, pressure broadening for these types of transitions also decrease with increasing rotational excitation.

By contrast, the elastic contribution is comparable to or larger than the population removal rate coefficient for the electronic transition. We find that the pressure broadening coefficients for lines in the $A - X$ electronic transition are approximately independent of OH rotational level. It is interesting to look at the rotational level dependence of pressure broadening for other radicals. Room-temperature pressure broadening coefficients have been measured for both the $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Pi$ transitions of the CN radical [31, 32]. The dependence of the pressure broadening coefficient in these band systems also appears to depend weakly upon rotational excitation.

Since calculations can be carried out for conditions not so readily achievable in the laboratory, we have reported coefficients for pressure broadening as a function of temperature of 200-500 K for selected pure rotational, vibrational, and electronic transitions of OH.

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References

- [1] J.-P. Hartmann, C. Boulet, D. Robert, Collisional Effects on Molecular Spectra, Elsevier, Amsterdam, 2008.

- [2] J. Kłos, M. H. Alexander, M. Brouard, C. J. Eyles, F. J. Aoiz, A new potential energy surface for $\text{OH}(A^2\sigma^+)-\text{Ar}$: The van der Waals complex and scattering dynamics, *J. Chem. Phys.* 129 (2008) No. 054301.
- [3] L. Scharfenberg, J. Kłos, P. J. Dagdigian, M. H. Alexander, G. Meijer, S. Y. T. van de Meerakker, State-to-state inelastic scattering of Stark-decelerated OH radicals with Ar atoms, *Phys. Chem. Chem. Phys.* 12 (2010) 10660–10670.
- [4] K. B. Gubbels, Q. Ma, M. H. Alexander, P. J. Dagdigian, D. Eanis, G. C. Groenenboom, A. van der Avoird, S. Y. T. van de Meerakker, Resonances in rotationally inelastic scattering of $\text{OH}(X^2\pi)$ with helium and neon, *J. Chem. Phys.* 136 (2012) No. 144308.
- [5] H. C. Schewe, Q. Ma, N. Vanhaecke, X. Wang, J. Kłos, M. H. Alexander, S. Y. T. van de Meerakker, G. Meijer, A. van der Avoird, P. J. Dagdigian, Rotationally inelastic scattering of OH by molecular hydrogen: Theory and experiment, *J. Chem. Phys.* 142 (2015) No. 204310.
- [6] J. P. Burrows, D. I. Cliff, P. B. Davies, G. W. Harris, B. A. Thrush, J. P. T. Wilkinson, Pressure broadening of the lowest rotational transition of OH studied by laser magnetic resonance, *Chem. Phys. Lett.* 65 (1985) 197–203.
- [7] K. V. Chance, D. A. Jennings, K. M. Evenson, M. D. Vanek, I. G. Nolt, J. V. Radostitz, Pressure broadening of the 118.455 cm^{-1} rotational lines of OH by H_2 , He, N_2 , and O_2 , *J. Molec. Spectrosc.* 146 (1991) 375–380.
- [8] K. Park, L. R. Zink, K. M. Evenson, K. V. Chance, I. G. Nolt, Pressure broadening of the 83.869 cm^{-1} rotational lines of OH by N_2 , O_2 , H_2 , and He, *J. Quant. Spectrosc. Radiat. Transfer* 55 (1996) 285–287.
- [9] A. Schiffman, D. J. Nesbitt, Pressure broadening and collisional narrowing in $\text{OH}(v=1 \leftarrow 0)$ rovibrational transitions with Ar, He, O_2 , and N_2 , *J. Chem. Phys.* 100 (1987) 2677–2689.
- [10] W. J. Kessler, M. G. Allen, S. J. Davis, Rotational level-dependent collisional broadening and line shift of the $A^2\sigma^+ - X^2\pi$ (1,0) band of OH in hydrogen-air combustion gases, *J. Quant. Spectrosc. Radiat. Transfer* 49 (1993) 107–117.

- [11] B. Shirinzadeh, D. M. Bakalyar, C. C. Wang, Measurement of collision-induced shift and broadening of the ultraviolet transitions of OH, *J. Chem. Phys.* 82 (1991) 2877–2879.
- [12] E. C. J. Rea, A. Y. Chang, R. K. Hanson, Shock-tube study of pressure broadening of the $A^2\sigma^+ - X^2\pi$ (0,0) band of OH by Ar and N₂, *J. Quant. Spectrosc. Radiat. Transfer* 37 (1987) 117–127.
- [13] V. L. Kasyutich, Pressure broadening parameters of the hydroxyl radical $A^2\sigma^+$ ($v'=0$) $\leftarrow$ $X^2\pi_{3/2}$ ($v''=0$) transitions at ca. 308 nm, *Eur. Phys. J. D* 33 (2005) 29–33.
- [14] G. Buffa, O. Tarrini, M. Inguscio, Predictions for collisional broadening of far-infrared rotational lines of atmospheric interest, *Appl. Opt.* 15 (1987) 3066–3068.
- [15] S. Beneč, J. Buldyreva, M. Chrysos, Pressure broadening and temperature dependence of microwave and far infrared rotational lines in OH perturbed by N₂, O₂, and Ar, *J. Molec. Spectrosc.* 210 (2001) 8–17.
- [16] L. S. Rothman, I. E. Gordon, Y. Babikov, A. Barbe, D. C. Benner, P. F. Bernath, et al., The HITRAN 2012 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer* 130 (2013) 4–50.
- [17] C. Hill, I. E. Gordon, R. V. Kochanov, L. Barrett, J. S. Wilzewski, L. S. Rothman, HITRANonline: An online interface and the flexible representation of spectroscopic data in the HITRAN database, *J. Quant. Spectrosc. Radiat. Transfer* 177 (2016) 4–14.
- [18] L. S. Rothman, C. P. Rinsland, A. Goldman, S. T. Massie, D. P. Edwards, J.-M. Flaud., A. Perrin, et al., The HITRAN molecular spectroscopic database and HAWKS (HITRAN atmospheric workstation 1996 edition), *J. Quant. Spectrosc. Radiat. Transfer* 60 (1996) 665–710.
- [19] R. Wehr, R. Ciurylo, A. Vitcu, F. Thibault, J. R. Drummond, A. D. May, Dicke-narrowed spectral line shapes of CO in Ar: Experimental results and a revised interpretation, *J. Molec. Spectrosc.* 235 (2006) 54–68.

- [20] R. Wehr, A. Vitcu, F. Thibault, J. R. Drummond, A. D. May, Collisional line shifting and broadening in the fundamental P -branch of CO in Ar between 214 and 324 K, *J. Molec. Spectrosc.* 235 (2006) 69–76.
- [21] N. H. Ngo, H. Tran, R. R. Gamache, J. M. Hartmann, Pressure effects on water vapour lines: beyond the Voigt profile, *Phil. Trans. R. Soc. A* 370 (2012) 2495–2508.
- [22] M. Baranger, General impact theory of pressure broadening, *Phys. Rev.* 112 (1958) 855–865.
- [23] A. Ben-Reuven, Impact broadening of microwave spectra, *Phys. Rev.* 143 (1966) 7–22.
- [24] R. Shafer, R. G. Gordon, Quantum scattering theory of rotational relaxation and spectral line shapes in H₂–He gas mixtures, *J. Chem. Phys.* 58 (1973) 5422–5443.
- [25] R. N. Zare, *Angular Momentum*, Wiley, New York, 1988.
- [26] M. L. Strekalov, Evaluation of the contribution of elastic dephasing processes in linewidths, *Chem. Phys. Lett.* 332 (2000) 525–530.
- [27] M. H. Alexander, Quantum treatment of rotationally inelastic collisions involving molecules in π electronic states: New derivation of the coupling potential, *Chem. Phys.* 92 (1985) 337–344.
- [28] G. Paterson, S. Marinakis, M. L. Costen, K. G. McKendrick, J. Kłos, R. Tobola, Orientation and alignment depolarization in OH($X^2\pi$) + Ar/He collisions, *J. Chem. Phys.* 129 (2008) No. 074304.
- [29] G. Paterson, S. Marinakis, M. L. Costen, K. G. McKenadricks, J. Kłos, R. Tobola, Erratum: orientation and alignment depolarization in OH($X^2\pi$) + Ar/He collisions [*J. Chem. Phys.* 129, 074304 (2008)], *J. Chem. Phys.* 131 (2009) No. 159901.
- [30] HIBRIDON is a package of programs for the time-independent quantum treatment of inelastic collisions and photodissociation written by M. H. Alexander, D. E. Manolopoulos, H.-J. Werner, B. Follmeg, and P. J. Dagdigian and others. More information and/or a copy of the code can be obtained from the website <http://www2.chem.umd.edu/groups/alexander/hibridon/hib43>.

- [31] D. Forthomme, C. P. McRaven, T. J. Sears, G. E. Hall, Argon-induced pressure broadening, shifting, and narrowing in the CN $A^2\pi - X^2\sigma^+$ (1-0) band, J. Phys. Chem. A 117 (2013) 11837–112846.
- [32] S. T. Wooldridge, R. K. Hanson, C. T. Bowman, Measurements of argon collision broadening in the CN $B^2\sigma^+ \leftarrow X^2\sigma^+$ (0,0) spectrum, J. Quant. Spectrosc. Radiat. Transfer 53 (1995) 481–492.