Observation of a Speed-Dependent Collisional Inhomogeneity in H_2 Vibrational Line Profiles

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(Received 3 April 1989)

We report observations of inhomogeneous broadening of the vibrational line profiles of a gas in the "impact" density regime. In measurements up to 27 amagat (where the spectra are dominated by collision broadening), non-Lorentzian, asymmetric features are observed in Raman Q-branch transitions of H_2 dilute in a heavy perturber gas. We compare these measurements with an inhomogeneous line-profile model based on collisional shifts that strongly depend on the (thermal) speed of the H_2 radiator. Quantitative agreement is obtained only when speed-changing collisions are considered, which result in spectral line narrowing.

PACS numbers: 33.70.Jg, 33.20.Fb

The collisional broadening of an isolated rotation-vibration transition of a gas is considered to be in the impact regime[1] when (a) the collision duration is small compared to the inverse of the collisional width, (b) the latter is large compared to the Doppler width, and (c) the collisional width and shift have no significant dependence on relative molecular speeds. Such conditions have been shown theoretically[2] to produce Lorentz profiles. Experimental studies[3] of collisional broadening in pure H_2 have successfully employed these assumptions for densities well above the Dicke minimum[4] for the Doppler effect (~2.5 amagat for pure H_2) and below densities where the finite duration of collisions becomes important (~100 amagat). However, measurements of the temperature dependence of H_2 collisional shift coefficients[3,5] indicate that such shifts depend significantly on relative speed, in apparent violation of (c). In considering spectra at densities in the Doppler regime, Berman,[6] Ward, Cooper, and Smith[7] and Nienhuis[8] demonstrated that such speed-dependent shifts (and/or speed-dependent collision widths) can lead to asymmetries and/or additional inhomogeneities in the profile. Berman,[6] Pickett,[9] and Luijendijk[10] showed theoretically that these effects generally persist to higher densities, i.e., to the collision-broadened regime. While examples of speed-dependent line profiles in the Doppler regime have been reported in atomic[11] Ca and rovibrational HF and HCl spectra,[12] to our knowledge none have been observed in a purely collision-broadened line.

In this Letter, we report observations of line profiles in Raman Q-branch transitions of H_2 perturbed by Ar that exhibit asymmetries and Gaussian-type cores at densities normally considered to be in the impact regime. For densities from 3.6 to 14 amagat at room temperature the non-Lorentzian features do not vary, although the width of the profile increases linearly. Spectra measured at constant density (~14 amagat) show a marked increase in the non-Lorentzian features with increasing temperature. The features occur at densities well above the Dicke minimum (~1 amagat for H_2-Ar) and yet below those for which finite collision-duration effects[13] or collision-induced scattering[14] contribute to the Raman spectrum. We show that the anomalies can be explained by inhomogeneous broadening that arises from strong variations in the collisional shift with radiator speed. This interpretation is supported by a line-profile model based on speed-dependent shift cross sections derived from measurements of the Q-branch line shifts of the H_2-H_2 and H_2-Ar systems at different temperatures. The model also incorporates the effects of speed-changing collisions, which coherently narrow the (speed dependent) inhomogeneous part of the profiles. Such collisions are most likely when the masses of radiator and perturber molecules are similar, explaining why these inhomogeneities are less important in self-broadened gases.

The high-resolution inverse Raman (IRS) experiment[15] employs a pulse-amplified, tunable pump laser (~22-ns pulse duration) and a cw probe laser, providing a spectral resolution of 45 MHz (FWHM). Q-branch transition frequencies were obtained using a traveling corner-cube wavemeter. The highest peak intensity produced at the focus of the beams was kept below ~2 GW/cm^2 to eliminate Stark effects, which have been known to produce asymmetries.[16] The sample gases were contained in a high-pressure, high-temperature furnace with temperature controlled to an accuracy of +50, − 25 K. We measured gas pressure with transducers accurate to better than 1% of the indication and computer amagat density units using virial coefficients given in Ref. 17. The gases were mixed in the sample chambers while monitoring partial pressures and the compositions were verified to within ±2% by mass spectrometry.

The most compelling experimental evidence for a radiator-speed-dependent mechanism is summarized as follows: We observed non-Lorentzian line profiles only for perturbers with masses much greater than that of the H_2 radiator (for Ar, Kr, and N_2, but not for He or H_2). For such systems, a radiator's absolute speed largely determines its relative speed in collisions.[7] Strong variations in the collisional shift with relative speed are evidenced by strong temperature dependences observed in

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TABLE I. Collisional line-shift coefficients $\delta(T)$ for the $Q(1)$ transition of H_2 at different temperatures, measured with IRS, and compared to fitted model results. The coefficients are expressed in 10^{-3} cm^{-1}/amagat; figures in parentheses indicate experimental uncertainties in the last digit(s).

Temperature (K)	H_2-Ar Expt. $\delta(T)$	H_2-Ar Theor. $\delta(T)$	H_2-H_2 Expt. $\delta(T)$[a]	H_2-H_2 Theor. $\delta(T)$
295	−12.0(1)	−11.4	−3.20(3)	−3.2
450	−8.2(1)	−8.3	0.70(1)	−0.05
750	−2.7(2)	−3.0	5.85(8)	5.4
1000	0.86(40)	1.0	9.16(14)	9.5

[a] Reference 18, except for the 295-K value, which is from Ref. 5. The value for 750 K is interpolated between measurements at 725 and 1000 K. Because of its simplicity, the uncertainty in the model is $\sim 0.5\times 10^{-3}$ cm^{-1}/amagat; thus the disagreement at 450 K is not considered significant.

the density-shift coefficients. Thus, radiators with different speeds will be characterized by different vibrational transition frequencies, giving rise to an inhomogeneity. The observed temperature dependence of the asymmetry further supports the speed-dependent mechanism. Finally, we observe rapid narrowing of the asymmetry with increasing H_2 partial pressure, which we believe indicates the important role of speed-changing collisions in determining the line profile. Only results that critically define the line-profile model will be presented here.

Experimental values of the H_2 $Q(1)$ line shifts for Ar and H_2 perturbers at temperatures from 295 to 1000 K are listed in Table I. The Ar line-shift coefficients were determined by measuring $Q(1)$ spectra in 1:1 mixtures of H_2 and Ar at densities from 14 to 46 amagat. We fitted the data by Lorentzian profiles (a good approximation for this mixture composition) to obtain observed shifts, then corrected these for self-shift contributions using the pure-H_2 coefficients measured by Rahn and Rosasco.[18]

We modeled the $Q(1)$ spectral profile, including the line shift, in H_2-Ar mixtures by assuming that the collisional shift depends on the relative speed between H_2 and the perturber. The speed-changing rate of H_2 resulting from H_2-Ar collisions was taken to be comparable to the rate of vibrational dephasing by Ar, but for H_2-H_2 collisions it was assumed to be much faster than the dephasing by H_2. Also, we assumed the following empirical form for the $Q(1)$ shift cross section averaged over impact parameter:

$$\sigma(v_{\mathrm{rel}}) = a v_{\mathrm{rel}} + b + c/v_{\mathrm{rel}} , \qquad (1)$$

where v_{rel} is the relative speed between radiator and perturber, and a, b, and c are adjustable parameters. Here, σ has units of cm^{-1}/amagat per cm/s. The radiator-speed-dependent shift coefficient was obtained from

$$\delta(v_{\mathrm{rad}},T) = \int f_m(\mathbf{v}_{\mathrm{rad}}+\mathbf{v}_{\mathrm{rel}},T)\, v_{\mathrm{rel}}\,\sigma(v_{\mathrm{rel}})\, d\mathbf{v}_{\mathrm{rel}} , \qquad (2)$$

in cm − 1/amagat, where $\mathbf{v}_{\mathrm{rel}}$ is the relativistic velocity. Note that if $f_m(\mathbf{v},T)$ is the Boltzmann distribution of perturber velocities, $f_m(\mathbf{v}_{\mathrm{rad}}+\mathbf{v}_{\mathrm{rel}},T)$ gives the distribution of relative velocities seen by a radiator of velocity $\mathbf{v}_{\mathrm{rad}}$. For comparison with the observed line shifts, we integrated $\delta(v_{\mathrm{rad}},T)$ over the Boltzmann distribution of radiator velocities:

$$\delta(T) = \int f_M(\mathbf{v}_{\mathrm{rad}},T)\,\delta(v_{\mathrm{rad}},T)\, d\mathbf{v}_{\mathrm{rad}} .$$

Two sets of parameters a, b, and c in Eq. (1) were adjusted[19] to obtain agreement between $\delta(T)$ and the line-shift measurements for each collider pair (H_2-Ar and H_2-H_2; see Table I). The resulting $\sigma(v_{\mathrm{rel}})$ for H_2-H_2 is in excellent agreement (better than ± 1 Å^2 from 0.005 to 0.1 eV) with the collision-energy-dependent shift cross section reported by Kelley and Bragg.[3]

We now show that the line profiles observed for the H_2-Ar system can be modeled using the speed-dependent shift cross section [Eq. (1)]. Examples of the non-Lorentzian nature of these profiles are shown in Figs. 1(a) and 1(c), where spectra of $Q(1)$ from mixtures of 2 mole% H_2 in Ar at total densities of 13.9 and 13.7 amagat, and temperatures of 295 and 1000 K, respectively, are plotted. The solid curves are best-fit Lorentzian profiles and associated fit residuals. Note that the residuals increase substantially at 1000 K, but maintain a similar shape. Similar effects were observed for $Q(0)$ and $Q(2\text{-}4)$.

An inhomogeneous line profile is computed using $\delta(v_{\mathrm{rad}},T)$ from Eq. (2) in the expression for a speed-dependent Lorentzian profile:[6,10]

$$\begin{aligned} I_{\mathrm{inhom}}(\omega) &= \frac{1}{2\pi} S(\omega,\gamma,T) + \text{c.c.} \\ &\equiv \frac{1}{2\pi}\int \frac{f_M(\mathbf{v}_{\mathrm{rad}},T)}{\gamma(T)\rho - i[\omega+\delta(v_{\mathrm{rad}},T)\rho]}\, d\mathbf{v}_{\mathrm{rad}} + \text{c.c.} \end{aligned} \qquad (3)$$

Here, γ is the coefficient for the dephasing width (HWHM), ω is the detuning from the zero-density Raman frequency, and ρ is the density in amagat. This expression is similar to that for a speed-dependent Voigt profile,[6-8] except that we have assumed that $\gamma(v_{\mathrm{rad}},T) \sim \gamma(T)$ and that the Doppler-shift term $(\mathbf{k}\cdot\mathbf{v}_{\mathrm{rad}})$ is much smaller than $\gamma\rho$ due to motional narrowing.[20] The former assumption is based only on the fact that no speed dependence of the broadening was required to describe our results.

The inhomogeneous profile given by Eq. (3), which neglects speed-changing collisions, is generally in poor agreement with experimental asymmetric spectra in that it overestimates linewidth and asymmetry. However, if speed-changing collisions are present and occur more frequently than dephasing collisions, scattering amplitudes associated with different speed groups can coherently interfere, resulting in spectral narrowing. This narrowing and symmetrization are analogous to

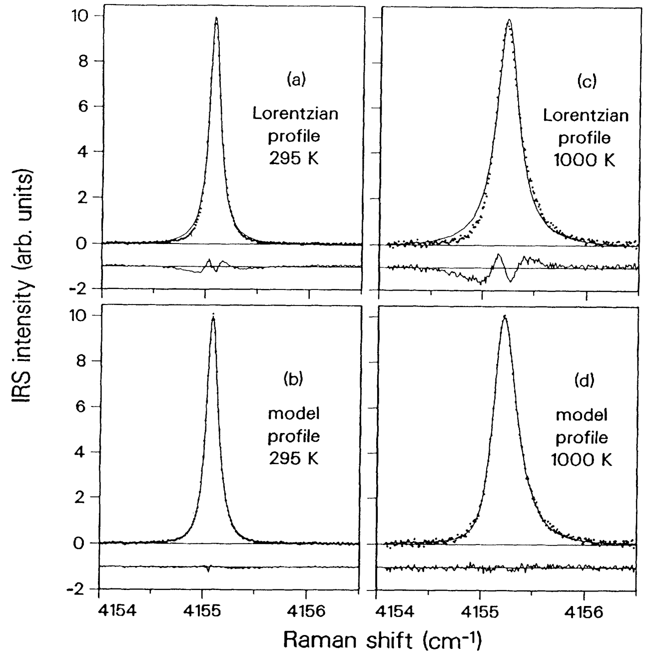

FIG. 1. Experimental IRS spectra (data points) of the $Q(1)$ transition of H_2 broadened by Ar at 295 and 1000 K. The H_2 mole fraction is 2% and the total densities are 13.9 and 13.7 amagat, respectively. The data are compared to best-fit Lorentzian profiles and to the model profile described in the text. The model includes inhomogeneous broadening arising from radiator-speed-dependent collisional shifts.

that produced in Doppler profiles by *velocity*-changing collisions, and can significantly alter the shape of the speed-dependent profile. We included speed-changing collisions using a hard-collision approximation analogous to that for Dicke narrowing,[21] resulting in a final expression for the line shape:

$$I(\omega)=\frac{1}{2\pi}\frac{S(\omega,\gamma+\nu,T)}{1-\nu\rho S(\omega,\gamma+\nu,T)}+\text{c.c.}\,, \qquad (4)$$

where ν is the frequency of speed-changing collisions. Note that as $\nu\rightarrow 0$, $I(\omega)\rightarrow I_{\rm inhom}(\omega)$, but as ν becomes larger than both γ and the width of $I_{\rm inhom}$, $I(\omega)$ narrows to a Lorentzian profile of half-width γ. Note that, unlike motional narrowing of the Doppler effect, varying the total density alone does not affect the degree of narrowing, since the width of $I_{\rm inhom}$ and $\nu\rho$ both scale linearly with density.

To calculate the model spectra in Figs. 1(b) and 1(d) (2% H_2 in Ar), we used Eq. (4) and varied γ, ν, and a frequency offset for best fit. (The latter is necessary because the model can vary from observer transition frequencies by up to 0.5×10^{-3} cm^{-1}/amagat.) The resulting γ and ν were, respectively, 2.4 and 8.3 at 1000 K, and 2.4 and 6.3 at 295 K, in units of 10^{-3} cm^{-1}/amagat. The temperature dependence of ν (the speed-changing frequency) is found to be comparable to that of β, the frequency of velocity-changing collisions.[20] However, the magnitude of ν is only ~8% of β, implying that the H_2 *speed* is conserved even after several velocity-changing collisions with Ar. The inefficiency of Ar in changing the speed of H_2 is presumably due to the large mismatch in mass and average speed. The best-fit values for γ (the dephasing frequency) were essentially the same; thus, the increased width observed at 1000 K results mostly from inhomogeneous broadening. Remarkably, we find that homogeneous (dephasing) broadening produces only ~25% of the total width in this case.

The model is also found to successfully describe the observed narrowing and symmetrization of the profiles as the H_2 concentration increases at constant temperature. We measured spectra from a series of gas mixtures at constant total density and temperature but with varying composition. The anomalies were strongest in mixtures of 0.5% H_2 in Ar (we did not investigate greater dilutions), but were nearly indiscernible in 20% mixtures at 295 K. For 50% H_2 at 295 K, the profile was Lorentzian to within our experimental uncertainty, ±1% of the peak intensity. Moreover, the linewidths of the profiles, as determined from either best-fit Lorentzian or spline functions, exhibited remarkable deviations from a linear mixing rule (i.e., a dependence on the mole-fraction-weighted sum of perturber broadening coefficients). This effect appears as a curvature in linewidths plotted against H_2 mole fraction [symbols in Fig. 2(b)]. We have observed similar nonlinear dependences in coherent anti-Stokes Raman spectroscopy (CARS) linewidths of H_2 in Kr, and in IRS linewidths of D_2 in Ar.

The line profiles corresponding to the IRS data in Fig. 2(b) were analyzed by varying the broadening and narrowing coefficients [γ and ν in Eqs. (3) and (4)] for best fit to each profile (described below), and by employing a mole-fraction-weighted sum of the previously determined H_2 and Ar shift functions [$\delta(v_{\rm rad},T)$] for each mixture. The results for 295 K are shown in Fig. 2(a). Using the linearly varying coefficients shown by the solid lines in Fig. 2(a), the model accurately describes the dependence of linewidth on H_2 mole fraction [Fig. 2(b)] and is also in excellent agreement with the observed spectral profile (not shown).

Some of the values for γ and ν indicated by data points in Fig. 2(a) could not be obtained by unconstrained fitting. At H_2 concentrations of 50% and higher the Lorentzian nature of the experimental profiles provided poor sensitivity to the relative magnitudes of γ and ν. Here, we used a linear extrapolation for ν which had an intercept for pure H_2 equal to the known velocity-changing collision rate, β.[20] [This line, shown in Fig. 2(a), was found to be consistent with the ν values for low-H_2 concentrations.] The associated coefficients for γ were obtained by fitting with fixed ν. Thus using $\nu=\beta$ for pure H_2, the model predicts that ~15% of the collision width is due to inhomogeneous broadening. For H_2-Ar collisions, about half of the width is found to be

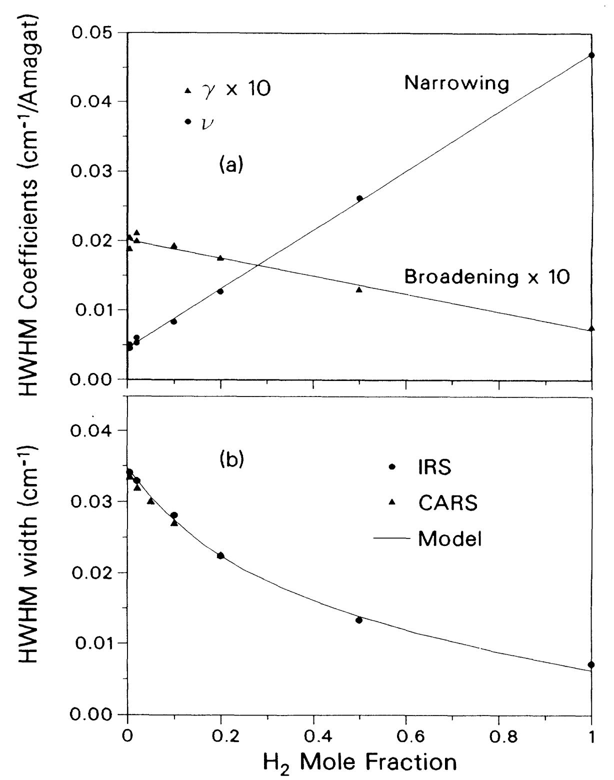

FIG. 2. (a) Best-fit collision-broadening (γ) and -narrowing (ν) coefficients, indicated by symbols, obtained from IRS spectra of the $Q(1)$ transition of H_2-Ar mixtures at 295 K and 7.3 amagat total density. (These coefficients are used by the proposed line-profile model.) Also plotted are best-fit straight lines through the data. (b) Spectral linewidths determined from fitting Lorentzian profiles to the data (symbols) and to the theoretical profiles (curve) calculated using the corresponding parameters in (a). The CARS measurements will be described fully elsewhere.

inhomogeneous, and ν is predicted to be ~ 10 times lower than the pure-H_2 value, corresponding to only $\sim 5\%$ of β for H_2-Ar.[20]

Similarly consistent results were obtained at 1000 K, although only three mixtures were investigated (2%, 50%, and 100% H_2). For pure H_2, $80(\pm 15)\%$ of the total linewidth was determined to be homogeneous, and ν was equal to $60(\pm 20)\%$ of β computed for 1000 K.[20]

We also investigated the dependence of the line profiles on total density, primarily in 2% H_2-Ar mixtures at ~ 295 K. Recall that the model [Eq. (4)] predicts an invariance of the line *shape* with respect to density. That is, if we normalize the detuning by density ($\omega = \omega' \rho$), then ρ enters the line profile only as a proportionality constant. Consistent with this property, we found that to within our uncertainties the best-fit values for γ and ν were independent of density over the range 2.8–14 amagat.

This research was supported by the U.S. Department of Energy, Department of Basic Energy Research, Chemical Sciences Division and, in part, by the U.S. Army Research Office.

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