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Effect of speed-changing collisions on spectral line shape

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High-resolution inverse Raman experiments for H_2 dilute in Ar [R. L. Farrow *et al.*, Phys. Rev. Lett. **63**, 746 (1989)] have revealed remarkable deviations from the usual linear mixing rule for the Q-line broadening. They have been interpreted using a line-profile model that takes into account the spectral narrowing induced by speed-changing collisions. The present approach includes the role of collisions changing both speed and phase, leading to an alternative interpretation of the above-noted experiments. This interpretation generalizes the earlier study and points out the various mechanisms of line formation.

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A recent high-resolution inverse Raman spectroscopy (IRS) investigation [1] of Q-branch transitions for H_2 dilute in a heavy perturber gas (Ar) has evidenced remarkable deviations from the usual linear mixing rule $[\gamma=\alpha\gamma_1+(1-\alpha)\gamma_2]$ for the line broadening coefficient γ as a function of concentration α. This nonlinearity is accompanied by an asymmetric feature of the Q-line profile. These effects were already observable in the collisional regime, at densities ρ such that the Doppler shift $(\mathbf{k}\cdot\mathbf{v})$ is much smaller than the γ value $(\equiv\hat{\gamma}\rho)$ due to motional narrowing [2,3]. These spectral features were interpreted by taking into account both the inhomogeneity coming from radiator speed dependence of the line shift $\delta(v)$ and the effect of speed-changing collisions, within the hard-collision approximation. The resulting profile was deduced [1] by a convenient transposition of the result for the effect of velocity-changing collisions in the Doppler regime [4]. Whatever the concentration, the profile is thus an inhomogeneous profile narrowed by the effects of exchange between different speed groups. The observed nonlinearity of $\gamma(\alpha)$ results from the strong difference between speed-changing frequencies (ν_1 for H_2-H_2 and ν_2 for H_2-Ar), since [1] ν_1 is one order of magnitude higher than ν_2. The aim of the present Rapid Communication is to propose an alternative interpretation of the IRS experiments of Ref. [1] and, of course, of those for other mixtures.

In the model of Farrow *et al.* [1] only two types of collision are considered, the speed-changing collisions (SC) and the dephasing collisions (D). A third type of collision, changing *both* speed and phase (SCD), may also be taken into account, as previously proposed by Rautian and Sobelman [4] in their study of the effects of velocity-changing collisions on spectral line shape. So, the probability per unit time of collisions involving a speed change $v'\rightarrow v$ and a phase change $\varphi'\rightarrow\varphi$ is taken as (cf. Ref. [4])

$$f(v',v,\varphi-\varphi')=f(v',v)\delta(\varphi-\varphi')+g(v',\varphi-\varphi')\delta(v-v')+f(v',v)B(v',\varphi-\varphi') . \tag{1}$$

Each of the contributions in Eq. (1) corresponds to a given type of collisions (SC, D, and SCD, respectively). All these types of collisions are inhomogeneous since the line shift δ and the linewidth γ are considered to be v dependent. We should note that for SCD collisions the changes of speed and phase are assumed to be not interrelated for a given incoming speed v'. The resulting kinetic impact equation for the radiating dipole characterized by a speed v at time t may be expressed from Eq. (1) in terms of the ν^{SC} and ν^{SCD} collision frequencies and of the line broadening $\gamma^{D}(v)$ and line shifting $\delta^{D}(v)$ due to the dephasing as

$$\begin{aligned}\frac{\partial}{\partial t}d(v,t)=&-\nu^{SC}d(v,t)+\int f(v',v)d(v',t)dv'\\&-[\gamma^{D}(v)+i\delta^{D}(v)]d(v,t)-\nu^{SCD}d(v,t)\\&+\int f(v',v)\tilde{B}(v')d(v',t)dv' ,\end{aligned} \tag{2}$$

where

$$\tilde{B}(v')=\int B(v',\psi)e^{-i\psi}d\psi . \tag{3}$$

In the hard-collision model [4], neglecting the possible speed dependence of the collision frequencies, one has $f(v',v)=\nu^{SC}\Phi(v)$ and Eq. (2) becomes

$$\begin{aligned}\frac{\partial}{\partial t}d(v,t)=&-[\nu^{SC}+\nu^{SCD}+\gamma^{D}(v)+i\delta^{D}(v)]d(v,t)\\&+\nu^{SC}\Phi(v)d(t)+\nu^{SC}\Phi(v)\int\tilde{B}(v')d(v',t)dv' ,\end{aligned} \tag{4}$$

where $\Phi(v)$ is the Boltzmann distribution of the radiator speed and $d(t)=\int d(v,t)dv$. This equation may be solved exactly using a Laplace transform, so that the line profile $I(\omega)=\pi^{-1}\text{Re}\{d(i\omega)/d(t=0)\}$ takes the form

$$I(\omega)=\pi^{-1}\mathrm{Re}\left\{\frac{\langle[i\omega+F(v)]^{-1}\rangle}{1-\nu^{\mathrm{SC}}\langle[i\omega+F(v)]^{-1}\rangle-\langle\nu^{\mathrm{SC}}\tilde{B}(v)[i\omega+F(v)]^{-1}\rangle}\right\} \tag{5}$$

with

$$F(v)=\nu^{\mathrm{SC}}+\nu^{\mathrm{SCD}}+\gamma^{\mathrm{D}}(v)+i\delta^{\mathrm{D}}(v)\ . \tag{6}$$

In Eq. (5), $\langle\ \rangle$ means an average over the radiator speed.

The quantity $\nu^{\mathrm{SC}}\tilde{B}(v)$ may be expressed in terms of ν^{SCD}, $\gamma^{\mathrm{SCD}}(v)$, and $\delta^{\mathrm{SCD}}(v)$, which are defined by

$$\gamma^{\mathrm{SCD}}(v)+i\delta^{\mathrm{SCD}}(v)=\nu^{\mathrm{SC}}[\bar{B}(v)-\tilde{B}(v)]\equiv\nu^{\mathrm{SCD}}(v)[1-\tilde{\mathscr{B}}(v)]\ ,\quad \tilde{B}(v)\equiv\tilde{B}(v)/\bar{B}(v) \tag{7}$$

where $\bar{B}(v)=\int B(v,\psi)d\psi$. In the approximation of speed-independent collision frequencies, one obtains

$$\nu^{\mathrm{SC}}\tilde{B}(v)\equiv\nu^{\mathrm{SCD}}\tilde{\mathscr{B}}(v)=\nu^{\mathrm{SCD}}-\gamma^{\mathrm{SCD}}(v)-i\delta^{\mathrm{SCD}}(v)\ . \tag{8}$$

The line profile is finally obtained from Eqs. (5) and (8) as

$$I(\omega)=\pi^{-1}\mathrm{Re}\left\{\frac{\langle[i\omega+F(v)]^{-1}\rangle}{1-\nu^{\mathrm{SC}}\langle[i\omega+F(v)]^{-1}\rangle-\langle[\nu^{\mathrm{SCD}}-\gamma^{\mathrm{SCD}}(v)-i\delta^{\mathrm{SCD}}(v)][i\omega+F(v)]^{-1}\rangle}\right\}\ . \tag{9}$$

We can examine the behavior of this profile [Eq. (9)] for some simple physical situations. First, if only SCD collisions are considered, we have $\langle[i\omega+F(v)]^{-1}\rangle^{-1}=i\omega+\nu^{\mathrm{SCD}}$ so that $I(\omega)=\pi^{-1}\mathrm{Re}[i\omega+\langle\gamma^{\mathrm{SCD}}(v)\rangle+i\langle\delta^{\mathrm{SCD}}(v)\rangle]^{-1}$ is the expected Lorentzian profile. In the opposite case where only SC and D collisions are considered, the resulting profile is identical to that given by Eq. (4) of Ref. [1]. Finally, if the speed dependence of the line broadenings and line shiftings are disregarded, the line is (homogeneous) Lorentzian with the parameters $\gamma=\gamma^{\mathrm{D}}+\gamma^{\mathrm{SCD}}$ and $\delta=\delta^{\mathrm{D}}+\delta^{\mathrm{SCD}}$. When this speed dependence is accounted for, both types of inhomogeneous processes coexist, even in the absence of SC collisions.

The present approach thus suggests an alternative interpretation of the experimental result of Farrow *et al.* [1]. If, for the sake of simplicity, SC collisions are disregarded, it is possible to define the ratio of frequencies for SCD and D collisions by [cf. Eq. (1)]

$$\xi\equiv\nu^{\mathrm{SCD}}/\nu^{\mathrm{D}}\ . \tag{10}$$

In the case $\xi\ll1$, the physical situation is similar (but not identical) to that of the analysis of Farrow *et al.* [1] for the high dilution limit. But the opposite case ($\xi\gg1$) may be considered as the realistic situation for most of molecular systems. If applied to pure hydrogen, the present analysis is consistent with the study of Rahn, Farrow, and Rosasco [5].

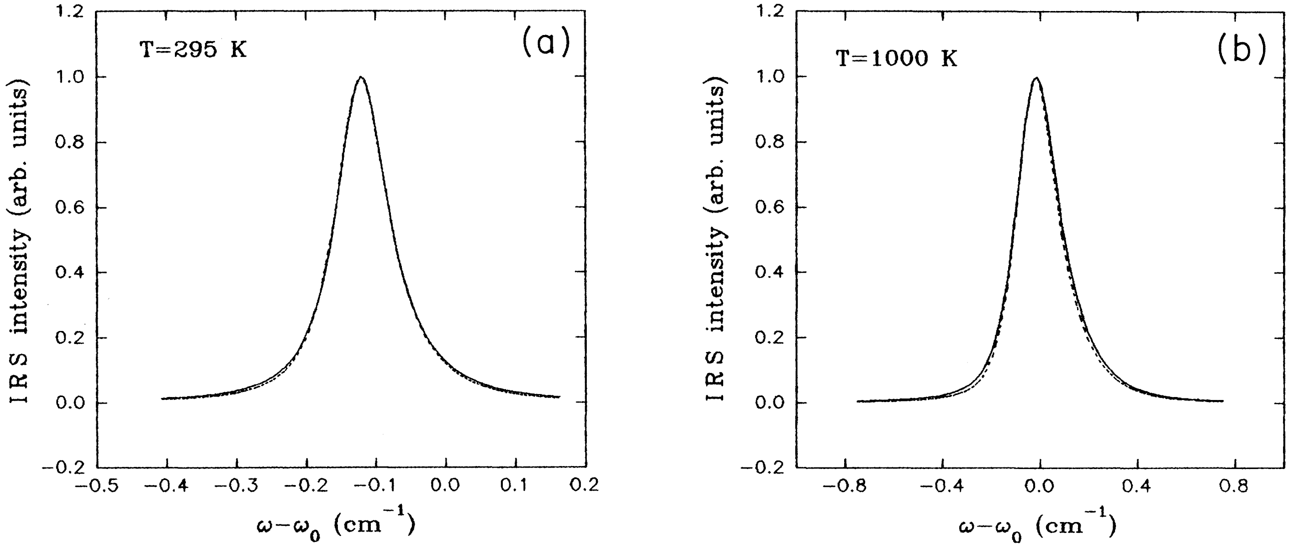

FIG. 1. Calculated profile for the $Q(1)$ transition of H_2 broadened by Ar at 295 and 1000 K. The H_2 mole fraction is $\alpha\simeq0$ and the total density is 10 amagat. ——, profile calculated from the model of Farrow *et al.* [1] with their parameters; — — —, the present calculation with $x_1=99.9\%$, $y_1=y_2=0$ and $x_2=10\%$, $\gamma_1=0.9$ mK/amagat and $\gamma_2=2.55$ mK/amagat at 295 K, and with $x_2=6\%$, $\gamma_1=4.4$ mK/amagat and $\gamma_2=3.4$ mK/amagat at 1000 K. The δ_1 and δ_2 parameters are taken from Ref. [1].

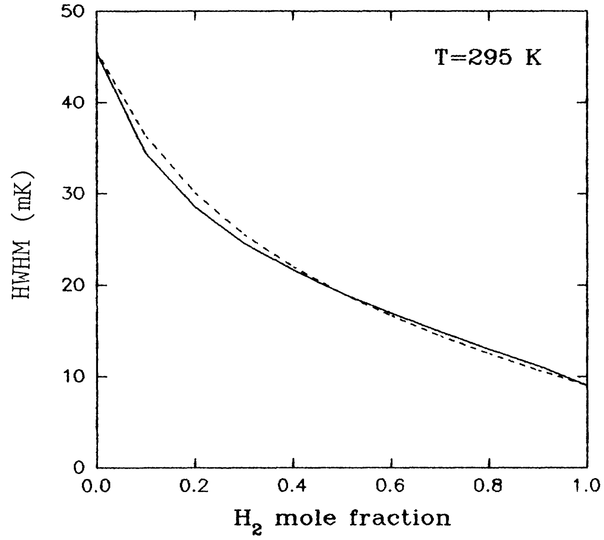

FIG. 2. Spectral linewidth at 295 K and 10 amagat calculated by using the same parameters as in Fig. 1. ——, the present calculations; — — —, the model of Farrow *et al.* [1].

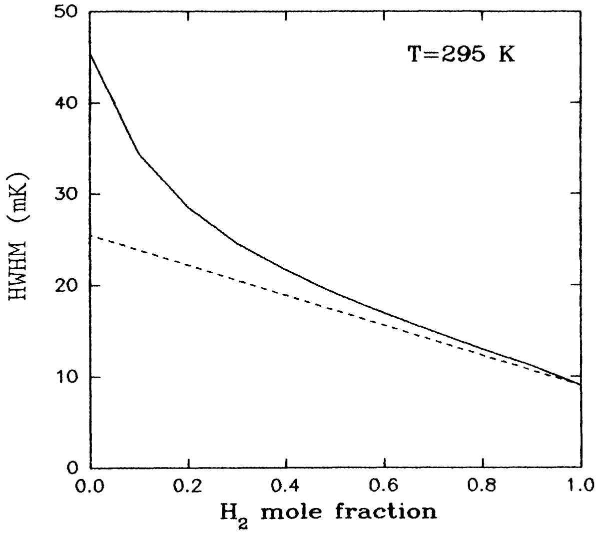

FIG. 3. Spectral linewidth at 295 K and 10 amagat in the present calculation. ——, identical to Fig. 2; — — —, fitted collisional broadening parameter.

Calculations have been performed which support the above interpretation. Let us introduce the ratios $x_i = \nu_i^{SCD}/\nu_i$ and $y_i = \nu_i^{SC}/\nu_i$ for each of the two pairs of colliding molecules, ν_i being the total collision frequency [6]: $\nu_i = \nu_i^{SC} + \nu_i^{D} + \nu_i^{SCD}$ [$\xi_i = x_i/(1-x_i-y_i)$, $i=1,2$]. Comparison between profiles calculated with the model of Farrow *et al.* [1] and with the present model is shown in Fig. 1 (in the limit where no SC collision arises, $y_1 = y_2 = 0$). The asymmetric features are correctly reproduced. Notice that the ratio of SCD H$_2$-Ar collisions decreases with increasing temperature, as is reasonable [$x_2(295\ \mathrm{K}) = 10\%$ and $x_2(1000\ \mathrm{K}) = 6\%$]. The main observed feature [1] is the deviation of γ from the usual mixing rule, so it is of central interest to check if the alternative interpretation proposed here is also appropriate to interpret such a feature. Figure 2 clearly indicates that it is. The line broadening coefficient for H$_2$-Ar is closer to the observed half width at half maximum (HWHM) in the present interpretation than in that of Farrow *et al.* [1] (2.55 instead of 2.0 mK/amagat at 295 K compared to 4.6 experimental value, cf. Fig. 3). For the pure H$_2$ limit, since $x_1 = 99.9\%$, the observed profile is purely Lorentzian and the HWHM thus coincides with the collisional broadening parameter (cf. Fig. 3).

To go further in the present analysis, it would be necessary to take into account in both interpretations the possible speed dependence of the line broadening coefficients and of the collision frequencies [7]. The simple addition approximation for the velocity-dependent impact operator for the two molecular pairs, in the case of mixtures, must be also examined. Direct experimental confirmation of the possible role of SCD collisions in H$_2$ dilute in heavy rare gases could be possible by using time-resolved nonlinear techniques [8].

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