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Intracollisional Interference in the Spectrum of HD Mixed with Rare Gases*

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We present the first observation and interpretation of an interference effect in the infrared absorption spectrum of HD—rare-gas mixtures. This effect, due to constructive or destructive interference between allowed and collision-induced dipoles during a collision, is referred to as "intracollisional interference." Is is manifested by the appearance of a narrow line at the $R_1(1)$ position which increases with rare-gas density. This interference has relevance to the determination of HD abundance in planetary atmospheres.

As was first pointed out by Wick[1] in 1935, the HD molecule has an allowed electric dipole vibration-rotation spectrum. Because the allowed dipole arises from the nonadiabatic breakdown of the Born-Oppenheimer approximation, it has a small magnitude of the order of 10^{-3} D. The infrared spectrum of HD was first observed by Herzberg[2] in 1950, and more recently by Trefler and Gush,[3] in the pure rotational, and by Bejar and Gush,[4] and by McKellar[5,6] in various vibrational bands.

Collision-induced spectra occur quite generally and are due to absorption by the transient dipole created in a pair of molecules during a collision (for a recent review see, e.g., Welsh[7]). Most work in this area has been done with molecules that do not have allowed infrared dipole spectra, e.g., H_2 and N_2. Mixtures of homonuclear diatomic molecules with inert gases have also been extensively studied. For the collision-induced spectrum of a dipolar gas, the possibility of an interference between the two types of dipoles (allowed and induced) discussed above should be considered. In the present paper we present experimental evidence for and a theoretical analysis of an interference effect of this kind for HD-Kr mixtures. Because the interference only takes place during collisions, we shall refer to this effect as "intracollisional interference." Intracollisional interference can be contrasted with intercollisional interference which has been known for some time,[8] and arises from the interference of collision-induced dipoles in successive collisions. Intercollisional interference is always destructive and gives rise to a dip in the collision-induced spectrum at the transition frequency of the free molecule; the width of the dip is of the order of the reciprocal of the time between collisions. Intracollisional interference can be either constructive or destructive and also occurs at the transition frequency of the free molecule; its width, however, is of the same order of magnitude as that of the allowed line.

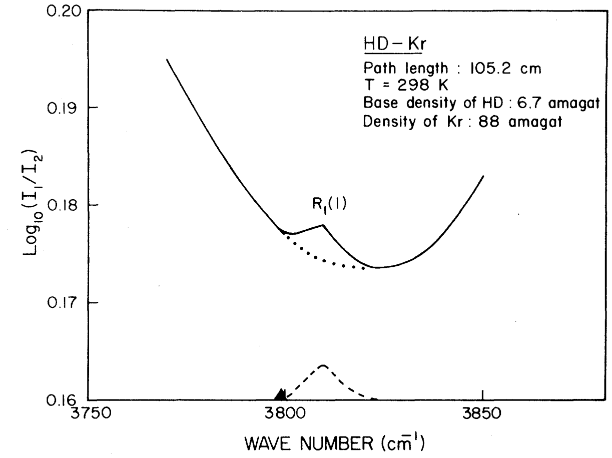

FIG. 1. An enlarged portion of the enhancement spectrum in the region 3770–3850 cm^{-1} taken with 3-cm^{-1} spectral resolution. The solid curve is the experimental profile. The dotted curve is obtained by extending smoothly the high-frequency wing of the Q branch and the low-frequency wing of the S branch. The dashed curve at the bottom represents the $R_1(1)$ line obtained from the difference between the solid and the dotted profiles. The free molecular position is indicated by the triangle.

We shall now discuss the intracollisional interference mechanism in more detail. We consider the case of an HD-Kr mixture for which there are quantitative experimental results available (see Fig. 1), although the effect has also been observed in HD-Xe mixtures. Our expressions will be valid for any interacting pair of molecules one of which has an allowed dipole spectrum. A general expression for the spherical components of the total dipole moment of an HD-Kr pair is given by[9]

$$\mu_\nu = (4\pi/\sqrt{3})\textstyle\sum_{L\lambda} A_{L\lambda}(rR)\sum_M C(\lambda L 1; \nu - M, M) Y_{\lambda,\nu-M}(\theta\varphi) Y_{LM}(\Theta\Phi), \tag{1}$$

where we refer to Fig. 2 for the geometry. The internuclear separation is denoted by $\vec{r}\ (r, \theta, \varphi)$ and the separation of centers of mass by $\vec{R}\ (R, \Theta, \Phi)$; all angles and dipole components are with respect to fixed space axes. $C(\lambda L 1; \nu - M, M)$ is a Clebsch-Gordan coefficient and the Y's are spherical harmonics. The expansion coefficients $A_{L\lambda}$ in (1) depend in general on both r and R and are independent of the coordinate system used. Because of parity considerations we must have $\lambda + L$ odd. The expansion (1) describes both the allowed HD and the collision-induced dipole moments.

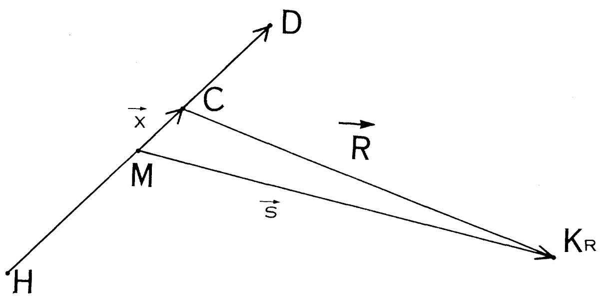

FIG. 2. The geometry of an HD-Kr binary collision. The points M and C denote the midpoint and center of mass of the HD molecule.

For the purpose of an order-of-magnitude calculation we will restrict ourselves to the consideration of the component of the allowed HD dipole along the direction of the internuclear axis. The spherical components of this dipole in a fixed space coordinate system are of the form

$$P_\nu = P_A(r)(4\pi/3)^{1/2} Y_{1\nu}(\theta\varphi), \tag{2}$$

where $P_A(r)$ is the dipole moment function.[10] It is clear that this dipole is incorporated in the coefficient A_{01}. For molecules which do not have a center of inversion symmetry, the induced dipole will also have a part which transforms like

(2); i.e., the coefficient A_{01} will be of the form

$$A_{01}=P_A(r)+P_I(r,R), \tag{3}$$

where $P_I(r,R)$ is the induced dipole moment function. (Note that P_I also depends on R.) In calculating the intensity no interference between different coefficients $A_{L\lambda}$ occurs because each corresponds to a different angular dependence of the dipole moment. The absorption associated with a particular coefficient $A_{L\lambda}$ is proportional to a configurational average of the square of rotation-vibrational matrix elements of that coefficient. According to (3) it follows that the intensity associated with A_{01} consists of the three contributions: an allowed part, a pure collision-induced part, and a part due to intracollisional interference.

A straightforward calculation of the integrated intensity of these three contributions for a particular rotation-vibrational transition yields, respectively,

$$\int \alpha(\nu)\,d\nu/\nu=(4\pi^2/3)n_A a_0^{\,2}\alpha_F P_J C(J1J';00)^2\times\begin{cases}\langle vJ|P_A|v'J'\rangle^2, & \text{(4a)}\\ n_I a_0^{\,3}4\pi\int_0^\infty\langle vJ|P_I|v'J'\rangle^2 g(R)R^2\,dR, & \text{(4b)}\\ 2n_I a_0^{\,3}\langle vJ|P_A|v'J'\rangle 4\pi\int_0^\infty\langle vJ|P_I|v'J'\rangle g(R)R^2\,dR, & \text{(4c)}\end{cases}$$

where $\alpha(\nu)$ is the absorption coefficient per unit path length; n_A and n_I the number densities of the dipolar and the perturbing molecules, respectively; a_0 the Bohr radius; α_F the fine-structure constant; P_J the probability for the rotational state J (normalization $\sum_J P_J=1$); and $g(R)$ the pair correlation function for an absorber-perturber pair. In (4) P_A, P_I, and R are in atomic units. The contribution from intracollisional interference, (4c), is, like the pure induced intensity (4b), proportional to the product $n_A n_I$. Furthermore, because the allowed dipole is diagonal in the translational states, it follows that the intensity of the intracollisional interference occurs at the position of and has a width of the same order of magnitude as the allowed line, and is, therefore, much narrower than the induced feature.

We now consider the particular case HD-Kr and show in Fig. 1 the experimentally observed enhancement spectrum in the region around 3800 cm^{-1}. The enhancement spectrum is obtained by subtracting the pure HD spectrum taken at the HD base density from the total observed absorption. The remaining intensity is therefore due to HD-Kr interactions only and in the absence of intracollisional interference would be expected to show the well-known broad features associated with induced absorption. This is indeed the case apart from the small sharp feature at the position of the $R_1(1)$ line. This feature is not due to pure HD because the HD spectrum[11] has been subtracted [in fact, the base density of HD used is so small that the allowed $R_1(1)$ was not observable with our apparatus]. Furthermore, the feature is not due to impurities, because runs with Kr alone also failed to show it. We therefore interpret the sharp feature in Fig. 1 as due to intracollisional interference because of its position and width.

By drawing in the background due to the broad components, the intensity of the intracollisional line can be determined. From (4c) it follows that $(\rho_{\rm HD}\nu)^{-1}\int\alpha(\nu)d\nu$ for this line should be proportional to $\rho_{\rm Kr}$, where ρ is the density in amagats. This is consistent with the experimental data as displayed in Fig. 3, although the scatter of the points is large. (Note that, by definition, the line drawn in Fig. 3 has to go through the origin.) From the slope of the graph the so-called binary absorption coefficient can be determined and has the value $(5\pm3)\times10^{-10}$ cm^{-1} amagat^{-2}. It turns out that this value is in good agreement with the theoretical estimate.

To estimate the theoretical intracollisional intensity we need values for both the allowed and the induced dipole matrix elements. For the

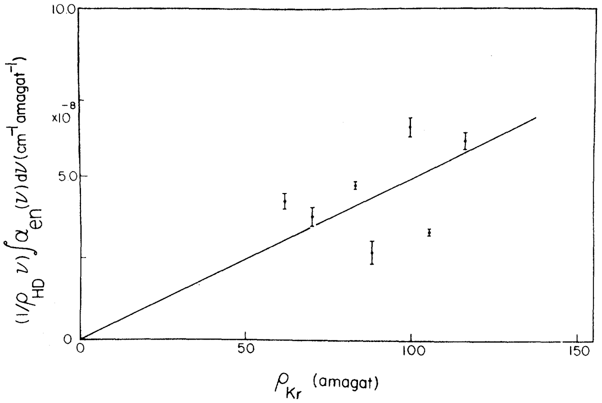

FIG. 3. A plot of the integrated absorption coefficient per unit density of HD versus the density of Kr for the $R_1(1)$ line at 298 K.

magnitude of the allowed matrix element of the $R_1(1)$ line, $|\langle 01|P_A|12\rangle|$, we adopt the experimental value of 2.17×10^{-5} a.u. obtained by McKellar.[6] The induced matrix element, $\langle 01|P_I|12\rangle$, can be expressed in terms of the induced dipole moment of an H_2-Kr pair. The reason for this is that, apart from very small nonadiabatic effects, the electronic charge distributions for H_2-Kr and HD-Kr are identical. More precisely, we assume that the dipole $\mu_v(\vec{r},\vec{s})$ for H_2-Kr is appropriate also for HD-Kr. The correct dynamical coordinates to be used for HD-Kr are $\vec{r}$ and $\vec{R}$ as used in (1). To obtain the dipole moment in this form we apply the coordinate transformation $\vec{s} = \vec{R}+\vec{x}$ (where $x=r/6$) to the H_2-Kr moment $\mu_v(\vec{r},\vec{s})$. To first order in the small quantity x we can write

$$\mu_v{}^{\text{HD-Kr}}(\vec{r},\vec{R}) = (1+\vec{x}\cdot\nabla_R)\mu_v{}^{\text{H}_2\text{-Kr}}(\vec{r},\vec{R}). \tag{5}$$

In principle both the coefficients A_{10} and A_{12} of H_2-Kr contribute to the desired coefficient A_{01} of HD-Kr. For the purpose of an estimate of the intensity, we confine ourselves to the contribution from the larger, i.e., from $A_{10}(r,R)$. We take the following model for $A_{10}(r,R)$:

$$A_{10}(r,R) = m(r)e^{-(R-\sigma)/\rho}, \tag{6}$$

where ρ is a range parameter and σ the Lennard-Jones diameter of the pair; $m(r)$ denotes the strength of the induced moment at $R=\sigma$. Combining (5) and (6) we find for the induced contribution to the coefficient A_{01} of HD-Kr

$$P_I = \tfrac{1}{3}x(2/R - 1/\rho)m(r)e^{-(R-\sigma)/\rho}. \tag{7}$$

The quantities $|\langle 01|m(r)|12\rangle|$ and ρ can in principle be determined from either the observed H_2-Kr or HD-Kr spectrum. A reasonable fit to these spectra can be obtained by taking $|\langle 01|m(r)|12\rangle| = 2\times 10^{-3}$ a.u. and $\rho/\sigma = 0.12$. Using the above results for P_A and P_I, we find for the intracollisional interference contribution to the binary absorption coefficient of the $R_1(1)$ line at room temperature

$$(\nu\rho_{\text{HD}}\rho_{\text{Kr}})^{-1}\int\alpha(\nu)\,d\nu = 4\times 10^{-10}\ \text{cm}^{-1}\ \text{amagat}^{-2}. \tag{8}$$

As pointed out above, this result is in good agreement with the experimental value.

The ratio of the intensity due to the intracollisional interference to that due to the usual collision-induced absorption is independent of the densities, whereas the ratio to the intensity of the allowed line is proportional to the density of the perturbing gas. In particular, in the case of the $R_1(1)$ line at 300 K in HD-Kr, we find this ratio to be approximately $0.04\rho_I$. This implies that for $\rho_I > 25$ amagats the intracollisional intensity dominates over the allowed one. The effect must therefore be taken into account in the analysis of line strengths in high-density media, as occur, for example, in planetary atmospheres.

An interesting feature of intracollisional interference is its linear dependence on the product of the matrix elements of P_A and P_I, the interference being constructive or destructive depending on the sign of this product being positive or negative. Since there is evidence that $\langle 01|P_A|12\rangle > 0$,[10] and in the present case the observed interference is constructive, $\langle 01|P_I|12\rangle > 0$ also. According to (7) this implies

$$[dm(r)/dr]_{r=r_e} < 0.$$

Observation of other bands will allow further signs to be determined.

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