Mixing of rotational levels and intracollisional interference in the pure rotational $R_0(J)$ transitions of gaseous HD

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A detailed theoretical analysis of the intensities of the pure rotational $R_0(J)$ transitions in gaseous HD is presented. These transitions all manifest small intracollisional interference effects arising from the cross product of the allowed– and the induced–dipole-moment matrix elements. Using recent *ab initio* calculations of the induced dipole moment in an HD-HD pair, this interference is found to be constructive for most transitions, thus implying a density-dependent increase in intensity. For the $R_0(0)$ transition, a small but significant additional contribution to the constructive intracollisional interference results from the mixing of rotational levels in a single molecule during collisions. Additionally, because of a near-resonance condition, simultaneous mixing of internal rotational levels in both molecules of a colliding pair leads to a large destructive interference affecting primarily the $R_0(2)$ transition. The present theoretical values of the interference parameter a_{theor} are compared with experimental data and it is concluded that while the low-temperature data are in reasonable accord with the present theoretical results, significant differences still remain both between different experimental determinations, and between theory and experiment for the room-temperature data. Possible theoretical refinements to explain the observed large temperature dependence of the intracollisional interference are discussed briefly.

I. INTRODUCTION

The first experimental observation of "intracollisional interference" was made in HD–rare-gas mixtures where it was manifested by the appearance of a sharp feature at the $R_1(1)$ frequency that increased in intensity as the rare-gas density was increased.[1,2] The notation $R_{v'}(J)$ denotes the transition $(v',J+1) \leftarrow (v''=0, J)$, where v and J are the vibrational and rotational quantum numbers, respectively. A similar effect was also observed in the fundamental band $(v'=1)$ of pure HD where the interference was found to be destructive.[3,4] For the roational band $(v'=0)$ of pure HD, it was suggested[4] that a destructive interference could reconcile the difference between values of the allowed– (nonadiabatic) dipole-moment matrix elements obtained previously by Trefler and Gush[5] from high-density experiments and the theoretical *ab initio* values.[6–9]

In recent years a number of experimental studies of the intensities of the $R_0(J)$ transitions in pure HD (Refs. 10–14) and in HD–rare-gas mixtures[11,15,16] at various temperatures and densities have been reported. Concomitant with these experimental studies, theoretical analyses of the effects of intracollisional interference on the intensities and line shapes have been published.[4,17,18] The overall theoretical work prior to 1985 has been reviewed by Poll.[19]

In 1985 Tabisz and Nelson proposed that rotational-level mixing by anisotropic intermolecular interactions could play an important role in the theoretical description of intracollisional interference.[20] This effect is described in the following section together with another mixing mechanism which is found to affect profoundly the intensity of the $R_0(2)$ transition.

In all the theoretical work cited above, the magnitude of the component of the induced dipole moment, which interferes with the allowed dipole moment, had to be obtained indirectly from the analyses of other collision-induced absorptions. The sign of this component (with respect to that of the allowed dipole) had to be inferred from the nature of the interference (i.e., constructive or destructive). However, recently an *ab initio* calculation of the various components of the dipole induced in an HD-HD pair and in HD–rare-gas pairs has been carried out.[21] This allows one to determine the sign as well as the magnitude of the intracollisional interference without the introduction of any free parameters as discussed in Sec. II.

Using a method similar to that of the present study, the effect of interference on the $R_0(0)$ transition in solid HD has recently been reported[22] and the theoretical predictions corroborated by experiment.[23,24] This suggests, at least for the solid, that the basic mechanism for intracollisional interferences is well understood.

The situation in gaseous HD, however, is not as clear. This is apparent from a comparison between the results of the present analysis and the experimental data. In particular, for some transitions, the observed interference

changes from constructive to destructive as the temperature is increased. Although this behavior is not predicted within the limitations of the present theory, we discuss briefly possible theoretical refinements which could contribute to a more dramatic temperature dependence. We feel, however, that while the ultimate resolution of the nature of intracollisional interference must be made experimentally, additional *ab initio* calculations of the induced–dipole-moment components, and especially the dependence on the internuclear separations of the individual molecules, would contribute to a better theoretical understanding of the temperature dependence of the interference.

II. THEORY AND RESULTS

We first consider the effect of intracollisional interference assuming no collisional mixing of rotational levels; i.e., we ignore the anisotropic interaction between the colliding HD molecules. The space-fixed spherical components of the induced dipole moment of a pair of molecules can be expressed in terms of appropriately coupled products of three spherical harmonics, Y_{lm}, describing the orientations of the individual internuclear axes, $\mathbf{r}_1 \equiv (r_1, \omega_1)$ and $\mathbf{r}_2 \equiv (r_2, \omega_2)$, and the orientation of the vector separation between their centers of mass $\mathbf{R} \equiv (R, \Omega)$,[25]

$$\mu_\nu^I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = [(4\pi)^3/3]^{1/2} \sum_{\lambda_1, \lambda_2, \Lambda, L} A_\Lambda(\lambda_1, \lambda_2, L; r_1, r_2, R)$$

$$\times \sum_{\mu_1, \mu_2, M} C(\Lambda, L, 1; \mu_1 + \mu_2, M, \nu) C(\lambda_1, \lambda_2, \Lambda; \mu_1, \mu_2, \mu_1 + \mu_2) Y_{\lambda_1 \mu_1}(\omega_1) Y_{\lambda_2 \mu_2}(\omega_2) Y_{LM}(\Omega) .$$

$$(1)$$

In this expression, the C's are Clebsch-Gordan coefficients and the dipole coefficients $A_\Lambda(\lambda_1, \lambda_2, L; r_1, r_2, R)$ provide a unique coordinate-independent representation of the strengths of the various induction mechanisms specified by the indices λ_1, λ_2, Λ, and L. In particular, we will be concerned with the induced coefficient $A_1(1,0,0; r_1, r_2, R)$ that arises primarily through the shifted overlap mechanism.[25,26] The allowed dipole moment

$$\mu_\nu^A(\mathbf{r}_1) = (4\pi/3)^{1/2} p^A(r_1) Y_{1\nu}(\omega_1) \tag{2}$$

also contributes to the coefficient $A_1(1,0,0; r_1, r_2, R)$. Because in the present paper we are interested only in the sharp $R_0(J)$ features, we can write the integrated intensity in the form[4]

$$\int \frac{\alpha(\omega)}{\omega} d\omega = \int \frac{\alpha^A(\omega)}{\omega} d\omega + \int \frac{\alpha^{AI}(\omega)}{\omega} d\omega$$

$$= (1 + a\rho) \int \frac{\alpha^A(\omega)}{\omega} d\omega , \tag{3}$$

where $\int [\alpha^A(\omega)/\omega] d\omega$ is the allowed intensity associated with the dipole in Eq. (2), and

$$\int \frac{\alpha^{AI}(\omega)}{\omega} d\omega = \frac{8\pi^2 N_0^2 \rho^2 V}{3\hbar c} \sum_{i, f, \nu} P_i \langle i | \mu_\nu^A | f \rangle \langle i | \mu_\nu^I | f \rangle^* \tag{4}$$

is the intensity of the intracollisional interference associated with the cross product of the allowed dipole and the induced dipole. In these expressions, $\alpha(\omega)$ is the absorption coefficient per unit pathlength at frequency ω, ρ is the density in amagats, N_0 is Loschmidt's number, V is the volume, and P_i are the Boltzmann factors normalized according to $\sum_J (2J + 1) P_J = 1$; $|i\rangle$ and $|f\rangle$ denote the initial and final states of the transition, respectively. Sub-

stituting the general form for μ_ν^I from Eq. (1) into Eq. (4) and carrying out the summations, one finds for the coefficient a describing the intracollisional interference

$$a = \frac{8\pi N_0 \int_0^\infty g(R) p_{0J_1, 0J_1+1}^I(R) R^2 dR}{p_{0J_1, 0J_1+1}^A} , \tag{5}$$

where $p_{0J_1, 0J_1+1}^{A,I}$ are the rotational matrix elements of the allowed dipole moment[6-9] and the Boltzmann-weighted induced dipole component of the same symmetry, $A_1(1,0,0; r_1, r_2, R)$, respectively, and $g(R)$ is the pair correlation function. An *ab initio* calculation of $A_1(1,0,0; \bar{r}_1, \bar{r}_2, R)$ where $\bar{r} = 1.4487 a_0$ (appropriate to the average internuclear separation in an isolated H_2 molecule) is available.[21] Implications of the difference between $A_1(1,0,0; \bar{r}_1, \bar{r}_2, R)$ and $p_{0J_1, 0J_1+1}^I(R)$ are discussed in Sec. III.

Numerical results obtained from Eq. (5), using the isotropic intramolecular potential from Norman *et al.*[27] for computing the pair correlation function, are presented in Table I for three temperatures (77, 195, and 295 K). Also listed are the experimental values a_{expt} determined by several different groups. It is clear from these results that there is significant J dependence of a_{expt}, although there are large differences in sign as well as magnitude between the values obtained by the different experimental groups.

In an effort to improve the agreement between theory and experiment, Tabisz and Nelson[20] considered the effects of mixing of the rotational levels of a single HD molecule due to the anisotropic interaction. The mixed levels are then connected by another induced dipole component, $A_2(2,0,1; r_1, r_2, R)$, thus leading to an additional contribution to the intracollisional interference denoted by Δa. Following their procedure, we find a different theoretical expression for Δa, which is only nonzero for

TABLE I. Comparison between theoretical and experimental values of the interference parameters (10^{-3} amagat^{-1}); the theoretical values a are from Eq. (5), Δa from Eq. (6), $\Delta a'$ from the additional mixing of levels (see text), and a_{theor} are the net theoretical values.

Parameter	$R_0(0)$	$R_0(1)$	$R_0(2)$	$R_0(3)$
		$T=77$ K		
a	0.9	0.9	0.9	
Δa	0.5	0	0	
$\Delta a'$	0	0	-3.4	
a_{theor}	1.5	0.9	-2.4	
a_{expt}[a]	0.6	0.6		
a_{expt}[b]	4.16(42)	2.59(23)	$-4.4(0.6)$	
		$T=195$ K		
a	1.4	1.4	1.4	1.4
Δa	0.7	0	0	0
$\Delta a'$	0	0	-3.1	-0.2
a_{theor}	2.1	1.4	-1.7	1.2
		$T=295$ K		
a	1.7	1.7	1.7	1.7
Δa	0.8	0	0	0
$\Delta a'$	0	0	-3.2	-0.2
a_{theor}	2.5	1.7	-1.4	1.5
a_{expt}[c]				260(70)
a_{expt}[d]		$-1.5(3)$	$-2.0(3)$	2.4(3)
a_{expt}[e]	$-2.5(19)$	$-1.1(2)$	1.3(1)	2.1(6)

[a] Reference 11.
[b] Reference 28.
[c] Reference 12.
[d] Reference 13.
[e] Reference 14.

the $R_0(0)$ transition, viz.,

$$\Delta a = -\frac{8\pi N_0}{P_{00,01}^A 2\sqrt{2}B_0}\int_0^\infty \langle 00| A_2(2,0,1;r_1,\bar{r}_2,R)|01\rangle$$

$$\times V_a'(R)g(R)R^2\,dR\ , \qquad (6)$$

where B_0 is the rotational constant of HD in the ground state, and $V_a'(R)$ is the magnitude of the anisotropic interaction. This can be approximated by[14,29]

$$V_{HD}(R)=V_{H_2}(R)+\frac{r_e}{6}\frac{dV_{H_2}(R)}{dR}\cos\theta$$

$$=V_{H_2}(R)+V_a'(R)\cos\theta\ . \qquad (7)$$

Here θ is the angle between r_1 and R (where r_1 is directed from H to D in molecule 1, and R from the center of mass of molecule 1 to the center of mass of molecule 2), and $V_{H_2}(R)$ is the potential of Norman et al.[27] Because of the perturbative nature of the calculation and the fact that the integral in Eq. (6) becomes unphysically large for small values of R, we adopted the same cutoff criteria as those of Tabisz and Nelson.[20] Again using the ab initio value $A_2(2,0,1;\bar{r}_1,\bar{r}_2,R)$ for

$$\langle 00| A_2(2,0,1;r_1,\bar{r}_2,R)|01\rangle\ ,$$

we find for the additional contribution to the intracol-

lisional interference of the $R_0(0)$ transition the values listed in Table I for the three temperatures.

There is another type of rotational-level mixing mechanism that one can consider which involves the rotational levels of both molecules in a colliding pair. In order to calculate this mixing, we assume that the unperturbed states (i.e., in the absence of anisotropic interactions) are of the form $|J_1M_1;J_2M_2;LM\rangle$ where LM designates the angular part of the relative translational wave function of the pair of colliding molecules. Because of the near-resonance between $|3M_1;00;LM\rangle$ and $|2M_1',2M_2';L'M'\rangle$ ($\Delta E=1.865$ cm^{-1}, an energy difference which is relatively small compared to the anisotropic interaction of the proper symmetry to mix these levels), this mixing can be appreciable. The theoretical expressions together with the computational details of this mixing will be published elsewhere,[30] but it is clear from the rotational levels involved that this mixing will affect primarily transitions having rotational quantum numbers 2 and 3, i.e., $R_0(2)$ and $R_0(3)$. The contribution to the intracollisional interference of this mixing is denoted by $\Delta a'$ and the magnitudes calculated using a similar perturbational approach as that used for calculating Δa are given in Table I. We note here that because of the perturbational approach and the need for a cutoff, the numerical values of $\Delta a'$ (and Δa also) are not as accurate as those for a. Nonetheless, it is clear that the contribution

$\Delta a'$ is large for the $R_0(2)$ transition and has a sign opposite to that of a, thus changing the interference from constructive to destructive. For $R_0(3)$, the magnitude of $\Delta a'$ is more than an order of magnitude smaller and the mixing in this case results only in a reduction of the constructive interference. The total theoretical values of the interference parameter $a_{\text{theor}} = a + \Delta a + \Delta a'$ for the $R_0(J)$ transitions are listed in the table for comparison with the experimental values.

III. DISCUSSION AND CONCLUSIONS

As can be seen from Table I, the two independent experimental determinations of a_{expt} for $R_0(0)$ and $R_0(1)$ at 77 K are all positive, indicating a constructive interference; a similar constructive interference has also been observed in the liquid[31] and in the solid.[23,24] These results are in qualitative agreement with the present theoretical values, although these latter are between the experimen-

tal values in magnitude. The recent measurement of destructive interference for the $R_0(2)$ transition[28] is also in qualitative agreement with the present theoretical results. Furthermore, for HD-H_2 enhancement spectra for which $\Delta a' = 0$, the observed interference for the $R_0(2)$ transition is constructive,[16] again in qualitative agreement with the present predictions. On the other hand, the agreement between the various experimental determinations at 295 K is quite poor, both in the sign of the interference and in its magnitude. The best agreement between theory and experiment is for the data of McKellar;[13] this agreement is reasonable except for the sign of the $R_0(1)$ transition.

A comparison of the experimental data for different temperatures suggests that there is an important temperature dependence. Within the present theory, the temperature enters only indirectly through the pair correlation function. However, additional temperature and J dependence would occur if one would use the actual *ab initio* values of $p^I_{0J_1,0J_1+1}(R)$. These are defined by

$$p^I_{0J_1,0J_1+1}(R) = \sum_{J_2} (2J_2+1)P_{J_2}\langle 0J_1;0J_2|A_1(1,0,0;r_1,r_2,R)|0J_1+1;0J_2\rangle \tag{8}$$

and, as mentioned previously, have been approximated by $A_1(1,0,0;\bar{r}_1,\bar{r}_2,R)$. As is well known,[4] the major contribution to $A_1(1,0,0;\bar{r}_1,\bar{r}_2,R)$ in HD arises from the anisotropic overlap component in H_2, $A_2(2,0,1;r_1,r_2,R)$, when the latter is transformed to the proper coordinate system for HD.[4,25] This is because the larger isotropic overlap characterized by the component $A_0(0,0,1;r_1,r_2,R)$ vanishes by symmetry for two identical molecules.[32] This component is not zero, however, for two slightly dissimilar molecules [e.g., HD-H_2 (Ref. 21) or two HD molecules in different rotational levels], and has not been calculated via *ab initio* methods. One would thus expect for higher temperatures at which collisions between HD molecules in different rotational levels are more common, and furthermore, because the larger the difference in J between colliding molecules, the larger the contribution of the isotropic overlap mechanism to the induced component $A_1(1,0,0;r_1,r_2,R)$, that

additional temperature dependence would be introduced. This refinement could easily be incorporated into the present theory if the induced component $A_1(1,0,0;r_1,r_2,R)$ were known at several internuclear separations, r_1 and r_2. This information would also allow one to calculate vibration-rotational matrix elements of the induced dipole, thus enabling one to extend the present theory to the fundamental $R_1(J)$ transitions for which extensive experimental data are available.

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