PHYSICAL REVIEW A VOLUME 31, NUMBER 2 FEBRUARY 1985

# Rotational-level mixing and intracollisional interference in the pure rotational spectrum of HD gas

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(Received 16 August 1984)

Rotational-level mixing by anisotropic intermolecular forces is found to be important to the mechanism which produces intracollisional interference effects in the pure rotational spectrum of HD and HD–inert-gas mixtures. The major contribution involves the anisotropic repulsive term in the potential and the anisotropic overlap-induced dipole moment. Improved agreement between calculation and experiment results when the mixing is included in the analysis.

## I. INTRODUCTION

The term "intracollisional interference" denotes the interference between spectral transitions involving permanent and collision-induced dipole moments. The theory of the effect has been developed by Poll, Tipping, and Herman.[1–3] It transpires that the infrared spectrum of HD is ideal for observation of the phenomenon. HD has a very small permanent dipole moment and, like the symmetric molecules $H_2$ and $D_2$, has a collision-induced[4] infrared spectrum produced by transient dipoles induced in clusters of interacting molecules. Intracollisional interference has been identified in the pure rotational[5,6] and vibrational-rotational spectra[1,7–9] of gaseous HD and HD–inert-gas mixtures.

For interference to occur, both the allowed ($p^A$) and induced ($p^I$) moments must follow the same selection rules. That this is possible is not immediately apparent as the rule on the angular momentum quantum number $J$ of one of the interacting molecules is $\Delta J = \pm 1$ for the allowed transitions and, in the case of homonuclear diatomic molecules, $\Delta J = 0, \pm 2$ for the induced transitions. In HD, however, the centers of mass and of charge are not coincident and additional components in the induced dipole arise[1,7] which permit the transitions $\Delta J = \pm 1, \pm 3, \ldots$ . The present authors[5,6] have made a comparison of the density behavior of the integrated intensity of the pure rotational spectrum of HD with the theory.[1] In the density range studied (6–60 amagats), the intensity decreases with increasing density consistent with a destructive interference effect (see Fig. 1 of Ref. 6). The magnitude of the interference is described by a parameter $a$ which is twice the ratio of the average induced moment to the allowed moment. General agreement between experiment and calculation is evident but differences of the order of 30% in the value of $a$ are found. A missing but presumed important ingredient to the theory as developed to date is rotational-level mixing by anisotropic intermolecular forces.[1,10] The present report is an attempt to assess the importance of the mixing effect for the pure rotational spectrum.

## II. GENERAL APPROACH

The theory developed by Poll, Tipping, and Herman[1–3] is summarized in this section. If purely collision-induced contributions are neglected, the absorption coefficient $\alpha(\omega)$ integrated over all frequencies $\omega$ is, for a homogeneous gas,

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

when $\rho$ is the density and $\alpha^A$ is the absorption coefficient of the allowed spectrum.

The integrated intensity of the intracollisional interference term is

$$\left[ \int \frac{\alpha(\omega)}{\omega} d\omega \right]_{\text{int}} = \frac{4N}{V} \frac{4\pi^2}{3\hbar c} \sum_{i,f,\nu} P_i \langle i | p_\nu^A | f \rangle \langle i | p_\nu^I | f \rangle^* \ . \tag{2}$$

$N$ is the number of pairs in volume $V$; $P_i$ is the Boltzmann factor normalized so that $\sum_J (2J+1) P_J = 1$. The sum is over all initial states $i$, final states $f$, and components of the dipole moment $\nu$. The interference parameter $a$ is defined by

$$a = \frac{2\langle p^I \rangle}{p^A} = \left[ \frac{8\pi N_0}{p^A} \right] \int_0^\infty p^I_{vJ,v'J'} g(R) R^2 dR \ , \tag{3}$$

where $N_0$ is Loschmidt's number, $g(R)$ the pair correlation function, $R$ the intermolecular distance, and $(v,J)$ and $(v',J')$ the lower and upper energy states involved in the transition.

Poll and Van Kranendonk[11] have given a general expression for the induced dipole moment in a pair of interacting molecules 1 and 2 in terms of spherical harmonics and Clebsch-Gordon coefficients.

$$p_\nu^I(r_1,r_2;R) = \frac{(4\pi)^{3/2}}{\sqrt{3}} \sum_{\lambda_1,\lambda_2,\Lambda,\lambda} A_\Lambda(\lambda_1,\lambda_2,\lambda;r_1,r_2,R) \times \sum_{\mu,\mu_2} C(\lambda_1,\lambda_2,\Lambda;\nu-\mu-\mu_2,\mu_2) C(\Lambda,\lambda,1;\nu-\mu,\mu) Y_{\lambda_1,\nu-\mu-\mu_2}(\omega_1) Y_{\lambda_2,\mu_2}(\omega_2) Y_{\lambda,\mu}(\Omega) . \tag{4}$$

TABLE I. Magnitude of the interference parameters $a\,(10^{-3}$ amagat$^{-1})$ and $b\,(10^{-9}$ cm$^{-1}$ amagat$^{-1})$.

| | HD-HD | | | HD-He | | |
|---|---|---|---|---|---|---|
| | $a$ | $a+\Delta a$ | Expt. | $b$ | $b+\Delta b$ | Expt. |
| $R(0)$ | 5.4 | 7.37 | $\cdots$ | $\cdots$ | $\cdots$ | $\cdots$ |
| $R(1)$ | 5.4 | 7.53 | $7.7 \pm 1.2$ | 7.3 | 10.2 | $19 \pm 0.8$ |
| $R(2)$ | 5.4 | 6.49 | $6.3 \pm 1.2$ | 5.6 | 5.9 | $5.7 \pm 0.7$ |
| $R(3)$ | 5.4 | 7.59 | $7.2 \pm 1.1$ | 2.2 | 3.0 | $2.8 \pm 0.9$ |

The angles $\omega_1$, $\omega_2$, and $\Omega$ describe the orientations of 1 and 2 and of the intermolecular axis relative to a laboratory fixed reference frame; $r_1$ and $r_2$ are the internuclear separations in 1 and 2. A number of terms in (4) have been quantitatively evaluated from experimental spectra: isotropic overlap $[A_0(0,0,1)]$, anisotropic overlap $[A_2,(2,0,1)]$, quadrupole-induction and anisotropic overlap $[A_2(2,0,3)]$, etc. For HD the additional components due to the noncoincidence of the centers of mass and charge are generated by

$$p^I_{\mathrm{HD}}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}) = [1+\tfrac{1}{6}(\mathbf{r}_1-\mathbf{r}_2)\cdot\nabla_R+\cdots]\,p^I_{\mathrm{H}_2}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}) \ . \tag{5}$$

The anisotropic overlap moment $A_2(201)$ is the leading term in (4) which both contributes to the $H_2$-$H_2$ (and HD-HD) induced rotational spectrum and has a component from (5) capable of interfering with $p^A$ as described by (2). It is usual to write overlap terms as exponentials; thus,

$$A_2(2,0,1;r_1,r_2,R) = \lambda \exp[-(R-\sigma)/R_0] \ , \tag{6}$$

where $\sigma$ is the molecular diameter, $R_0$ the range of the interaction, and $\lambda$ the strength of the dipole at $R=\sigma$. Equation (5) yields

$$A_1(1,0,0;r_1,r_2,R) = \lambda\frac{\sqrt{2}}{18}\left[\frac{1}{R_0}-\frac{2}{R}\right] r_e \exp\left[-\frac{R-\sigma}{R_0}\right] \ , \tag{7}$$

where $r_e$ is the equilibrium internuclear distance. Substitution of (7) in (3) gives $a$. Numerical values can be obtained for the magnitude of $a$ with the parameters $\lambda$ and $R_0$ deduced from the $H_2$-$H_2$ rotational spectrum by Poll and Hunt[12] assuming a Lennard-Jones potential (see Table III of Ref. 6); $p^A$ is taken from *ab initio* calculations.[13] The magnitude of $a$ is found to be $5.4\times10^{-3}$ amagat$^{-1}$ and is compared with experimental determinations from Ref. 6 in Table I. The calculated value is of the correct order but is low for all $R(J)$ lines studied.

## III. ROTATIONAL-LEVEL MIXING

In Ref. 1 the total wave function used to evaluate (2) is the product of rotational, vibrational, and translational wave functions and is an eigenfunction of the Hamiltonian

$$H = H_{\mathrm{molec}} + V_i \ ,$$

where $H_{\mathrm{molec}}$ is the Hamiltonian of the isolated molecules and $V_i$ the isotropic intermolecular potential. If the anisotropic potential $V_a$ is included in the Hamiltonian, then mixing of rotational energy levels ensues and $p^A$ may interfere directly with the principal components of $p^I$ as given by (4) and not just minor ones arising through (5). To estimate the effect of this mixing, we report here a first-order perturbation theory calculation performed in the spirit of the work of Herman[10] on the redistribution of the intensity in the infrared spectrum of HCl–inert-gas mixtures by anisotropic molecular interactions. The mixing is expected primarily to give additional contributions to the intracollisional interference effect and not significantly affect the allowed transition elements.[1]

The anisotropic potential is taken as the sum of the quadrupole-quadrupole interacton $V_{Q_1Q_2}$, an anisotropic dispersion term and an anisotropic repulsion term; the latter two depend on $\cos\theta$ where $\theta$ is the angle between the internuclear axis in HD and the intermolecular axis.

$$V_a = V_{Q_1Q_2} - 24\epsilon\left[\frac{\sigma^6}{R^7}-\frac{2\sigma^{12}}{R^{13}}\right] d\cos\theta = V_{Q_1Q_2} + V_a'\cos\theta \ . \tag{8}$$

$d$ is the separation between the center of mass and the center of charge. These particular forms for the anisotropic dispersion $(R^{-7})$ and repulsion $(R^{-13})$ terms have been devised by Herman[10] and used with success[10,14] for treatment of collision effects in HCl–inert-gas spectra.

An adiabatic approximation is made to treat the rotational and translational motion. The mixing is calculated for a fixed intermolecular separation and an average over $R$ is then performed. The rotations are, thus, assumed to occur much more rapidly than the translational motion. While certainly not good, the approximation is perhaps not outrageous for HD, for which the characteristic time of rotation ($\sim 1/2cB$, where $B$ is the rotational constant) is $3.8\times10^{-13}$ sec and is of the order of the duration of an intermolecular collision $\sim 10^{-13}$ sec.

The rotational wave function is written as

$$\psi_{JM} = \phi_{JM} + \sum_{J'',M''}{}' \frac{\langle J''M''|V_a|JM\rangle}{E_{J''}-E_J}\phi_{J''M''} \tag{9}$$

and substituted along with (5) in (2). The calculation of $\{\int[\alpha(\omega)/\omega]d\omega)\}_{\mathrm{int}}$ proceeds as in Ref. 1. One molecule of the pair is considered to be the active absorber and an average over coordinates of the other molecule is made. The possibility of double transitions arising from the mixing is, therefore, excluded. The quantum numbers of the translational states do not change in the mixing process. This would be an unacceptable approximation in the calculation of the line shape but is adequate for the total intensity considered here.

The additional contributions to the intensity of the interference term involve the $\cos\theta$ term in $V_a$ and the isotropic $[A_0(001)]$ and anisotropic $[A_2(201)]$ overlap components in $p^I_{\mathrm{HD}}$. The quadrupole-quadrupole term in the potential participates with the $A_1(100)$ component of $p^I_{\mathrm{HD}}$ obtained through (5) and, thus, gives essentialy a second-order contribution.

Equations (1)–(3) yield for the revised interference parameter, which is the ratio

$$2\left[\int\frac{\alpha(\omega)}{\omega}d\omega\right]_{\text{int}}\Big/\rho\int\frac{\alpha^{A}(\omega)}{\omega}d\omega\ ,$$

$$a+\Delta a=\frac{8\pi N_0}{p^A}\left[\int A_1(1,0,0;R)g(R)R^2dR+\frac{1}{6B}\int\left(\frac{2J+1}{J+1}-\frac{2J+3}{J+1}\right)A_0(0,0,1;R)V_a'(R)g(R)R^2dR\right.$$
$$+\frac{1}{6\sqrt{2}B}\int\left(\frac{-J(2J+1)}{(J+1)(2J+3)}+\frac{(J+2)(2J+3)}{(J+1)(2J+1)}\right)A_2(2,0,1;R)V_a'(R)g(R)R^2dR$$
$$\left.+\frac{1}{2\sqrt{2}B}\int\left(\frac{2J+5}{2J+3}-\frac{2J-1}{2J+1}\right)A_2(2,0,1;R)V_a'(R)g(R)R^2dR\right]\ . \tag{10}$$

The first integral gives $a$ in the absence of anisotropic interactions. The two terms in the second and third integrals arise, respectively, from the mixing of the state $J''=J$ into the upper state $J+1$ of the transition and from mixing $J''=J+1$ into the lower state $J$; here, the isotropic and anisotropic overlap-induced moments associated with the selection rule $\Delta J=0$ interfere with the allowed transition moment. The terms in the fourth integral come from mixing $J''=J+2$ into the upper state $J+1$ and from mixing $J''=J-1$ into the lower state $J$; the latter term does not contribute when $J=0$. The anisotropic overlap-induced moment ($\Delta J=\pm 2$) participates in the interference described by this integral. In all cases the contribution of the mixing terms vary as $(1/J)$ at large $J$.

In the evaluation of the last three integrals in (10), the interaction cannot be taken to small $R$ where the perturbation becomes large; it must be cut off so that the first-order wave function (9) remains accurate. Again, following Herman,[10] an intensity conservation criterion is adopted which has the effect of normalizing the perturbed wave function. It is assumed that the maximum amount of intensity that can be borrowed from a transition starting at level $J$ is equal to the intensity in the transition in the absence of anisotropic interactions. The total spectral intensity available must remain unchanged. As a result, for example, in the fourth integral of (10), the intensity lost to the transition $J\rightarrow J+2$ decreasing the intensity of the $R(J)$ line appears at the frequency of $R(2J+2)$ line; similarly, intensity lost to the $J-1\rightarrow J+1$ transition appears at the frequency of the $R(2J)$ line. The second and third integrals in (10) make no contribution to $\Delta a$ in this approximation as they borrow and return intensity at the same frequency. Therefore, the only contribution to $\Delta a$ comes from the term involving $\cos\theta$ in $V_a$ and the anisotropic overlap-induced moment. It must be emphasized that in the present treatment, it is intensity which is conserved; $\Delta a$, which varies as the intensity borrowed or gained at a given frequency divided by the intensity of the allowed $R(J)$ line at that frequency, is not conserved.

The condition that the maximum amount of intensity borrowed is equal to the intensity in the absence of anisotropic interactions reduces from (2) to the statement that

$$A_1(1,0,0;R)\geq\frac{f(J)}{2\sqrt{2}b}V_a'(R)A_2(2,0,1;R)\ , \tag{11}$$

where $f(J)$ is the quantity in large brackets in the fourth integral of (10). The equal sign applies at $R=R_c$. At values of $R$ less than $R_c$ where the inequality no longer holds, the right-hand side (RHS) of (11) and, thus, the borrowed intensity is kept at its value at $R=R_c$.

Equation (10) is evaluated at 295 K with $g(R)=\exp[-V_i(R)/kT]$ and a Lennard-Jones potential;[1,6,12] $d$ is taken[15] as 0.12 Å. The first integral gives $a$ as in Sec. II. The cutoff distance $R_c$ applied to the fourth integral is for the various $R(J)$ lines: $R(0)$, $1.042\sigma$; $R(1)$, $1.021\sigma$; $R(2)$, $1.012\sigma$; and $R(3)$, $1.006\sigma$. These $R_c$ correspond to values of the perturbation parameter $V_a'(R)/B$ of 0.24, 0.38, 0.58, and 0.78 for the respective $R(J)$ lines. In the average over $R$, the anisotropic repulsion term in the potential dominates the dispersion term and provides the larger contribution to $\Delta a$. Results for $a+\Delta a$ are shown in Table I. It is evident that accord between calculation and experiment is greatly improved by inclusion of rotational-level mixing in the intracollisional interference mechanism.

## IV. HD-He MIXTURES

Enhancement spectra are available for HD-He and HD-Ar mixtures.[6] The enhancement intensity, that due to HD-$X$ encounters, is given by[6,7]

$$\int\frac{\alpha^{en}(\omega)}{\omega}d\omega=b\rho_p\ , \tag{12}$$

where

$$b=8\pi N_0Kp^A\int p^I(R)g(R)R^2dR\ , \tag{13}$$

$$K=(8\pi^3N_0/3hcZ)[\exp(-E_J/kT)-\exp(-E_{J+1}/kT)](J+1)\ . \tag{14}$$

$\rho_p$ is the perturber density, $Z$ the state sum, and $E_J$ the energy of state $J$. In a like manner to $a$, the interference parameter $b$ is altered when rotational-level mixing is taken into account and, to first order, the contribution to $\Delta b$ comes again from the anisotropic overlap-induced moment and the $\cos\theta$ term in the potential.

$$\Delta b=[f(J)/2\sqrt{2}B]\int V_a'(R)A_2(2,0,1;R)g(R)R^2dR\ . \tag{15}$$

Equation (15) is evaluated with a Lennard-Jones potential[6,12] for $V_i$ and Eq. (8) for $V_a$. Wormer and Van Dijk[16] have calculated the dipole moment $p^I$ for H$_2$-He in an *ab initio* manner. It is the isotropic[5,6] $[A_1(001)]$, rather than anisotropic, moment of HD-He that gives the component from (5) which interferes with $p^A$ in the absence of anisotropic interactions. Results for $b+\Delta b$ are compared with experiment in Table I. Agreement for $R(2)$ and $R(3)$ is found but the value for $R(1)$, while increased, remains lower than experiment. It must be admitted that to achieve this result, the sign of the $A_2(201)$ anisotropic component is assumed to be the same as the isotropic $A_1(001)$ component, although Wormer and Van Dijk find these signs opposite in the range of $R$ probed by the experiment. It is not clear whether the difficulty lies with the experimental results (only three densities studied), the *ab initio* calculation, or the proposed mixing mechanism.

To our knowledge, information on the anisotropic overlap-induced moment for HD-Ar is unavailable. Of course, the data[6] could be used to deduce $\lambda$ and $R_0$ for this interaction.

## V. CONCLUSIONS

The addition of rotational-level mixing to the mechanism of intracollisional interference makes significant and measurable changes to the interference parameters $a$ and $b$. The promise is that study of the interference will lead to information on anisotropic molecular interactions in hydrogen, which will supplement that obtained through other experimental techniques such as the measurement of scattering cross sections[17] and the spectroscopy of the solid[18] and of Van der Waals complexes.[19]

## ACKNOWLEDGMENTS

This research was performed while G.C.T. was at the National Research Council of Canada. He wishes to thank Dr. Willem Siebrand and the members of the Theoretical Chemistry Section for their warm and generous hospitality. Discussions with R. M. Herman, J. D. Poll, and R. H. Tipping are gratefully acknowledged.

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