COLLISIONAL INTERFERENCE IN THE INFRARED ABSORPTION SPECTRUM OF HD

G.C. Tabisz, Lorenzo Ulivi, P. Drakopoulos and Z. Lu
Department of Physics, University of Manitoba
Winnipeg, Manitoba, R3T 2N2, Canada

ABSTRACT

The small dipole moment of HD makes it an almost unique case for the study of the interference between collision-induced and allowed transitions. Normally, such effects are overshadowed by strongly allowed absorption. Experimental and theoretical aspects of the problem are reviewed with emphasis on the temperature dependence of the interference and line shape parameters of the pure rotational far-infrared spectrum. The observations are not fully explainable in terms of the currently available theory.

INTRODUCTION

The hydrogen molecular isotope HD has a small permanent dipole moment of the order of 10^{-3} D. Much interest, in the infrared spectrum of HD, has been motivated by the need to measure this moment. The smallness of the moment, in addition, makes HD an almost unique case for the study of the interference between allowed and collision-induced transitions. Understanding of the interference promises to level to an increased knowledge of the anisotropic interactions between hydrogen molecules and its elucidation has thereby become an important reason for study of the HD spectrum. Unlike the purely collision-induced profile, which in the low density limit is independent of pressure, here consideration of the spectral profile immediately involves all of the difficulties of pressure broadening.

The general outline of this paper is as follows: It begins with a discussion of the infrared spectrum of H_2. Then differences between the properties of H_2 and HD and the theory of the spectrum of HD are considered. The second half of the paper is devoted to the presentation and discussion of experimental results. Roger Herman[1] gave a discussion of the theory of the problem at the Williamsburg meeting four years ago with stress on the vibration-rotation spectrum. The intention here is to present recent progress, emphasizing our own experimental work on the far-infrared pure rotational spectrum in dense gases. There have been, as well, reports on the measurement and interpretation of the interference effect in liquid and solid HD[2,3].

SPECTRUM OF H_2

First, let us look briefly at the concept of collision-induced absorption. H_2 is a symmetric molecule and does not have a dipole allowed infrared spectrum. It has, however, a collision-induced spectrum which has been extensively studied; George Birbaum reviewed it for us at the Torun meeting in 1988[4]. Collision-induced spectra occur quite generally and are due absorption by the transient dipole created in a pair or larger cluster of interacting molecules. The mechanisms which generate the induced dipole are clearly related to interaction terms in the intermolecular potential: induction, dispersion and exchange. For two interacting molecules, the pair dipole moment can be expressed as follows[5]:

$$\mu_{\nu}^{I}(r_1 r_2;R) = \frac{(4\pi)^{3/2}}{\sqrt{3}} \sum_{\lambda_1,\lambda_2,\Lambda,\lambda} A_{\Lambda}(\lambda_1,\lambda_2,\lambda;r_1,r_2,R)$$

$$\times \sum_{\mu,\mu_2} C(\lambda_1,\lambda_2,\Lambda;\nu-\mu-\mu_2,\mu_2)C(\Lambda,\lambda,1;\nu-\mu,\mu)$$

$$Y_{\lambda_1,\nu-\mu-\mu_2}(\omega_1)Y_{\lambda_2,\mu_2}(\omega_2)Y_{\lambda,\mu}(\Omega) \quad . \tag{1}$$

The angles ω, ω_2, Ω describe orientations of molecules 1 and 2 and of the intermolecular axis relative to the laboratory frame; r_1 and r_2 are internuclear separations; R is the intermolecular distance; the C and the Y are Clebsch-Gordon coefficients and spherical harmonics. The coefficients A_{Λ} depend only on r_1, r_2 and R and provide a co-ordinate independent classification of various components of the dipole moment. Several of these coefficients have been evaluated quantitatively.

$A_2(223)$ describes anisotropic quadrupolar induction and depends on the dipole polarizability of one molecule and the quadrupole moment of the other; it varies as R^{-4}.

$A_0(001)$ describes the isotropic overlap contribution which varies exponentially.

$A_2(201)$ is an anisotropic overlap contribution and also varies exponentially.

$A_1(100)$ describes a dipole along the internuclear axis of one of the molecules. It vanishes for a H_2-H_2 pair.

SPECTRUM OF HD

Now let us turn to HD. HD possesses a small permanent dipole moment μ^A due to non-adiabiatic coupling of electronic and nuclear motions. Wick[6] predicted its existence in the 1930's and these have been many *ab initio* calculations of it[7].

The value of $\mu^A(r)$ at the r_e, the equilibrium separation, is termed the permanent dipole moment and is about 8×10^{-4} D. Remember that a typical polar molecule has a permanent moment of one-tenth to several debyes; so this moment is indeed small. It lies along the internuclear axis in the direction H^+D^-, thus pointing from H to D and negative in a co-ordinate system whose z-axis points from D to H.

In the following discussion of the HD spectrum, we shall rely on the development of the theory by Herman, Poll and Tipping[1,8-11].

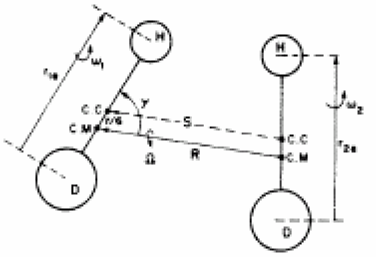

Fig. 1. HD-HD interaction. CM is the center of mass; CC is the center of charge.

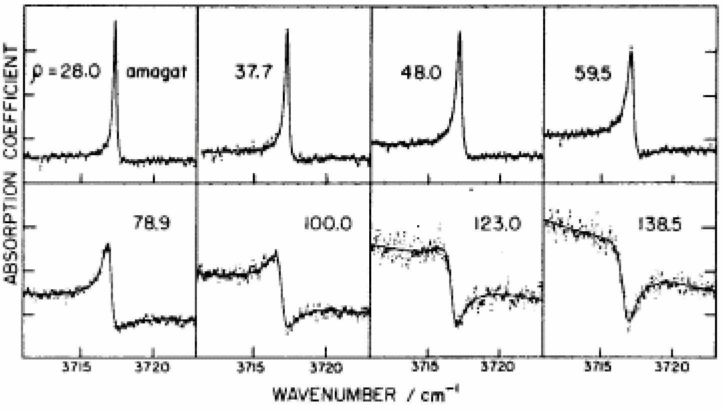

Fig. 2. $R_1(0)$ line of pure HD at 77 K (ref.14). Points are experimental and solid curves are fitted Fano profiles. One division on the vertical axis represents an absorption coefficient of 0.001 cm^{-1}. The origin of the absorption scale for each trace has been shifted to center the $R_1(0)$ feature.

The pair HD-HD within the adiabatic approximation is the same as H_2-H_2. The same induced moment function applies to both situations provided a requisite co-ordinate transformation is made. Induced moments are analyzed with respect to molecular centers of mass to facilitate incorporation of translational motion. For HD, the centers of mass and of charge are displaced by a small distance $r/6$ (Fig. 1). $\vec{S}$ is the distance between the mid points of two molecules (center of charge),

$$\vec{S} = \vec{R} + 1/6\ (\vec{r}_1 - \vec{r}_2) \tag{2}$$

and to a first approximation,

$$\vec{\mu}^I(\text{HD-HD}) = \{1 + (1/6)(\vec{r}_1 - \vec{r}_2) \cdot \vec{\nabla}_R\}\ \vec{\mu}^I(\text{H}_2\text{-H}_2) \quad . \tag{3}$$

New components of A_Λ are generated which permit transitions $\Delta J = \pm1, \pm3$, ... in addition to the $\Delta J = 0, \pm2$ for the collision-induced transitions allowed in H_2-H_2. (J is the total angular momentum quantum number of one of the molecules of the pair.) These new symmetries are responsible for the unusual spectral features which appear for the HD system.

The total dipole moment for a system of N molecules

$$\vec{\mu}(t) = \vec{\mu}(t)^A + N\vec{\mu}^I(t) \tag{4}$$

The absorption coefficient $\alpha(\omega)$ depends on the Fourier transform of the autocorrelation function $C(t) = \langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle$ and the spectrum thus consists of several parts.

The allowed spectrum arises from terms of the type $\langle \vec{\mu}_1^A(0) \cdot \vec{\mu}_1^A(t) \rangle$. In the impact approximation the line shape is a pressure broadened Lorentzian contour. These contributions to $\alpha(\omega)$ vary as the density ρ.

Cross terms, such as $\langle \vec{\mu}_1^A(0) \cdot \vec{\mu}_{12}^I(t) \rangle$ and $\langle \vec{\mu}_{12}^I(0) \cdot \vec{\mu}_1^A(t) \rangle$ represent interference between allowed and induced moments (12 refers to the moment in a pair). Their contribution to $\alpha(\omega)$ depends on the density squared. This effect was identified experimentally by Reddy, Prasad[12] and McKellar[13] and elucidated theoretically by Herman, Poll and Tipping[1,8-12] in the late 1970's and early 1980's. If interference is to occur both allowed and induced moments must be of the same symmetry. The allowed moment has symmetry designated by $A_1(100)$. Through the co-ordinate transformation(3), the isotropic and anisotropic overlap induced moments contain components of that symmetry. (For example, the $A_0(001)$ term for H_2-H_2 gives $A_1(102)$ and $A_1(100)$ terms for HD-HD.) The $A_1(100)$ component of the induced moment is always parallel or antiparallel to the allowed moment, producing constructive or destructive interference.

Within the impact approximation, the line shape is Lorentzian. The profile is sharp, the reasons for which, at least in the opinion of the present authors, have not been quantitatively enunciated[1,9]. In the now 'famous' experimental results of Rich and McKellar[13,14], the fundamental band showed a line shape of the Fano type, whose asymmetry increased with increasing density (Fig. 2). If an

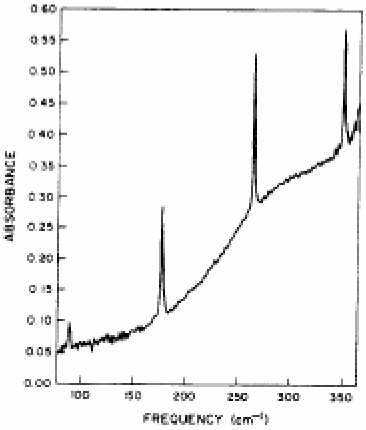

Fig. 3. Pure HD spectrum at 68 amagat and 295 K.

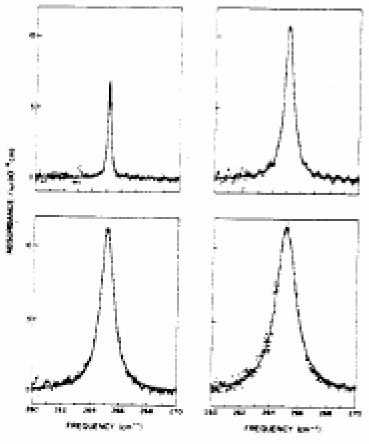

Fig. 4. $R_0(2)$ line of pure HD at 6.9, 31.4, 46.5, and 68.3 amagat (from left to right and top to bottom).

isolated normal line were displayed as in Fig. 2, the result would be a Lorentzian whose peak decreased linearly with density and whose width increased linearly with density in order to maintain a constant area. Above 80 amagat, the $R_1(0)$ line shows an anomalous dispersion shape and finally turns upside down becoming an 'emission' feature. Their results for HD-rare gas mixtures are even more dramatic[14].

To account for these profile features, Herman et al.[10] introduced into C(t), dipole weighted phase factors which represent the influence of phase shifts occurring at the end points of the time interval of dipole inducing collisions. The correlation function is multiplied by a complex quantity $\Delta = \Delta' + i\Delta''$ and the line shape is a sum of Lorentzian and dispersion contours. The Δ, which depends on the interacting species and on T, has as yet not been evaluated.

There is also a purely collision-induced spectrum with broad features as in H_2 arising from the terms like $< \vec{\mu}^{I}_{12}(0)\cdot\vec{\mu}^{I}_{12}(t) >$. Again, the contribution to $\alpha(\omega)$ varies as the density squared. The terms $< \vec{\mu}^{I}_{12}(0)\cdot\vec{\mu}^{I}_{13}(t) >$ involve three molecules and give contributions to $\alpha(\omega)$ varying as the density cubed. The collisions are still binary as the molecules do not collide simultaneously. This effect is known as intercollisional interference[1]. Again, the spectral features are characterized by the same parameters as allowed lines and the line shape is the sum of Lorentzian and dispersion profiles. As a result of this ρ^3 term, the same line may show net destructive and constructive interference, in different density regions. Roger Herman[1] has given an excellent exposition of his view of the physical mechanisms responsible for these two types of interference in the Proceedings of the Williamsburg meeting.

The total spectrum of present interest then consists of allowed, allowed-induced and intercollisional components with Lorentzian and Lorentzian plus dispersion contours

$$\begin{aligned}\alpha(\omega) = {} & \rho N_0 (4\pi^2/3\hbar c)\omega(J+1)P(J)\left|\langle J\left|\mu^A(r)\right|J'\rangle\right|^2 \\ & \times \left[\left[1+2\rho N_0\Delta' I+\rho^2N_0^2(\Delta'^2-\Delta''^2)I^2\right] \frac{(\gamma/2\pi)}{(\gamma/2)^2+(\omega-\omega_0)^2} \right. \\ & \left. + (\rho N_0\Delta'' I + \rho^2N_0^2\Delta'\Delta'' I^2) \frac{2(\omega-\omega_0)/\pi}{(\gamma/2)^2+(\omega-\omega_0)^2} \right] \end{aligned} \tag{5}$$

with

$$I = 4\pi \frac{\int_0^\infty \langle J \left|\mu^I(R)\right|J'\rangle g(R)R^2 dR}{\langle J\left|\mu^A\right|J'\rangle} \quad . \tag{6}$$

ω_0 is the shifted peak frequency, γ is the FWHM, p(J) is the normalized Boltmann factor, I is essentially the ratio of the average induced moment to the allowed moment, g(R) is the pair distribution function; ρ is the density in amagat and N_0 is

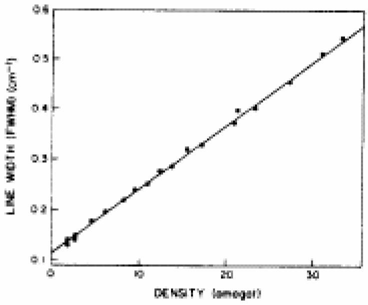

Fig. 5. FWHM of $R_0(2)$ for HD-HD at 195 K. Points are experimental and the solid line is the fitted curve.

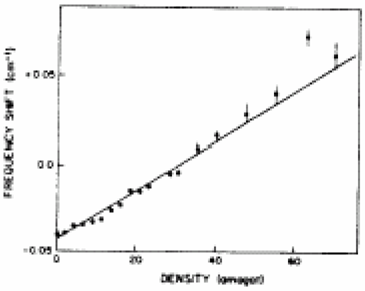

Fig. 6. Frequency shift of $R_0(1)$ for HD-Ne at 77 K. Points are experimental and the solid line is the fitted curve. The shift is plotted relative to 177.844 cm^{-1}.

Loschmidt's number. The integrated absorption coefficient may be written as

$$\int_{-\infty}^{\infty}[\alpha(\omega)/\rho N_0\omega]d\omega = \int_{-\infty}^{\infty}[\alpha^A(\omega)/\rho N_0\omega]d\omega[1+2\rho N_0\Delta' I+\rho^2 N_0^2(\Delta'^2-\Delta''^2)I^2]$$

$$= C_0+C_1\rho+C_2\rho^2 \tag{7}$$

$\alpha^A(\omega)$ is the absorption coefficient due to the allowed moment alone.

EXPERIMENTAL RESULTS

We have measured the four purely rotational lines $R_0(0)$ to $R_0(3)$, which fall at frequencies from 85 cm^{-1} to 375 cm^{-1}, in pure HD and HD-inert gas mixtures at 295 K, 195 K and 77 K. Total sample densities ranged between 2 and 70 amagat. A Michelson interferometer with theoretical resolution of 0.06 cm^{-1} was used[15-17].

Figure 3 shows the sharp features $R_0(0)$ to $R_0(3)$ superimposed on the broad collision-induced background of the $S_0(0)$ to $S_0(1)$ lines.

The purely collision-induced background was removed and rotational lines were fitted with Fano profiles. Examples are shown in Fig. 4. Little asymmetry was observed, the profiles being nearly symmetric Lorentzians. Line broadening B_0 and frequency shift S_0 coefficients were obtained assuming a linear density dependence (Figs. 5 and 6).

The measured integrated absorption coefficient was expressed in the form (7). From C_0, the magnitude of the dipole moment of isolated molecular may be obtained. It is also convenient to define two interference parameters,

$$\underline{a} = C_1/C_0 = 2N_0\Delta' I \tag{8}$$

$$\underline{b} = C_2/C_0 = N_0^2(\Delta'^2 - \Delta''^2)I^2 \tag{9}$$

In Table I, the values of dipole moment averaged over the three experimental temperatures are presented; errors shown are statistical[17]. There is an apparent increase with increasing J. The values on the whole are about 5% less than the ab initio values which show considerably less dependence on J.

When the integrated absorption coefficient is plotted versus density, the result is a sloping line. It would be horizontal for a purely allowed transition. This interference effect may be small (Fig. 7), positive (Fig. 8), or negative (Fig. 9). The slope can be related to the interference parameters (eqs.(8) and (9))[15-17].

The sign of $\underline{a}$ changes with increasing J at all temperatures for pure HD. It also changes from 77 K to 195 K with 295 K and 195 K having the same sign (Table II). For mixtures with inert gases, $\underline{a}$ is positive for all T and all $R_0(J)$ for He, Ne and Ar, the sole exception is $R_0(0)$ for Ar at 195 K. At 295 K, $\underline{a}$ is negative for Kr and Xe (Table III).

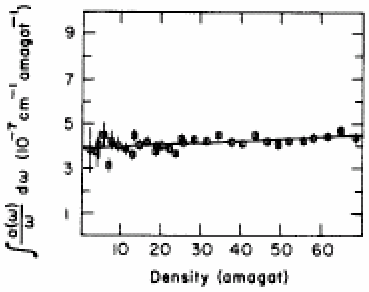

Fig. 7. Integrated absorption coefficient of $R_0(3)$ for pure HD at 295 K. Points are experimental and the solid line is the fitted curve.

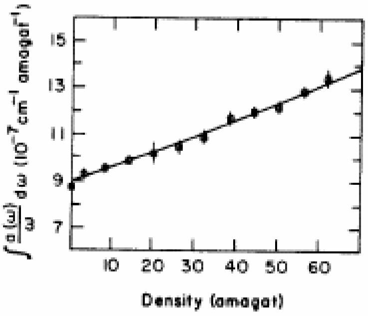

Fig. 8. Integrated absorption coefficient of $R_0(2)$ for HD-Ne at 295 K.

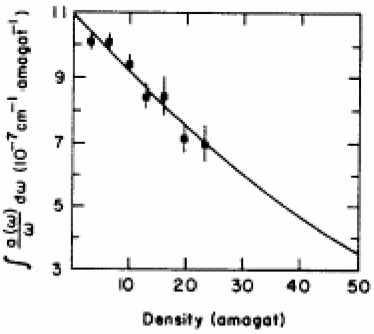

Fig. 9. Integrated absorption coefficient of $R_0(1)$ for HD-Kr at 295 K.

Table I. Dipole moment of HD (10^{-4} D).

	$R_0(0)$	$R_0(1)$	$R_0(2)$	$R_0(3)$
this work	7.26(3)	7.91(2)	8.07(2)	8.34(10)
ref.24				8.47(9)
ref.25		7.5(4)	7.8(4)	7.4(4)
ref.26	8.18(26)	7.9(4)		
Calc.(ref.7)	-8.463	-8.455	-8.440	-8.420

CALCULATION OF THE INTERFERENCE PARAMETER

The interference parameter may be calculated using the theory developed above. We have used ab initio calculations of Borysow, Frommhold and Meyer[18] for the HD-X induced moments. It is, of course, necessary to choose induced moments of the same symmetry as the allowed moment in order that the interference, i.e. the cross terms, be non-zero. For HD-HD, only the anisotropic overlap moment yields of compoent of the required symmetry. For HD-X both isotropic and anisotropic overlap moments contribute. The intermolecular potential used to evaluate g(R) was that for H_2-X, corrected to apply to HD-X. The quantity *a* was calculated from (8) assuming the phase factor $\Delta' = 1$. Results are shown for HD-HD in Table IV. In general, the order of magnitude agrees with experiment, but details of size and sign do not. For $R_0(0)$ a correction can be made for the leading contributions to rotational level mixing by the anisotropy of the intermolecular potentials[19,20]. In addition, Ma, Tipping and Poll[20] have described a resonance mixing effect, due to the near-resonance of between the levels ($J_1=3$, $J_2=0$) and ($J_1=2$, $J_2=2$) in a pair of colliding HD molecules. This results in simultaneous mixing of internal levels in both molecules and leads to a large destructive interference affecting primarily the $R_0(2)$ transition, to the extent that the sign of interference can change. It should be noted that while the effect of the resonance mixing on the sign of *a* is clearly seen in the HD-HD calculations, the agreement between calculation and experiment is only consistent at 77 K.

An interesting comparison is between HD-HD and HD-H_2. Experimentally there is frequently a difference of magnitude or sign or both between the two systems. Calculations indicate that *a* should always be larger in magnitude for HD-HD but this prediction cannot be confirmed because of the large error bars.

Mixtures with atoms are perhaps more amenable to analysis since the atoms lack the possible complications due to internal vibrational and rotational degrees of freedom. Here, for the calculations involving Kr and Ar, only empirical isotropic overlap parameters were available (Table V).

Table II. Interference parameter a for HD-HD and HD-H_2 (10^{-3} amagat^{-1}).

	T (K)	$R_0(0)$	$R_0(1)$	$R_0(2)$	$R_0(3)$
			Experiment		
HD-HD	77	+3.1(4)	+2.2(2)	−3.7(8)	
	195	−5.5(22)	−0.2(6)	+1.1(8)	+7.4(36)
	295	−2.5(19)	−1.1(2)	+1.3(1)	+2.1(6)
HD-H_2	77	+5.4(15)	+2.2(14)	+0.8(29)	
	295		−2.4(5)	−0.9(3)	+4.3(18)

Table III. Interference parameter a for HD inert gas systems (10^{-3} amagat^{-1}).

Perturber	T (K)	$R_0(0)$	$R_0(1)$	$R_0(2)$	$R_0(3)$
			Experiment		
He	77	+6.0(16)	+6.2(7)	+4.4(15)	
Ne	77	+5.8(15)	+8.5(9)	+7.4(24)	
Ar	195	−33.0(40)	+3.0(5)	+4.6(6)	+ 8.4(30)
He	295		+5.7(9)	+3.9(8)	+10.0(19)
Ne	295		+2.1(4)	+6.9(4)	+ 5.3(12)
Ar	295		+1.8(3)	+6.1(2)	+ 9.4(11)
Kr	295		−17.4(24)	−4.3(36)	− 6.7(59)
Xe	295		−23.9(19)	−10.0(23)	− 8.2(44)

Table IV. Calculated interference parameter $\underline{a}$ for HD-HD and HD-H_2 (10^{-3} amagat^{-1}).

	T (K)	$R_0(0)$	$R_0(1)$	$R_0(2)$	$R_0(3)$
HD-HD					
$\underline{a}$	77	1.03	1.03	1.03	
$\underline{a} + \Delta\underline{a}$		1.5	0.9	-2.4	
$\underline{a}$	195	1.47	1.47	1.47	1.47
$\underline{a} + \Delta\underline{a}$		2.1	1.4	-1.7	1.2
$\underline{a}$	295	1.84	1.84	1.84	1.84
$\underline{a} + \Delta\underline{a}$		2.5	1.7	-1.4	1.5
HD-H_2					
$\underline{a}$	77	0.72	0.72	0.72	0.72
$\underline{a}$	195	1.15	1.15	1.15	1.15
$\underline{a}$	295	1.50	1.50	1.50	1.50

For $R_0(0)$, $\Delta\underline{a}$ corrects for mixing of rotational levels by the anisotropic potential. For $R_0(2)$ and $R_0(3)$, Δa is the contribution of a resonance interaction. For $R_0(1)$, $\Delta\underline{a}$ is zero (ref.20).

Table V. Calculated interference parameter $\underline{a}$ for HD inert gas systems (10^{-3} amagat^{-1}).

Perturber	T (K)	$R_0(0)$	$R_0(1)$	$R_0(2)$	$R_0(3)$
He	77	+4.47	+4.47	+4.47	
Ar	195	+8.80	+8.80	+8.80	+8.80
He	295	+7.38	+7.38	+7.38	+7.38
Ar	295	+9.44	+9.44	+9.44	+9.44
Kr	295	(?)11.6	(?)11.6	(?)11.6	(?)11.6
Xe	295	(?)13.4	(?)13.4	(?)13.4	(?)13.4

DISCUSSION

Let us now look into the question of the sign of a̲ in more detail for the mixtures with inert gases. The sign of the interference depends on the relative orientation of the allowed moment and the $A_1(100)$ component of the induced moment, both of which lie along the direction of the internuclear axis. The allowed moment is always in the direction H^+D^- and therefore the sign of the interference will depend on the direction of the overlap component. A positive isotropic overlap moment $A_0(001)$ which point from the perturber to HD molecule (for example, He^+HD^-) will give a $A_1(100)$ component pointing from H to D in HD and result in positive interference. For the anisotropic overlap component $A_1(201)$, the opposite is true; when it is negative, the resulting interference is positive. The sign of the induced moment is available from ab initio calculations for HD-He, HD-Ne and HD-Ar and we conclude that the interference should be positive as observed[16]. Unfortunately for the mixtures with Kr and Xe, the sign of overlap moment is not available from calculation.

Nevertheless, a qualitative picture can be given[16]. The overlap induced moment originates at short intermolecular distances as a result of the exclusive principle. Electrons of outer orbitals of both molecules are pushed outward. If the two molecules differ, a pair moment appears which is the algebraic sum of two moments. Short range forces generally give a moment with the more polarizable molecule negative since it suffers the more distortion. It is expected then that collisions with molecules lighter than HD will give an induced moment that points toward HD and positive interference. Perturbers much heavier than HD will give negative interference. Indeed, this is the predominant pattern observed (Table III).

An important result then is that one can deduce the sign of the overlap moments for HD-X pairs; this information cannot be supplied from ordinary collision-induced spectroscopy.

In our calculations, we have taken $\Delta' \sim 1$. If we assign discrepancy between calculation and experiment to Δ', then we can estimate Δ'. In only about one-half of the cases studied is $\Delta' < 1$, as required by the theoretical framework. The HD- inert gas mixture results tend to have $\Delta' < 1$ more consistently than do the pure HD data.

It is interesting to compare the results for the pure rotational band with those for the fundamental bands[13,14]. The studies of McKellar and Rich[14] on the fundamental band were extended to densities higher than those for our investigations of the rotational spectrum. They found that at 77 K, the integrated absorption coefficient of $R_1(1)$ decreases more rapidly with increasing density than that of $R_1(0)$ at low density but then turns up above 100 amagat due to the ρ^3 term. The asymmetry of these lines also varies differently with density. McKellar and Rich conclude that Δ' is about the same for HD-He, HD-Ne and HD-Ar for a given $R_1(J)$ line but that variations in Δ''I do not follow a simple pattern. Overall, the theory of Herman et al.[8-11] provides a very satisfactory basis for description of their data.

In the pure rotational case, a smaller a and smaller profile asymmetry with respect to the vibration-rotation lines are found. Part of this result is expected as $\mu^A_{0-0} \sim 10 \times \mu^A_{1-0}$ and a is inversely proportional to μ^A. By ab initio calculations, μ^A_{0-0} is in the sense H^+D^- and μ^A_{1-0} is in the sense H^-D^+. For the 1-0 band in HD-He, the $A_1(100)$ component of the isotropic overlap component is in the direction H^+D^- and therefore a is predicted to be negative. Experimentally a is less than zero for HD-He, HD-Ne and HD-Ar[14] and greater than zero for HD-Kr[12]. Therefore, it would seem that the same trends are evident in the rotational and fundamental bands, but opposite in sign because of the opposite signs of the allowed moments. Why there is a greater asymmetry, and hence larger Δ'', for the fundamental band is not apparent. Roger Herman[21] and his colleagues are attempting to clarify this situation through a direct calculation of Δ.

There are still unexplained aspects of the magnitude of a. Additional mechanisms may affect the line profile at medium densities. Such a mechanism which is capable of modifying the intensity of the spectral line involves the effect of the finite duration of collisions. In the impact approximation, the time of duration is, of course, assumed negligible compared to the time between collisions. Boulet, Robert and Galatry[22] have taken the time of duration into account in a general theory of line broadening. Then one obtains a Lorentzian plus a dispersion profile and intensity modification in the same manner as gotten for the interference effect. We tried a calculation of the intensity modification for HD allowed lines and compared it to the interference parameters. The effect was generally in the right direction but an order of magnitude too small to explain discrepancies between theory and experiment.

PROFILE PARAMETERS

Let us now turn to the broadening coefficient B_0. It generally decreases with increasing J at all temperatures and systems[17]. The universal exception is $R_0(0)$ at 77 K. At all J and for all systems, B_0 increases with T. A power law dependence of B_0 on T does not give a good representation of this behaviour (Fig. 10).

For HD-He, Green[23] has computed pressure broadening cross sections for $R_0(0)$ and $R_0(1)$ following the impact theory approach (Fig. 11). The calculated B_0 curves lie somewhat above experimental values but the principal features of the temperature and J-dependence are the same. B_0 is greater for $R_0(1)$ at low T; at intermediate T, B_0 is slightly greater for $R_0(0)$.

Generally, the frequency shifts go from positive to negative, that is from blue to red, as J increases for all systems at all T. The asymmetry of the profiles was quantitatively described; it increases with increasing density but the data show much scatter due to the difficulties of measuring such a small symmetry[16,17].

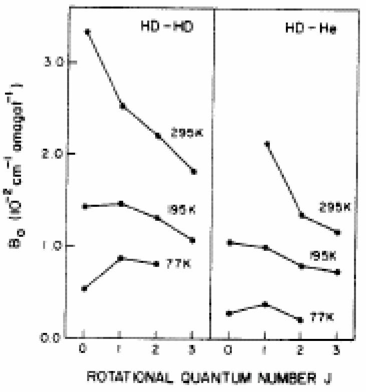

Fig.10. Broadening coefficient B_0 versus J. Points are deduced from experiment. Straight line segments connect the points.

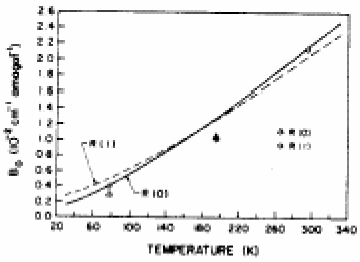

Fig.11. B_0 for pure HD. Points are experimental. Lines are from theory (ref.23). $R_0(0)\Delta$; $R_0(1)$ ◇

SUMMARY

(i) The measured value of the permanent dipole moment shows a possible J-dependence not predicted by the ab initio calculations.

(ii) Characterization of the density and temperature dependence of the absorption coefficient and spectral line parameters is reasonably complete. The integrated absorption coefficient has a more complicated behaviour than predicted by present theory. The temperature dependence of the interference parameter a, particularly its change in sign for HD-HD, cannot be explained by a theory where temperature enters only through the pair distribution function.

(iii) The temperature dependence of the line widths agrees with the predictions of impact theory in the few quantitative assessments which could be made. The frequency shifts are in qualitative agreement with theory.

(iv) In general, the HD-inert gas results conform better with present theory than do the pure HD data.

Several themes on which future studies can be built come to mind.

(a) Experimentally, data on both the rotational and fundamental bands at more temperatures would be desirable given the strong variation of a with temperature for several lines.

(b) Theoretically, a methodical calculation of the widths and shifts for HD-X systems is needed, both within the impact approximation and with unified theories.

(c) Ma et al.[20] have pointed out the desirability of having ab initio calculations of the $A_1(100)$ component of the induced moment at several internuclear separations. Their availability would allow the extending of the theory of the interference to the vibration-rotation region and permit the inclusion of more refined temperature-dependent rotational level mixing effects in the calculations.

ACKNOWLEDGEMENTS

This research was supported by grants from the Natural Sciences and Engineering Research Council (Canada), the Consiglio Nazionale delle Richerche (Italy) and NATO.

REFERENCES

1. R.M. Herman, in Spectral Line Shapes, Vol. 4, edited by J. Exton (Deepak, Hampton, 1987), p.351.
2. M.J. Clouter and A.R.W. McKellar, Can. J. Phys. 65 1, 1987.
3. J.D. Poll, this volume;
   A.R.W. McKellar and M. J. Clouter, Chem. Phys. Lett. 140, 117 (1987);
   R.H. Tipping and J.D. Poll, Phys. Rev. B35, 6699 1987);
   S.K. Bose and J.D. Poll, Can. J. Phys. 65, 1577 (1987);
   S.Y. Lee, S.I. Lee, J.R. Gaines, R.H. Tipping and J.D. Poll, Phys. Rev. B37, 2357 (1988).

4. G. Birnbaum, L. Frommhold and G.C. Tabisz, in Spectral Line Shapes, Vol. 5, edited by J. Szudy (Ossolineum, Wroclaw, 1989) p.623.
5. J.D. Poll and J. van Kranendonk, Can. J. Phys. 39, 189 (1961).
6. G.C. Wick, Atti R. Accad. Naz. Lincei, Mem. Cl. Sci. Fis. Mat. Nat. 21, 708 (1935).
7. W.R. Thorson, J.H. Choi and S.K. Knudson, Phys. Rev. A31, 22 (1985); 31, 34 (1985).
8. R.M. Herman, Phys. Rev. Lett. 42, 1206 (1979).
9. R.H. Tipping, J.D. Poll and A.R.W. McKellar, Can. J. Phys. 56, 75 (1978).
10. R.M. Herman, R.H. Tipping and J.D. Poll, Phys. Rev. A 20, 2006 (1979).
11. R.H. Tipping and J.D. Poll in Molecular Spectroscopy: Modern Research, edited by K.N. Rao (Academic, New York, 1985), Vol. III, p.421.
12. J.D. Poll, R.H. Tipping, R.D.G. Prasad and S.P. Reddy, Phys. Rev. Lett. 36, 248 (1976).
13. A.R.W. McKellar, Can. J. Phys. 51, 3889 (1973).
14. N.H. Rich and A.R.W. McKellar 61, 1648 (1983).
    A.R.W. McKellar and N.H.Rich 62, 1665 (1984).
15. P.G. Drakopoulos and G.C. Tabisz, Phys. Rev. A36, 5556 (1987).
16. P.G. Drakopoulos and G.C. Tabisz, Phys. A36, 5566 (1987).
17. L. Ulivi, Z. Lu and G.C. Tabisz, Phys. Rev. A40, 642 (1989).
18. A. Borysow, L. Frommhold and W. Meyer, J. Chem. Phys. 88, 4855 (1988).
19. G.C. Tabisz and J.B. Nelson, Phys. Rev. A31, 1160 (1985).
20. Q. Ma, R.H. Tipping and J.D. Poll, Phys. Rev. A38, 6185 (1988).
21. R. Herman, private communication
22. C. Boulet, D. Robert and L. Galatry, J. Chem. Phys. 72, 751 (1980); C. Boulet and D. Robert, ibid. 77, 4288 (1982).
23. S. Green, Physica 76, 609 (1974).
24. P. Essenwanger and H.P. Gush, Can. J. Phys. 62, 1680 (1984).
25. A.R.W. McKellar, Can. J. Phys. 64, 227 (1986).
26. A.R.W. McKellar, J.W.C. Johns, W. Majewski, and N.H. Rich, Can. J. Phys. 62, 1673 (1984).

53
1237

Authorization to photocopy items for internal or personal use, beyond the free copying permitted under the 1978 US Copyright Law (see statement below), is granted by the American Insitute of Physics for users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service, provided that the base fee of $2.00 per copy is paid directly to CCC, 27 Congress St., Salem, MA 01970. For those organizations that have been granted a photocopy license by CCC, a separate system of payment has been arranged. The fee code for users of the Transactional Reporting Service is: 0094-243X/87 $2.00.

© 1990 American Institute of Physics.

Individual readers of this volume and non-profit libraries, acting for them, are permitted to make fair use of the material in it, such as copying an article for use in teaching or research. Permission is granted to quote from this volume in scientific work with the customary acknowledgment of the source. To reprint a figure, table or other excerpt requires the consent of one of the original authors and notification to AIP. Republication or systematic or multiple reproduction of any material in this volume is permitted only under license from AIP. Address inquiries to Series Editor, AIP Conference Proceedings, AIP, 335 E. 45th St., New York, NY 10017.

L.C. Catalog Card No. 90-85194
ISBN 0-88318-791-4
DOE CONF-9006278

Printed in the United States of America.

This book was put into production on 3 October 1990 and was published on 17 December 1990.