

Intracollisional interference in the pure rotational spectrum of HD: Determination of the permanent electric dipole moment

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The intensity of the pure rotational absorption spectrum of gaseous HD is measured as a function of density for pure HD and HD-He and HD-Ar mixtures. The decrease in the absorption coefficient with increasing density is consistent with a destructive intracollisional interference between the transitions involving the permanent and collision-induced dipole moments. The permanent dipole moment of the molecule in its ground vibrational state is found to be J dependent and in the range $(8-10) \times 10^{-4}$ D.

I. INTRODUCTION

The molecular hydrogen isotope HD possesses a small permanent electric dipole moment due to nonadiabatic effects coupling electronic and nuclear motions. Wick¹ predicted its existence and several authors have carefully attempted its calculation by *ab initio* methods.²⁻⁹ While the symmetric molecules H₂ and D₂ have no dipole moment and show no allowed infrared spectrum, HD thus does. Herzberg¹⁰ first observed the fundamental and overtone spectra due to this moment. Trefler and Gush¹¹ deduced a value for the moment of the ground vibrational state from the intensity of the pure rotational spectrum. This determination is lower than the presumably best *ab initio* calculations^{7,9} by 30–50%. In a recent letter,¹² the present authors reported new measurements on the pure rotational spectrum and demonstrated that this discrepancy between experiment and calculation may be accounted for through an intracollisional interference effect.¹³⁻¹⁶ This paper gives a fuller account of that work, extends the measurements to higher resolution and to mixtures of HD with inert gas atoms, refines slightly the values of the dipole moment, and continues the elucidation of the phenomenon of intracollisional interference.

II. INTRACOLLISIONAL INTERFERENCE

While H₂ does not have an allowed infrared spectrum, its collision-induced vibration-rotation spectrum, which arises from transient dipoles induced in clusters of in-

teracting molecules, has been the subject of exhaustive study.¹⁷ The induced moment depends on intermolecular separation and is described in terms of short-range overlap and long-range multipole interactions. Poll, Tipping, and Herman, basing their theory on the experimental results of Reddy, Prasad, and McKellar, have described an intracollisional interference effect.¹³⁻¹⁶ They show that, for a pair of interacting molecules with permanent dipole moments, there can be interference between the transitions involving the allowed (p^A) and induced (p^I) moments. The spectral intensity then depends on the square of the total moment $(p^A + p^I)^2$. The term in $(p^A)^2$ yields the allowed spectrum of sharp lines whose intensity is proportional to the density ρ ; the term in $(p^I)^2$ gives rise to a broad collision-induced spectrum whose intensity at moderate density is proportional to ρ^2 . The cross term $2p^A p^I$, which describes the interference effect, also varies as ρ^2 ; since it involves p^A , it contributes to the sharp features at the frequencies of the allowed transitions. Herman¹⁵ has discussed the physical basis for the interference and has detailed the nature of various contributions to the spectrum. The interference results from a resonance between the discrete allowed spectrum and the quasicontinuous translationally broadened spectrum.¹⁸ The line profiles are then expected to be of the Fano type, a density-dependent superposition of a Lorentzian and an anomalous dispersion profile.^{16,18,19}

In general, the integrated absorption coefficient is related to the dipole moment involved in a transition by the well-known relationship^{11,14,16}

$$\int [\alpha(\omega)/\omega] d\omega = (8\pi^3 N_0 / 3hcZ) [\exp(-E_1/kT) - \exp(-E_2/kT)] (J+1) (p_{vJ,v'J'})^2 = K_{vJ,v'J'} (p_{vJ,v'J'})^2. \quad (1)$$

Here $\alpha(\omega)$ is the absorption coefficient²⁰ at frequency ω , $p_{vJ,v'J'}$ is the total dipole moment between vibration-rotation states (v,J) and (v',J') , Z is the state sum, E_1 and E_2 are the energies of the lower and upper states, and J is the angular momentum quantum number of the lower state.

Therefore, in the case of a homogeneous gas, when the

purely collision-induced component is not considered, the integrated absorption coefficient can be written as¹⁴

$$\int [\alpha(\omega)/\omega] d\omega = \int [\alpha^A(\omega)/\omega] d\omega (1 + a\rho). \quad (2)$$

Here $\alpha^A(\omega)$ is the absorption coefficient of the allowed spectrum when no interference is present. The interfer-

ence may be positive or negative, according to the relative signs of p^I and p^A . It is characterized by the parameter a which is essentially twice the ratio of the averaged induced moment to the allowed moment. Explicitly,

$$a = \left[8\pi N_0 \int_0^\infty p_{wJ,v'J'}^I(R)g(R)R^2dR \right] / p_{wJ,v'J'}^A, \quad (3)$$

where $g(R)$ is the pair-distribution function, R is the intermolecular separation, and N_0 is the number density at STP.

In the case of a mixture of absorber and perturber molecules, (1) must take into account all possible moments; thus for the total moment p , one has

$$p = p_a^A + p_p^A + p_{aa}^I + p_{pp}^I + p_{ap}^I,$$

where the subscripts refer to the absorber (a) and to the perturber (p). If the perturber has no permanent moment, and if the purely collision-induced components are again neglected, then (1) gives

$$\int [\alpha(\omega)/\omega]d\omega = \int [\alpha^A(\omega)/\omega]d\omega(1+a\rho_a) + b\rho_p, \quad (4)$$

where ρ_p is the perturber density and

$$b = 8\pi N_0 K_{wJ,v'J'} p_{wJ,v'J'}^A \int_0^\infty p_{wJ,v'J'}^I(R)g(R)R^2dR. \quad (5)$$

The absorption intensity that is due to the interaction of the absorber and perturber and, hence, additional to that due to the interaction of absorber molecules alone is designated as the absorption enhancement²⁰ $\alpha^{en}(\omega)$, and

$$\int [\alpha^{en}(\omega)/\omega]d\omega = b\rho_p. \quad (6)$$

Both p^A and p^I must satisfy the same selection rules if interference is to occur. The allowed spectrum is governed by the dipole rule $\Delta J = \pm 1$ for the total angular momentum quantum number of one of the molecules of the pair. For homonuclear diatomic molecules, transitions involving p^I follow $\Delta J = 0$ and ± 2 .¹⁷ In HD, however, the centers of mass and symmetry do not coincide. Thus a component appears in p^I which can interfere with the allowed dipole, even if anisotropic interactions are not taken into account.^{13,14,16,21} Anisotropic interactions, when present, can cause rotational-level mixing which affects the spectral intensities; this mixing effect has not been incorporated into the present theory.

The R dependence of the overlap contribution to the induced moment is customarily written as $\lambda_n \exp[-(R-\sigma)/R_0]$, where λ_n is the value of the moment at $R = \sigma$, the molecular diameter, and R_0 is the effective range parameter. The overlap-induced moment must be anisotropic in a symmetric encounter such as for HD-HD or H₂-H₂. In this case the component essential for interference is¹⁴

$$p^I(R) = \lambda_n (\sqrt{2}/18) r_e [(1/R_0) - (2/R)] \times \exp[-(R-\sigma)/R_0], \quad (7)$$

where r_e is the equilibrium bond length of the HD molecule (0.738 Å). For HD-inert-gas collisions, the major contribution to the induced absorption comes from the isotropic, rather than anisotropic, overlap-induced moment, and the required component is^{13,14}

$$p^I(R) = \lambda_n (r_e/18) [(1/R_0) - (2/R)] \exp[-(R-\sigma)/R_0]. \quad (8)$$

The intracollisional interference effect was first identified in the fundamental spectrum of HD^{14,18} and HD-rare-gas mixtures.¹³ In the current study, the pure rotational spectrum of HD is measured over a wide density range in pure HD, and in HD-Ar and HD-He mixtures. The presence of the interference effect is confirmed, and the results used to deduce values of the dipole moment of the ground vibrational state which are in reasonable agreement with *ab initio* calculations.

III. EXPERIMENTAL DETAILS

The sample gases were dried and contained in a 1-m stainless-steel absorption cell equipped with polyethylene windows.²² The hydrogen gas used was 96% HD, supplied by Merck, Sharpe, and Dohme Canada Ltd. Absorption spectra were taken in the frequency range 80–450 cm⁻¹ with a Nicolet FTIR (Fourier transform infrared) interferometer modified to accept the long-path-length sample cell. All experiments were performed at 295 K. Pure HD was studied in a density range of from 12 to 60 amagats at resolutions of 1 cm⁻¹ (10), $\frac{1}{2}$ cm⁻¹ (4), $\frac{1}{4}$ cm⁻¹ (1), and $\frac{1}{8}$ cm⁻¹ (1). (The figures in parentheses give the number of different densities at which data were taken.) High-purity argon (99.999%) was added to HD at a density fixed at about 13 amagats to prepare the HD-Ar mixtures; spectra were taken at argon

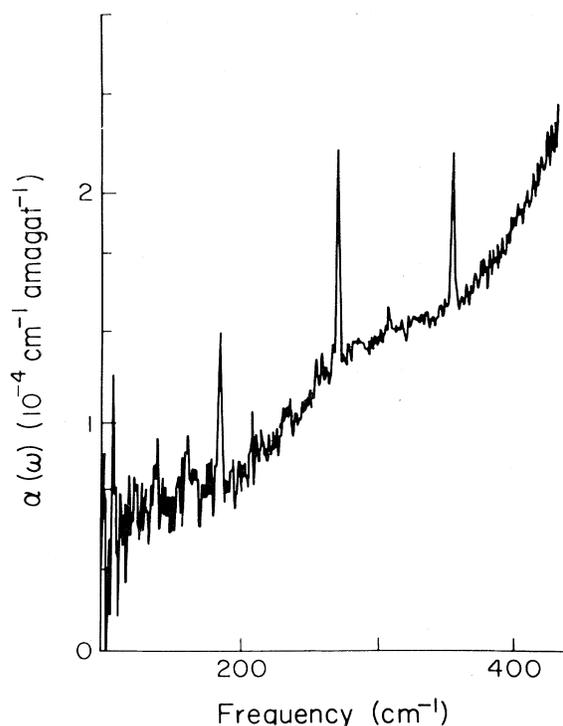


FIG. 1. Rotational spectrum of pure HD at 55.2 amagats. $R(1)$, $R(2)$, and $R(3)$ appear as sharp features at about 178, 265, and 351 cm⁻¹, respectively.

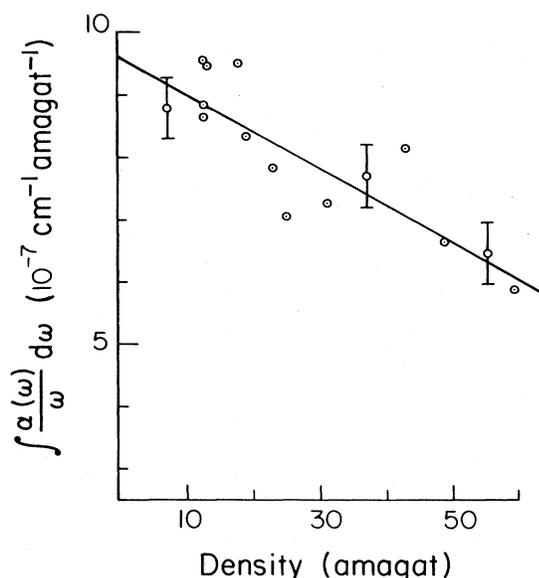


FIG. 2. Integrated intensity of the $R(2)$ line of pure HD as a function of density.

densities in the range of from 11 to 46 amagats at 1 cm^{-1} (5) and $\frac{1}{4}\text{ cm}^{-1}$ (2) resolution. Helium (99.999%) was mixed with HD at 23.3 amagats; spectra were recorded at three helium densities from 14 to 43 amagats at $\frac{1}{4}\text{ cm}^{-1}$ resolution. For the determination of the densities involved in the mixtures, the partial pressures were assumed additive and the densities computed from the equations of state of the pure gases.²³

The HD rotational lines appeared as sharp features on a broad collision-induced background which had to be removed before their integrated intensities could be determined (Fig. 1). To accomplish this subtraction, the broad background was estimated by a smooth curve over a frequency range of $\pm 25\text{ cm}^{-1}$ about a given $R(J)$ line. The specification of this background level was the largest single source of error (3–10%) in the determination of the integrated intensity. The $R(1)$, $R(2)$, and $R(3)$ rotational lines at approximately 178, 265, and 351 cm^{-1} were analyzed; the profiles of $R(0)$ and $R(4)$ at 89 and 437 cm^{-1} could not be detected with sufficient precision for reliable analysis.

IV. DIPOLE MOMENT OF HD

The integrated absorption coefficients of the pure HD spectra $\int [\alpha(\omega)/\omega]d\omega$ were plotted versus density (Fig. 2).²⁴ For all three lines, they decreased with increasing density compatible with a negative interference effect.

TABLE I. Comparison of experimental and theoretical dipole moments in units of 10^{-4} D .

	Experimental	Theoretical	
		Wolniewicz (Ref. 7)	Ford and Browne (Ref. 9)
$R(0)$		8.36	8.31
$R(1)$	8.78 ± 0.2	8.38	8.30
$R(2)$	8.47 ± 0.2	8.39	8.28
$R(3)$	10.21 ± 0.2	8.41	8.26

The consistency between the absorption coefficients of spectra taken at different resolutions was good except for $R(1)$ where the low density (≤ 10 amagats) results for 1 cm^{-1} resolution were greater than those taken at higher resolutions. The linear relationship described by (2) was fitted to the data, and the intercept at zero density, $\int [\alpha^A(\omega)/\omega]d\omega$, was related to the dipole moment of the isolated molecule through (1). The values, thus obtained, of the dipole moment of the ground vibrational state, ($p_{0J,0J'}^A$), are given in Table I. These are slightly different from those reported earlier by the present authors¹² because of the inclusion of data from further experimentation in this analysis. The error quoted represents the standard deviation obtained in the weighted least-squares fit. The estimated random error of the integrated absorption coefficient at a given density is 5–12%. A source of systematic error was the presence of water lines in the wings of $R(1)$ and particularly $R(3)$; the $R(2)$ region was clear of impurity lines and provided the best data for analysis. The values of $p_{0J,0J'}^A$ for $R(1)$ and $R(2)$ are in excellent accord with the latest *ab initio* calculations^{7,9} ($\leq 6\%$); the value of $R(3)$ is about 20% higher. The magnitude of this agreement is similar to that found in the case of the transition dipoles involved in the fundamental and overtone bands.^{7,9,25} The J dependence of the moment is larger than calculated. Both Bunker⁴ and Karl²⁶ have argued that the variation in the moment between different $R(J)$ transitions at low J should be of the order of 10^{-6} D .

V. INTERFERENCE PARAMETERS

Equations (2) and (6) show that the interference parameters a and b (Table II) may be obtained, respectively, from the slope of the graph of $\int [\alpha(\omega)/\omega]d\omega$ vs ρ (Fig. 2) and $\int [\alpha^{en}(\omega)/\omega]d\omega$ vs ρ_p (Fig. 3). The error quoted is again the standard deviation obtained from a weighted least-squares fit; in the case of the enhancement spectra, the straight line was constrained to pass through the origin

TABLE II. Interference parameters a and b in units of $\text{cm}^{-1}\text{ amagat}^{-1}$.

	a (10^3)		b (10^9)			
	HD-HD		HD-Ar		HD-He	
	Expt.	Calc. " ^a	Expt.	Calc. " ^a	Expt.	Calc. " ^a
$R(1)$	-7.7 ± 1.2	5.4	-17 ± 3	7.6	-19 ± 0.8	7.3
$R(2)$	-6.3 ± 1.2	5.4	-6.4 ± 0.7	5.8	-5.7 ± 0.7	5.6
$R(3)$	-7.2 ± 1.1	5.4	-2.4 ± 0.5	2.3	-2.8 ± 0.9	2.2

^aThe calculation gives the magnitude only and not the sign.

TABLE III. Intermolecular parameters required in the calculations.

	ϵ/k (K)	σ (Å)	λ_n (10^{-2} D)	R_0/σ
HD-HD	37 ^a	2.928 ^a	0.65 ^a	0.11 ^a
HD-Ar	66.6 ^b	3.17 ^b	1.0 ^b	0.11 ^b
HD-He	12.9 ^c	3.038 ^c	0.53 ^d	0.107 ^d

^aReferences 14 and 27.^bReference 27.^cReference 29.^dReference 28.

[(6)]. Both a and b are negative in all cases; p^A and p^I are therefore opposite in sign [(3) and (5)].

The magnitude of a and b may be calculated from (3), (5), (7), and (8) once $p^I(R)$ and p^A are provided. For $p^A_{\omega, \omega'}$ the average calculated values (Table I) were used. The zeroth-order approximation to $g(R)$, i.e., $\exp[-V(R)/kT]$, was taken, where $V(R)$ is the intermolecular potential. For HD-HD and HD-Ar, the induced moment parameters have been derived from induced rotational spectra of H₂-H₂ and H₂-Ar with a 12-6 Lennard-Jones potential.²⁷ The moment parameters²⁸ and isotropic intermolecular potential²⁹ for H₂-He have been calculated in an *ab initio* manner by Wormer *et al.* The necessary potential and induced moment parameters are collected in Table III; the calculated values of a and b are compared with experiment in Table II. These calculations have an estimated accuracy of no better than 10% due to the uncertainty in the moment parameters and to the use of the Lennard-Jones potential. Agreement is, therefore,

satisfactory for the $R(2)$ and $R(3)$ lines, while the values calculated for $R(1)$ are all somewhat low.

VI. DISCUSSION

Both the dipole moments and the interference parameters are of the same magnitude as predicted by theory. Thus, it would appear that it is a valid approach to attribute the decrease in absorption intensity to the mechanism of intracollisional interference and to extrapolate to zero density to determine the dipole moment of the isolated molecule. Most encouraging is the consistent agreement with theory which occurs for $R(2)$, the line with the least experimental uncertainties.

The theory of intracollisional interference as currently developed neglects rotational-level mixing by anisotropic intermolecular forces. Such an effect would be most important for low J levels^{14,21} and would yield a stronger J dependence of a and b than predicted by (3) and (5). The present result that the interference parameters differ most from calculation for $R(1)$ is perhaps, therefore, expected. Herman¹⁵ discussed contributions to the intensity which depend on powers of the density higher than ρ [Eqs. (2), (4), and (6)], but the present results were not performed at densities sufficiently high to identify them.

Surprisingly, no unambiguous evidence for a Fano profile was found. For pure HD, only the $R(2)$ profile in the midrange of densities was somewhat asymmetric (Fig. 4). McKellar and Rich^{16,18,30} have observed a dramatic evolution with density of the Fano profiles of the rotational lines of the fundamental band in pure HD and HD-inert-gas mixtures. It may be that the low resolution of the present experiments masks the shape of the profile; the highest resolution experiments ($\frac{1}{8}$ cm⁻¹) were performed only at low densities (~ 12 amagats).

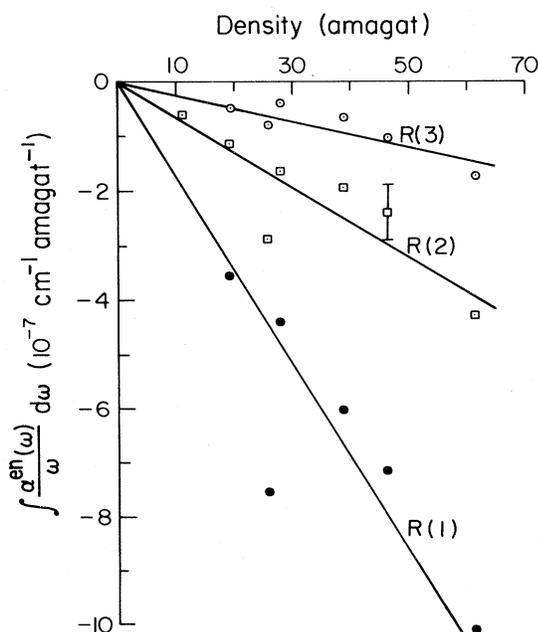


FIG. 3. Integrated intensity of the enhancement spectrum for HD-Ar mixtures as a function of argon density.

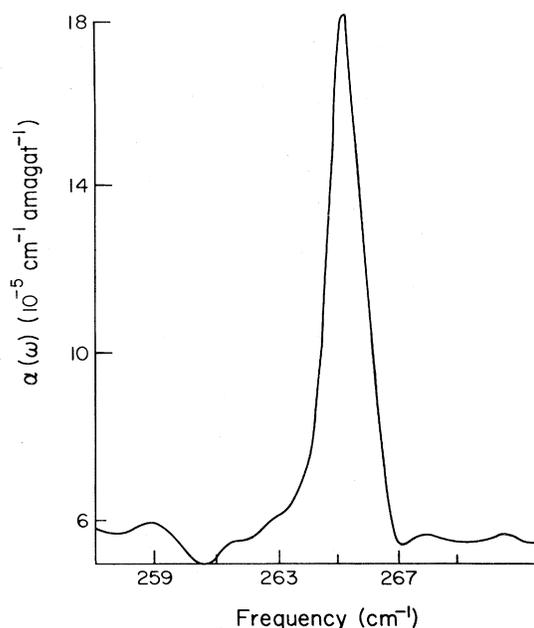


FIG. 4. Profile of the $R(2)$ pure HD at 31 amagats.

The large J dependence of the moment is not confirmed by theory. Trefler and Gush¹¹ measured the absorption coefficient at high densities (50–135 amagats) and determined what may be termed the apparent dipole moment, i.e., a value which is uncorrected for intracollisional interference effects. When the present results are extrapolated to these densities by (2), then excellent agreement is obtained with their moments,¹² including the same marked dependence on J .

The goal of the present analysis was to confirm the existence of the intracollisional interference effect and to test the theory of it as developed to date. Therefore, the quantities required to calculate a and b through (3) and (5) were taken from sources external to the present experiment. The data could, of course, be used in other ways. For example, $p_{0J,0J'}$ may be obtained from the measured b when the induced moment is specified. The mixture spectra were more free of water contamination than the spectra of the pure gas. The value of the dipole moment for $R(3)$ obtained in this manner is lower than that deduced from the pure HD case. This result supports the statement in Sec. IV that the presence of water lines systematically affected the determination of the integrated intensity of $R(3)$. Similarly, the measurements could be used to deduce information on the induced moment. In this regard, the accord found between experimental and calculat-

ed values of a demonstrates that the parameters of the H_2 - H_2 anisotropic overlap-induced moment, deduced from the intensity of the rotational absorption spectrum by Poll and Hunt,²⁷ provide a model of the moment which consistently accounts both for the induced absorption and the interference effect. A very recent investigation of the H_2 - H_2 rotational spectrum by Bachet, Cohen, Dore, and Birnbaum³¹ reveals that the overlap parameters depend markedly on the potential used in the analysis and concludes that the magnitude of the overlap interaction is smaller than found in the earlier study.²⁷ Further experimental study of the intracollisional interference effect together with refinement of the theory should help to resolve the controversy over the magnitude of the overlap-induced moment in hydrogen.

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²⁰The absorption coefficient is $\alpha(\omega) = (1/\rho l) \ln[I_0(\omega)/I(\omega)]$. $I_0(\omega)$ is the intensity transmitted in the absence of the ab-

sorber, $I(\omega)$ is the intensity transmitted through the absorber, l is the path length, and ρ is the gas density. The absorption coefficient of the enhancement spectrum is $\alpha^{en}(\omega) = (1/\rho_a l) \ln[I'_0(\omega)/I'(\omega)]$. $I'_0(\omega)$ is the intensity transmitted by the absorber alone, $I'(\omega)$ is the intensity transmitted by the mixture of the absorber and the perturber, and ρ_a is the density of the absorber. Amagat units of density are used throughout the paper.

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²⁴Figure 2 of Ref. 12 is a presentation of similar data. Its vertical axis is mislabeled and should read $\int \alpha(\omega) d\omega$ ($\text{cm}^{-2} \text{amagat}^{-1}$).

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