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New Spectroscopic Determination of the Dipole Moment of HD in the Ground Vibrational State

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The intensity of the pure rotational spectrum of gaseous HD is measured as a function of density to determine the dipole moment in the ground vibrational state. J-dependent values are found in the range $(8.0\text{–}9.8)\times 10^{-4}$ D which, contrary to previous determinations of Trefler and Gush, agree reasonably with *ab initio* calculations. Intracollisional interference is taken into account and its J dependence determined.

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It is well known that symmetric diatomic molecules such as H_2 and D_2 display no electric-dipole–allowed vibration-rotation spectra. During the vibrational motion of HD, the mass difference between the H and D atoms results in a displacement between the centers of the electronic and nuclear charge creating a small attendant dipole moment.[1,2] HD is, thus, the lightest polar molecule. Herzberg[3] was the first to observe the fundamental and overtone spectra due to this moment. In 1968, Trefler and Gush[4] measured the pure rotational spectrum and deduced a value for the dipole moment of the ground vibrational state. Their average value of 5.85×10^{-4} D differed by more than a factor of 2 from the presumably best *ab initio* calculation then available.[5] Considerable computational effort[6-10] has subsequently been expended to account for their result. Although these calculations agree well ($\lesssim 10\%$) with values of the transition dipoles deduced from the fundamental and overtone spectra, the experimental and calculated values of the ground-state moment still disagree by 40%.

While H_2 does not have an allowed infrared spectrum, its collision-induced vibration-rotation spectrum, arising from transient dipoles in clusters of interacting molecules, has been exhaustively studied.[11] The induced moment is considered to be caused by short-range overlap and long-range electric multipole interactions. Recently, Poll, Tipping, and their collaborators[12-14] have shown that, for a pair of interacting molecules with permanent dipole moments, there can be interference between the allowed (p^A) and induced (p^I) moments. The spectral intensity depends then 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; the term in $(p^I)^2$ gives rise to a broad collision-induced spectrum whose intensity at moderate density is proportional to the square of the density. The cross term $2p^A p^I$ is the contribution of the interference effect and is also proportional to the square of the density; since it involves p^A, it gives sharp lines at the frequencies of the allowed transitions. Then, when the pure induced spectrum is ignored, we have

$$\int[\alpha(\omega)/\omega]\,d\omega = \int[\alpha^A(\omega)/\omega]\,d\omega\,(1 + a\rho), \qquad (1)$$

where $\alpha(\omega)$ is the absorption coefficient at frequency ω,[15] $\alpha^A(\omega)$ is the absorption coefficient without inclusion of interference, and ρ is the density. The interference may be positive or negative and is characterized by the parameter a which is essentially twice the ratio of induced to

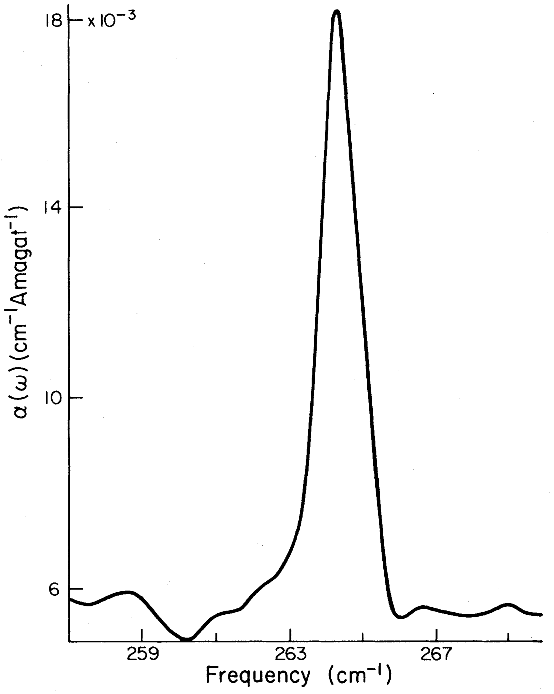

FIG. 1. The profile of the $R(2)$ line at 31.6 amagats.

allowed moments. For two interacting molecules,

$$a=[8\pi N_0\int_0^\infty g(R)p_{vJ,v'J'}{}^I(R)R^2dR]/p_{vJ,v'J'}, \qquad (2)$$

where $p_{vJ,v'J'}$ is the dipole moment between vibration-rotation states (vJ) and $(v'J')$, $g(R)$ is the pair distribution function, R is the intermolecular distance, and N_0 is the number density at STP. The resulting rotational line shape should be of the Fano type,[16] consisting of a density-dependent superposition of a Lorentzian and an anomalous dispersion profile.

Both p^A and p^I must satisfy the same selection rules if interference is to occur. The allowed spectrum follows the usual rule $\Delta J=\pm 1$ for the total angular momentum quantum number of one of the molecules. For homonuclear diatomic molecules, p^I has been shown[11] to yield $\Delta J=0,\pm 2$. For HD, however, since the centers of mass and charge are not coincident, a component appears in p^I which can interfere with the allowed dipole, even if anisotropic intermolecular interactions are not taken in account.

This intracollisional interference effect has been identified in the fundamental spectrum of HD and caused values of $p_{0J,1J'}{}^A$ to be raised by 2% compared with estimates made ignoring it.[13] In the present study, the pure rotational spectrum of HD was measured over a wide density range to determine whether the effects of intracollisional interference can reconcile the discrepancy between theory and experiment for the ground-state moment $p_{0J,0J'}{}^A$.

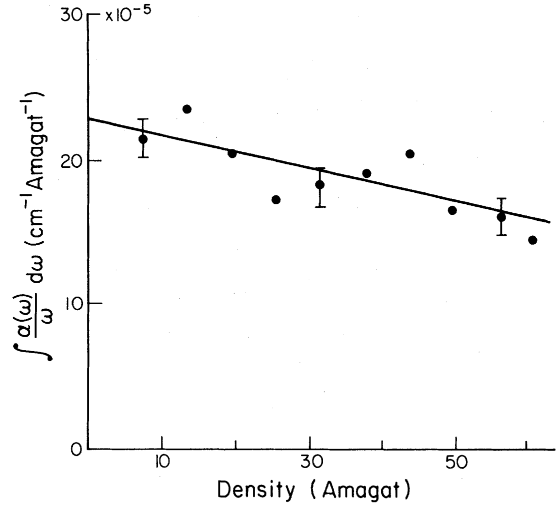

FIG. 2. The integrated intensity of the $R(2)$ line as a function of density.

Absorption spectra were taken in the range 80 to 450 cm^{-1} with a modified Nicolet scanning Michelson interferometer at spectral resolution of 1 cm^{-1}. The 98% isotopically pure HD was dried and contained in a 1-m absorption cell. Experiments were performed at 295 K at ten pressures in the range 7 to 60 atm. The $R(1)$, $R(2)$, and $R(3)$ rotational lines at 178, 265, and 351 cm^{-1} were analyzed; $R(0)$ and $R(4)$ could not be detected with sufficient precision for reliable analysis. The lines appeared as sharp features on a broad collision-induced background, which had to be removed before their integrated intensities could be determined. To accomplish this subtraction, the broad background was estimated by a smooth curve over a range of ± 25 cm^{-1} about a given $R(J)$ line. The specification of the background level was the largest single source of error (3%–10%) in the determination of the integrated intensities. Only the $R(2)$ line, in the midrange of densities, had a pronounced Fano profile (Fig. 1); otherwise the profiles appeared quite symmetric.

The integrated intensities $\int[\alpha(\omega)/\omega]d\omega$ were plotted versus density (Fig. 2). In all cases, they decreased with increasing density, consistent with a negative interference effect. A straight line, predicted by (1), was fitted to the data and the intercept at zero density, $\int[\alpha^A(\omega)/\omega]d\omega$, found. It was related to the dipole moment of the

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

	Experimental			Theoretical	
	Present	Trefler and Gush (Ref. 4)	Apparent moment[a]	Wolniewicz (Ref. 9)	Ford and Browne (Ref. 10)
$R(0)$	⋯	5.42	⋯	8.36	8.31
$R(1)$	9.36 ± 0.3	5.52	5.4 ± 0.5	8.38	8.30
$R(2)$	8.00 ± 0.2	6.18	6.3 ± 0.6	8.39	3.28
$R(3)$	9.79 ± 0.3	6.41	7.0 ± 0.5	8.41	3.26

[a] Apparent dipole moment at 70 amagats and 295 K determined through Eqs. (1) and (3).

isolated molecule by[4,13,14]

$$\int \alpha^{A}(\omega)\,d\omega = (8\pi^3\omega_0 N_0/3hcZ)[\exp(-E_1/kT) - \exp(-E_2/kT)](J+1)(p_{0J,0J}{}'^{A})^2, \tag{3}$$

where ω_0 is the central frequency of the line, Z is the state sum, E_1 and E_2 are the energies of the lower and upper states in the transition, and J is the angular momentum quantum number of the lower state.

The values of $p_{0J,0J}{}'^{A}$ obtained from this analysis are larger than the earlier results and much closer to *ab initio* calculations (Table I). The errors quoted represent the standard deviations obtained from the weighted least-squares fits. A source of systematic error was the presence of weak water lines in the wings of $R(1)$ and $R(3)$; although $R(2)$ was clear of water lines, there was the difficulty of integrating over its Fano profile. Such systematic errors cannot suffice to explain the apparent J dependence of $p_{0J,0J}{}'^{A}$ absent in the *ab initio* values. Compared with the *ab initio* results, $R(1)$ and $R(3)$ are 10%–13% high and $R(2)$ is 3% low. These magnitudes are typical of the agreement found in the case of the transition dipoles involved in the fundamental and overtone vibrational bands.[9,10]

For the interference parameters a, we obtained (in units of inverse amagat) $R(1)$, $(-9.6 \pm 0.5)\times 10^{-3}$; $R(2)$, $(-5.5 \pm 1.3)\times 10^{-3}$; and $R(3)$, $(-6.9 \pm 1.2)\times 10^{-3}$. If the sign of the calculated moment $p_{0J,0J}{}'^{A}$ is defined as positive[9] and since a is found to be negative, then, from Eq. (2), $p_{0J,0J}{}'^{I}$ is negative. Tipping, Poll, and McKellar[13] estimated $|a|$ from (2) to be 5.4×10^{-3} amagat^{-1} using the value[8] of 8.4×10^{-4} D for $|p_{0J,0J}{}'^{A}|$. Their calculation neglects mixing of rotational levels by anisotropic intermolecular forces which is important mainly at low J. Thus, the reasonable agreement for $R(2)$ and $R(3)$ and pronounced disagreement for $R(1)$ could be expected.

Trefler and Gush[4] made their observations at 77 and 295 K at elevated densities in the range 55–135 amagats and their final values of $p_{0J,0J}{}'^{A}$ (Table I) represent an average over all experiments. Their 295-K data were obtained at a mean density of about 70 amagats. The results of the present study may be used to obtain a value of the apparent dipole moment at this density, that is, to find the value which would be deduced from experiment, if the density-dependent interference is ignored. The extrapolation is performed with Eqs. (1) and (3) with our values of $p_{0J,0J}{}'^{A}$ and a (at 295 K); the results are given in Table I. The close agreement between the results of Trefler and Gush and the extrapolations shows that the anomalously low values obtained by those authors arise largely, if not exclusively, from their failure to account for the destructive interference effect.

The long-standing discrepancy between experiment and calculation for a fundamental property of a simple molecule, HD, has been resolved. The slight J dependence of the moment indicated by the experiment is, however, not confirmed by the calculations. Intracollisional interference has been identified in the pure rotational spectrum and for the first time its J dependence has been measured.

We wish to thank Professor J. D. Poll of the University of Guelph, who brought this problem to our attention, for continuing counsel and interest. Gratitude is expressed to Dr. M. S. Mathur for his invaluable advice on far-infrared spectroscopy and to Professor F. M. Kelly for discussion on the properties of HD.

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Statistical Properties of Light from a Dye Laser

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Recent experimental results of Kaminishi *et al.* on the photon statistics of a dye laser are compared with the exact solution of a laser model with fluctuating pump parameter.

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One of the great successes of quantum optics was the theoretical derivation of the statistical properties of laser light and the subsequent detailed experimental confirmation. The laser was thereby established as a source of light with statistical properties fundamentally different from all thermal light sources.

The well-known theoretical model which was successful in explaining all details of the photon statistics of a single-mode laser near threshold is the simple Van der Pol oscillator in rotating wave approximation[1]:

$$\dot{\beta} = [(a_1 + ia_2) - (A_1 + iA_2)|\beta|^2]\beta + \xi(t). \tag{1}$$

Here $\beta(t)$ is the complex amplitude of the laser mode, a_1, a_2, A_1, and A_2 are real parameters, a_2 and A_2 are different from zero only for nonzero detuning, a_1 is the pump parameter and positive (negative) above (below) threshold, and $A_1 > 0$ provides for stabilization above threshold due to saturation. $\xi(t)$ in Eq. (1) is a Gaussian white-noise source with the properties $\langle\xi(t)\rangle = 0$, $\langle\xi(t)\times\xi(0)\rangle = 0$, $\langle\xi^*(t)\xi(0)\rangle = Q\delta(t)$, which turns Eq. (1) into a stochastic differential equation. Henceforth, we always use the Stratonovich calculus of such equations.

Equation (1) should apply to any single-mode laser, and is in this sense universal, provided that the laser is sufficiently close to its threshold, where corrections due to higher-order nonlinearities or to time derivatives and deviations of $\xi(t)$ from white noise become irrelevant. In particular, the form of Eq. (1) is independent of any microscopic details of the laser process, and already follows from general symmetry principles of the theory of continuous instabilities.[2]

Recently, Kaminishi *et al.*[3] reported very interesting experimental results on the photon statistics of a dye laser near threshold. Their results differ completely from what one would expect on the basis of model (1). For instance, in Ref. 3 it was found that the relative mean square of the intensity fluctuations $\langle\Delta I^2\rangle/\langle I\rangle^2$ increases up to values of ~ 1000 for sufficiently small average photon number $\langle n\rangle$, whereas model (1) predicts an upper bound $\langle\Delta I^2\rangle/\langle I\rangle^2 \leq 1$. The model which adequately describes a dye laser near threshold must therefore differ from Eq. (1) by terms which do not become irrelevant, even very close to the laser threshold.

In the present Letter we propose such a model, which turns out to be exactly solvable, and compare its predictions with the available experimental data. The good agreement which we find supports the idea that the dye-laser threshold belongs to the new class of continuous instabilities with fluctuating control parameter which is described, again in a universal way, by our model.