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ELECTRIC DIPOLE MOMENT OF HD

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The electric dipole moment of HD in its ground vibrational and electronic state has been obtained from the intensity of the pure rotational spectrum. Its value is $(5.85 \pm 0.17) \times 10^{-4}$ D.

A free molecule of HD is known to possess a weak, vibrating electric dipole moment in the ground electronic state because it exhibits a rotation-vibration spectrum which obeys the selection rule $\Delta J = \pm 1$.¹ This may be explained as follows¹: The center of positive charge oscillates along the axis of the molecule during a molecular vibration because the excursions of the proton are greater than those of the deuteron; since the electrons do not follow exactly the motion of the positive charge, a weak, vibrating dipole moment results. A permanent dipole moment μ_0 may be expected as a result of this mechanism when anharmonicity of the nuclear vibrations is taken into account, and two calculations of μ_0 have appeared in the literature. Blinder,² using second-order perturbation theory and relatively simple wave functions, obtained the value $\mu_0 = 5.67 \times 10^{-4}$ D, and Kołos and Wolniewicz,³ using the complete four-particle Hamiltonian, found $\mu_0 = 1.54 \times 10^{-3}$ D. Up to the present, however, there has been no experimental value with which to compare these results.

We have recently investigated the far-infra-

red spectrum of compressed HD, as part of a general study of pressure-induced translational-rotational absorption spectra of gases.⁴ The absorption coefficient⁵ of HD is plotted over a wide frequency range in Fig. 1, and a detail of one of the sharp features of the spectrum is shown in Fig. 2. The most prominent

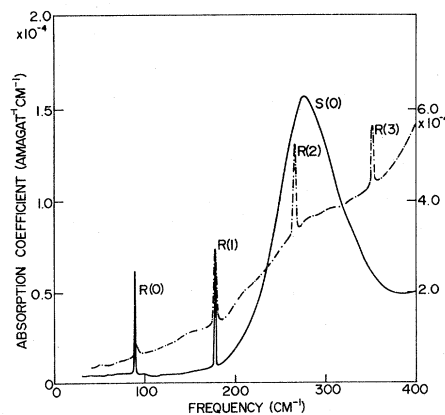


FIG. 1. The rotational spectrum of gaseous HD at 295°K and a density of 57 amagat (dot-dashed line), and at 77.3°K and density of 100 amagat (solid line; use right-hand scale).

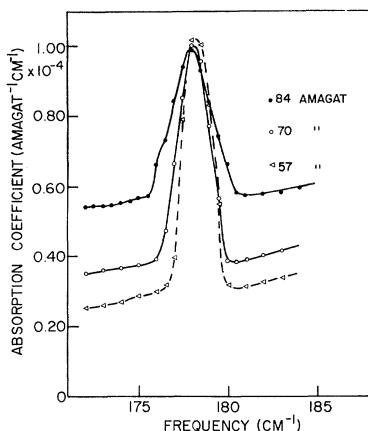


FIG. 2. The line $R(1)$ at 295°K at three different densities.

feature of the spectrum in Fig. 1 is a quasicontinuum, expected on the basis of results in hydrogen,⁴ which is identified as the collision-induced rotational spectrum obeying the selection rule $\Delta J=2$. This part of the spectrum, denoted by $S(J)$, arises from transient electric dipole moments induced in pairs of closely colliding molecules and is not of interest here. The remaining features, indicated by $R(J)$, may be identified on the basis of frequency as pure rotational transitions in single molecules according to the selection rule $\Delta J=1$. Supporting evidence for this identification is supplied by the fact that the width of the lines is comparatively small, implying that they arise from a permanent dipole moment. The finite width of the lines, which increases with the density, as is evident from Fig. 2, and which decreases with temperature, as is evident from Fig. 1, may be ascribed to normal pressure broadening. As may be seen from Table I, there is a small difference, which increases with J value, between the observed frequency σ_0 and the frequency σ_R obtained from the Raman effect of the low-pressure gas⁶; this difference, which is presumably a pressure shift, is independent of the density over the range studied.

A significant consequence of the identification of these features as the pure rotational spectrum is that from their intensity may be deduced an experimental value for the permanent electric dipole moment of HD. The integrated absorption coefficient of each R line was obtained from graphs similar to those of Fig. 2 in which the quasicontinuum was extended smoothly underneath the sharp feature; the

Table I. Rotational lines of HD.

Line	σ_0	σ_R	n	Area $\times 10^4$	$\mu_0 \times 10^4$
$R(0)$	89.36	89.23	3	1.53	5.42
$R(1)$	178.21	177.84	7	0.96	5.52
$R(2)$	265.64	265.19	4	1.37	6.18
$R(3)$	351.42	350.72	4	0.78	6.41

continuum was then subtracted from the observed profile and the area of the remaining sharp peak was evaluated. These areas were independent of the density within experimental error; this is consistent with the interpretation of the R lines as arising from transitions in single molecules. The results of a number n of experiments were consequently averaged and appear in Table I. The magnitude of the electric dipole moment may now be calculated from the theoretical formula written below. The integrated absorption coefficient of a gas of rigid rotators making transitions from the state $|J\rangle$ to the state $|J+1\rangle$ equals

$$\int_{\text{line}} A(\sigma) d\sigma = \frac{8\pi^3 \sigma_0 N_0 (e^{-E_1/kT} - e^{-E_2/kT}) (J+1) \mu_0^2}{3hcQ},$$

where σ_0 is the central frequency of the line, N_0 is Loschmidt's number, Q is the state sum, E_1 is the energy of the lower state, and E_2 is the energy of the upper state. For each experiment a value of μ_0 was obtained from the intensity of a given R line; the experimental values were subsequently averaged giving the results shown in Table I. The dipole moment appears to depend on J value, but the rather large scatter in the areas of the R lines from experiment to experiment makes it difficult to assert this conclusively. We have consequently averaged all our determinations of μ_0 to yield $\bar{\mu}_0 = (5.85 \pm 0.17) \times 10^{-4}$ D. The quoted error is the rms deviation of all our observations (18 in number) from the mean.

The mean dipole moment is very close to the result of Blinder,² but is only about one-third of the result of the more elaborate, and presumably more precise, calculation of Kołos and Wolniewicz.³ It should be noted, however, that the theoretical calculations are carried out in a reference frame attached to the nuclei and apply to the case $J=0$ only.⁷ The large discrepancy between the measured dipole

moment and the dipole moment calculated in the frame of the molecule implies that the latter is strongly dependent on J value. This being the case, it is clear that a comparison between theory and experiment can be made only if the matrix elements of the dipole moment operator between states of different J in the laboratory frame are calculated.

It would seem relevant to point out here the importance to astronomy of the fact that HD has a comparatively strong rotational spectrum. This permits, in principle, the detection of small amounts of HD, present, for example, in hydrogen clouds. This is in contrast to hydrogen itself, which exhibits only the very weak quadrupole spectrum in the infrared, and is hence difficult to detect. It would consequently be reasonable to include in a program of far-infrared astronomy a search for the $R(0)$ and $R(1)$ lines of HD. Such a program would naturally have to be carried out at high altitude to avoid absorption by water vapor in the lower atmosphere.

¹R. A. Durie and G. Herzberg, *Can. J. Phys.* **38**, 806 (1960).

²S. M. Blinder, *J. Chem. Phys.* **32**, 105, 582 (1960).

³K. Kołos and L. Wolniewicz, *J. Chem. Phys.* **45**, 944 (1966).

⁴D. R. Bosomworth and H. P. Gush, *Can. J. Phys.* **43**, 751 (1965).

⁵The absorption coefficient $A(\sigma)$ was calculated using the equation $A(\sigma) = (l\rho/\rho_0)^{-1} \ln_e [I_0(\sigma)/I(\sigma)]$. $I_0(\sigma)$ is the intensity of radiation transmitted by the evacuated absorption cell, $I(\sigma)$ is the transmitted intensity with gas in the cell, and l is the path length. The gas density in the cell is denoted by ρ , and ρ_0 is the gas density at normal pressure and temperature; their ratio (ρ/ρ_0) is called the gas density in amagat. In these experiments (ρ/ρ_0) was in the range 55 to 135 and the path length was 1 m. The intensities were obtained as a function of the frequency by a numerical Fourier analysis of interferograms produced by a two-beam interferometer [D. R. Bosomworth and H. P. Gush, *Can. J. Phys.* **43**, 729 (1965)]. The limit of resolution was about 0.4 cm^{-1} .

⁶B. Stoicheff, *Can. J. Phys.* **35**, 730 (1957).

⁷This was pointed out to us by Professor Wolniewicz.

NEGATIVE-MUON DEPOLARIZATION IN LOW-Z ELEMENTS AND HYDROGEN COMPOUNDS*

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A polarized negative muon is known to depolarize strongly in the process of forming a muonic atom in the ground state. Several calculations¹⁻³ have been made in which this effect is treated as the net result of successive spin-orbit interactions encountered in the muonic cascade. Barring further magnetic mechanisms in the muonic ground state,⁴ the muon's polarization at time of decay is predicted to be $P \approx \frac{1}{6}$ that of its precascade magnitude. Precession measurements of μ - e decay asymmetry involving spin $I=0$ elements have, in general, confirmed this value, the chief exception occurring in helium. Agreement with theory has been reported for C, H₂O, Mg, Si, S, Zn, Cd, and Pb, as well as the hydrocarbons of paraffin and polyethylene, and the hydrides of Mg and Pd.⁵⁻⁸

In this Letter we report μ - e asymmetry results for the elements C and Mg, and the following hydrogenous materials: H₂O, C₇H₈ (toluene and polyvinyltoluene), and CH₂ (paraffin and polyethylene). In contrast to the metals, measurements in each of the insulators dem-

onstrated about one-half the free μ^- precession signal anticipated on the basis of the spin-orbit process alone. We feel that this effect, which was not observed in previous experiments for water, paraffin, and polyethylene,^{5,7} might give evidence of an additional depolarization mechanism in certain insulators. Systematic effects in our experimental method were analyzed, but none was capable of resolving this disagreement.

Other insulators studied by us were (i) liquid O₂ which totally depolarized the negative muon, as one might expect of a strong paramagnetic medium, and (ii) liquid He which, lacking such an apparent mechanism, nevertheless, caused similar polarization loss as previously observed.^{9,10} A second phase to the experiment involved an attempt in helium and a few of the hydrocarbons to obtain direct precessional evidence for the muon-unpaired-electron spin-spin coupling of Ref. 4.

The precession of longitudinally polarized muons in a transverse magnetic field leads to the following modification in the time dependence