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## Electric Dipole Moments of Several Molecules from the Stark Effect\*

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The following molecular electric dipole moments, in Debye units, have been obtained from the Stark effect of pure rotational spectra observed in the microwave region:  $0.234 \pm 0.004$  for  $\text{NF}_3$ ;  $1.03 \pm 0.01$  for  $\text{PF}_3$ ;  $1.77 \pm 0.02$  for  $\text{POF}_3$ ;  $3.00 \pm 0.02$  for  $\text{HCN}$ ;  $3.92 \pm 0.06$  for  $\text{CH}_3\text{CN}$ ;  $3.83 \pm 0.06$  for  $\text{CH}_3\text{NC}$ ;  $1.79 \pm 0.02$  for  $\text{CH}_3\text{F}$ ;  $0.75 \pm 0.01$  for  $\text{CH}_3\text{CCH}$ ;  $1.26 \pm 0.01$  for  $\text{SiF}_3\text{H}$ . All values apply to the ground vibrational state.

THE Stark effect in microwave rotational spectra is now a well-known method for measurement of molecular dipole moments. Unlike that of other gaseous methods the accuracy obtainable is not affected by impurities in the sample. The limiting factor upon the accuracy is either the precision with which the electrode spacing can be maintained and measured, or the accuracy with which the Stark splitting of the lines can be measured. If the molecule exhibits a first-order Stark effect, as do symmetric-top molecules when  $K \neq 0$ , a relatively large Stark splitting can be obtained with moderate field strengths. The electrode spacing then becomes the limiting factor in the accuracy. If a second-order Stark effect must be employed, as is always the case with linear molecules in the ground vibrational state, and if in addition the dipole moment is small, as it is in  $\text{N}_2\text{O}$  and  $\text{CO}$ , it is not possible to produce a wide splitting with a reasonable voltage, and the line separation becomes the limiting factor on the accuracy. Frequently dipole moment determinations are complicated by nuclear quadrupole hyperfine structure.

In the present work the dipole moments of nine molecules have been evaluated from the Stark splitting of their rotational lines. Six of these have been previ-

ously measured, either with the Stark effect or with other methods.

### EXPERIMENTAL METHOD

Our measurements were made with a *K*-band waveguide Stark cell with a plane electrode supported across the center of the guide by Teflon<sup>1</sup> so that the conducting surfaces were perpendicular to the  $\mathcal{E}$ -lines of the microwave radiation.

A 100-kc square wave modulation method was used for all measurements except that for  $\text{HCN}$ . For the  $\text{HCN}$  line, 4-kc square wave modulation was employed. All line splittings were measured by standard frequency markers in the usual manner.

The electrode spacing as well as the over-all spectrometer was calibrated with  $\text{OCS}$ . Because  $\text{OCS}$  has a moderately large dipole moment, a rotational spectrum which is devoid of fine or hyperfine structure, and low *J* lines which fall in the centimeter wave region, this molecule provides a convenient standard for calibration. The dipole moment of  $\text{OCS}$  has been carefully measured by several workers.<sup>2</sup> The value obtained by Shulman and Townes<sup>2c</sup> is  $0.7085 \pm 0.004$  debye units. Since this is an accuracy equal to or greater than that to which the electrode spacing in our cell could be directly measured, we have used  $\text{OCS}$  to calibrate the spectrometer for each measurement.

### RESULTS

For all symmetric-top molecules investigated we have used only rotational lines with  $K=0$ . The  $K=0$  lines of symmetric-top molecules have only a second-order Stark effect, which makes them similar in the present measurements to linear molecules.

In  $\text{CH}_3\text{NC}$  the nuclear quadrupole coupling is too small to produce an observable hyperfine structure, and hence it can be ignored in the present considerations. In  $\text{HCN}$  and  $\text{CH}_3\text{CN}$  the  $\text{N}^{14}$  coupling  $eqQ$  is of the order of 4 Mc and produces an observable splitting of the line. Nevertheless, the large dipole moments of these molecules make it easy to impose a field of sufficient

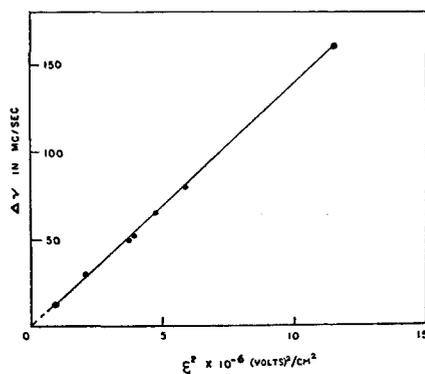


FIG. 1. Line displacement *versus* Stark field squared for  $\text{HCN}$ ,  $J=0 \rightarrow 1$ ,  $\Delta M_J=0$ ,  $M_I=1$ .

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<sup>1</sup> McAfee, Hughes, and Wilson, *Rev. Sci. Instr.* **20**, 821 (1949).

<sup>2</sup> (a) Dakin, Good, and Coles, *Phys. Rev.* **71**, 640 (1947);

(b) Strandberg, Wentink, and Kyhl, *Phys. Rev.* **75**, 270 (1949);

(c) R. G. Shulman and C. H. Townes, *Phys. Rev.* **77**, 500 (1950);

(d) J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.* **82**, 95 (1951).

TABLE I. Transitions and  $B$  values used.

Molecule	Transition employed	$\nu$ (Mc/sec)	$B_0$ (Mc/sec)	Reference
NF <sub>3</sub>	$J=0 \rightarrow 1$	21 361.92	10 680.96	a
PF <sub>3</sub>	$J=1 \rightarrow 2$	31 279.60	7 819.90	b
POF <sub>3</sub>	$J=1 \rightarrow 2$	18 377.0	4 594.25	c
HCN	$J=0 \rightarrow 1$	88 631.94	44 315.97	d
CH <sub>3</sub> CN	$J=1 \rightarrow 2$	36 793.64	9 198.83	e
CH <sub>2</sub> NC	$J=0 \rightarrow 1$	20 105.80	10 052.90	e
CH <sub>3</sub> F	$J=0 \rightarrow 1$	51 071.69	24 862.37	f
CH <sub>3</sub> CCH	$J=1 \rightarrow 2$	34 183.37	8 545.84	g
SiF <sub>4</sub> H	$J=1 \rightarrow 2$	28 831.90	7 207.98	h

a J. Sheridan and W. Gordy, Phys. Rev. 79, 513 (1950).  
 b Gilliam, Edwards, and Gordy, Phys. Rev. 75, 1014 (1949).  
 c Williams, Sheridan, and Gordy, J. Chem. Phys. 20, 164 (1952).  
 d Simmons, Anderson, and Gordy, Phys. Rev. 77, 77 (1950); 86, 1055 (1952).  
 e Kessler, Ring, Trambarulo, and Gordy, Phys. Rev. 79, 54 (1950).  
 f Gilliam, Edwards, and Gordy, Phys. Rev. 75, 1014 (1949).  
 g R. Trambarulo and W. Gordy, J. Chem. Phys. 18, 1613 (1950).  
 h See reference 4.

magnitude to break down the nuclear coupling and to produce the simple strong-field case.

The usual second-order formulas,

$$E_{JM_J}^{(2)} = -\frac{\mu^2 \mathcal{E}^2}{2hB} \frac{[3MJ^2 - J(J+1)]}{J(J+1)(2J-1)(2J+1)} \quad (1)$$

$$E_{00}^{(2)} = -\frac{\mu^2 \mathcal{E}^2}{6hB}$$

for linear molecules (or the symmetric-top formula with  $K=0$ ) without nuclear coupling apply to the strong field case, but a small correction given by

$$E_Q^{(1)} = -eqQ \left\{ \frac{[3MJ^2 - J(J+1)][3MI^2 - I(I+1)]}{4I(2I-1)(2J-1)(2J+3)} \right\} \quad (2)$$

must be added<sup>3</sup> to the energies to correct for the nuclear perturbations. In our experiments with the electrode placed so that the Stark field  $\mathcal{E}$  was parallel to the electric vector of the microwave radiation, only the  $M \rightarrow M$  transitions are allowed.

The strong-field displacement observed for the  $J=0 \rightarrow 1, M_J=0$  line is then

$$\Delta\nu_{M_J=0}^{(J=0 \rightarrow 1)} = \frac{4}{15} \frac{\mu^2 \mathcal{E}^2}{h^2 B} + \text{term independent of } \mathcal{E}. \quad (3)$$

It is readily seen that  $\Delta\nu$  plotted as a function of  $\mathcal{E}^2$  is a straight line in the strong field region with slope  $S$ :

$$S_{M_J=0}^{(J=0 \rightarrow 1)} = \frac{d(\Delta\nu)}{d(\mathcal{E}^2)} = \frac{4}{15} \frac{\mu^2}{h^2 B}. \quad (4)$$

The nuclear effects do not influence the slope in the strong-field region but only the projected intercepts. The dipole moment can then be found readily if the line displacements are plotted against  $\mathcal{E}^2$  (or  $V^2$  since the electrode spacing is held constant) for both the standard

<sup>3</sup> U. Fano, J. Research Natl. Bur. Standards 40, 215 (1948).

OCS molecule and the molecule  $X$  being investigated, and if the ratios of the two slopes are then taken.

For the  $J=1 \rightarrow 2$  transition of linear molecules (or of symmetric tops with  $K=0$ ) there are two  $\Delta M_J=0$  Stark components corresponding to  $M_J=0$  and  $M_J=1$ . The strong-field  $\Delta\nu$  versus  $\mathcal{E}^2$  plots of these have slopes,

$$S_{M_J=0}^{(J=1 \rightarrow 2)} = \frac{d(\Delta\nu)}{d(\mathcal{E}^2)} = -\frac{8}{105} \frac{\mu^2}{h^2 B}, \quad (5)$$

and

$$S_{M_J=1}^{(J=1 \rightarrow 2)} = \frac{d(\Delta\nu)}{d(\mathcal{E}^2)} = \frac{13}{210} \frac{\mu^2}{h^2 B}. \quad (6)$$

It was found most convenient to employ the  $J=1 \rightarrow 2$  transition of OCS for all calibrations. However, the  $J=0 \rightarrow 1$  transition was used for some of the molecules under investigation. For the  $J=0 \rightarrow 1, K=0, \Delta M=0$ , transition of the molecule  $X$  (symmetric top or linear) used with the  $J=1 \rightarrow 2, M_J=0$ , line of OCS, Eqs. (4) and (5) are combined to give the unknown moment,

$$\mu_X = \mu_{\text{OCS}} \left( \frac{2}{7} \frac{B_X}{B_{\text{OCS}}} \frac{|S_X|}{|S_{\text{OCS}}|} \right)^{\frac{1}{2}} \begin{cases} J=0 \rightarrow 1 \text{ for } X \\ J=1 \rightarrow 2, M_J=0 \text{ for OCS.} \end{cases} \quad (7)$$

When the same rotational transition with the same second-order Stark component is measured for both the unknown molecule  $X$  and for OCS, the formula for the unknown moment in terms of the measured parameters becomes

$$\mu_{\text{OCS}} \left( \frac{B_X}{B_{\text{OCS}}} \frac{|S_X|}{|S_{\text{OCS}}|} \right)^{\frac{1}{2}} \begin{cases} J=1 \rightarrow 2 \text{ and same second-} \\ \text{order Stark component} \\ \text{for } X \text{ and OCS.} \end{cases} \quad (8)$$

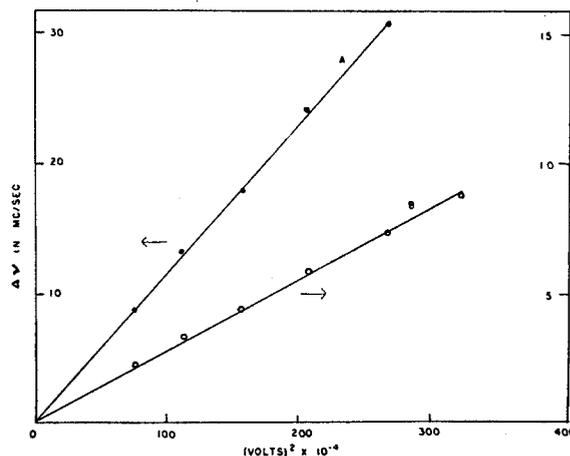


FIG. 2. Line displacement versus Stark voltage squared:  
 A. OCS,  $J=1 \rightarrow 2, M_J=0 \rightarrow 0$   
 B. NI<sup>2</sup>F<sub>4</sub>,  $J=0 \rightarrow 1, M_J=0 \rightarrow 0$ .

TABLE II. Electric dipole moments.

Molecule	Moment in debye units	
	Present study	Previous value and method
NF <sub>3</sub>	0.234±0.004	0.21–0.25 (Dielectric const) <sup>a</sup>
PF <sub>3</sub>	1.03 ±0.01	1.03±0.01 (Stark) <sup>b</sup>
POF <sub>3</sub>	1.77 ±0.02	1.74±0.04 (Stark) <sup>c</sup>
HCN	3.00 ±0.02	2.957 (Stark) <sup>d</sup>
	(Ground vib. state)	(Excited bending vib. state)
CH <sub>3</sub> CN	3.92 ±0.06	3.97 (Stark) <sup>e</sup>
CH <sub>3</sub> NC	3.83 ±0.06	
	(Ground vib. state)	
	3.78 ±0.06	
	(Excited bending vib. state)	
CH <sub>3</sub> F	1.79 ±0.02	1.81–1.84 (Dielectric const) <sup>f</sup>
CH <sub>3</sub> CCH	0.75 ±0.01	
SiF <sub>3</sub> H	1.26 ±0.01	

<sup>a</sup> K. L. Ramaswamy, Proc. Indian Acad. Sci. **2A**, 364 (1934).

<sup>b</sup> Shulman, Dailey, and Townes, Phys. Rev. **78**, 145 (1950).

<sup>c</sup> S. J. Senatore, Phys. Rev. **78**, 293 (1950).

<sup>d</sup> R. G. Shulman and C. H. Townes, Phys. Rev. **77**, 421 (1950).

<sup>e</sup> Coles, Good, and Hughes, Phys. Rev. **79**, 224 (1950).

<sup>f</sup> C. P. Smyth and K. B. Alpine, J. Chem. Phys. **2**, 449 (1934); R. L. Ramaswamy, Proc. Indian Acad. Sci. **4A**, 108 (1936).

The  $B_0$  values for all the molecules included in the present study have been previously measured by means of microwave spectroscopy. The values used, with the references, are listed in Table I.

Although the Stark effect of HCN in an excited bending vibrational state has been measured earlier, that of the normal or ground vibrational state has not. For HCN we have used the OCS data to calibrate the electrode separation and have plotted in Fig. 1 the Stark displacement against the square of the field, in volts<sup>2</sup>/cm<sup>2</sup>. For other molecules, the splitting is plotted simply as a function of the voltage squared along with a similar plot of the OCS data. Figure 2 shows the plot for N<sup>15</sup>F<sub>3</sub>. Plots for the other molecules are similar and are not given. A few moments, namely, those for POF<sub>3</sub>, PF<sub>3</sub>, and CH<sub>3</sub>CN already measured with the Stark method in other laboratories, were remeasured as a check. In all instances the agreement with the previous values was within the estimated experimental error. Because of the exceptionally small dipole moment of NF<sub>3</sub> it did not prove easy to obtain the necessary field strength to breakdown completely the N<sup>14</sup> nuclear quadrupole coupling even though the coupling con-

stant,  $eqQ$ , is only  $-7.07$  Mc/sec.<sup>4</sup> Rather than solve the complex intermediate case we chose the easier course of measuring the splitting for N<sup>15</sup>F<sub>3</sub>, which has no nuclear hyperfine structure.

The electric dipole moments obtained for the different molecules in the present study are listed in Table II with earlier values from the literature. The moment of CH<sub>3</sub>CN was measured for both the ground state and the lowest excited bending vibrational state. The moment was found to be less for the bending state by about 1.5 percent than for the ground state. Although the combined absolute errors are greater than this amount, the possible error in the relative value is slightly less. Hence, the difference appears to be significant. Also the value obtained for the HCN ground vibrational state is correspondingly larger than that of the first excited bending mode.

The interpretation of molecular dipole moment in terms of the electronic structures of the molecules is a formidable task on which but little progress has been made, even for simple diatomic molecules. It is to be hoped that the dependable moment-values now being obtained from the microwave Stark effect in many different laboratories will stimulate new theoretical efforts to understand them. The very small dipole moment of NF<sub>3</sub> provides strong evidence for the importance of the atomic hybridization moments predicted quantum mechanically by Coulson.<sup>5</sup> Both the N<sup>14</sup> nuclear coupling and the bond angles<sup>4</sup> in this molecule suggest a large amount, about 17 percent of *s*-hybridization of the bonding orbitals of N. The two electrons in the nonbonding orbital (which has complementary hybridization of about 50 percent *p* character) produce a large N atomic moment which is opposed to, and almost cancels, the primary moment expected from the high ionic character of the NF bonds.

We wish to thank Dr. John Sheridan who prepared some of the chemicals used, Mr. W. C. King who helped with the measurements on HCN, and Dr. M. Mizushima for helpful discussion of theory.

<sup>4</sup> J. Sheridan and W. Gordy, Phys. Rev. **77**, 719 (1950).

<sup>5</sup> C. A. Coulson, Trans. Faraday Soc. **38**, 433 (1942).