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Molecular Dipole Moments and Stark Effects. III. Dipole Moment Determinations*

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Dipole moments of eight molecules were determined by the Stark splittings of the rotational transitions in the microwave region. The molecules and their moments in Debye units are: AsF_3, 2.815±0.025; CH_3I, 1.647±0.014; CH_3Cl, 1.869±0.010; CH_3Br, 1.797±0.015; CH_3CF_3, 2.321±0.034; PF_3, 1.025±0.009; N_2O, 0.166±0.002; and ClCN, 2.802±0.020. In all cases Stark effects followed very closely theoretical expectations.

INTRODUCTION

The determination of molecular electric dipole moments from a study, in the microwave region, of the splitting of rotational energy levels by an electric field has a number of advantages over older methods. First of all, the moment is determined for a certain vibrational and rotational state and is not the average over all states as found by the previous methods. The variation of charge distribution and molecular shape with vibrational and centrifugal distortion may therefore be studied. The chemical purity of the sample is no longer an important requirement. Actually, since the sample is examined as a dilute gas and the rotational transition of different substances are quite easily resolved, "impurities" may be more abundant than the sample and the molecule of interest may be decomposing at a fairly rapid rate without seriously inconveniencing the microwave measurements. Microwave measurements are made at a gas pressure of approximately 0.01 mm of Hg and many substances may be studied in the vapor state which by other methods would have to be examined in solution, with the consequent complication of solvent effects. The microwave method has especial advantages for molecules having small dipole moments, since in these cases the fractional accuracy remains the same, i.e., one percent or less. As is well known, when the dipole moment is measured from the temperature dependence of the dielectric constant, large uncertainties arise when small dipole moments are measured. In this investigation the dipole moments of eight different molecules were determined by the Stark splitting of their rotational transitions observed in the microwave region. This splitting is a function of the applied field and the permanent electric moment of the molecule. The molecules considered can be divided in two groups, those without and those with hyperfine structure caused by nuclear quadrupole interaction. The former and simpler cases were the molecules CH_3CF_3, PF_3 and in the approximation used also $N^{15}N^{14}O^{16}$ and $Cl^{36}C^{12}N^{14}$. The molecules with appreciable quadrupole coupling were CH_3Cl, CH_3Br, CH_3I and AsF_3.

EXPERIMENTAL METHOD

The detailed experimental method was described in Part II of this series.[1] In that paper the dipole moment of the linear molecule OCS was determined by measuring the splitting as a function of applied voltage in three different wave guides whose internal dimensions had been measured. The average value of the OCS dipole was used to calibrate the spacings and corrections in all three guides. From this calibration the corrected values of dipole moments quoted below are derived. Thus the dipole moments reported here are all measured relative to the OCS dipole moment (assumed to be 0.7085±0.004) rather than being dependent on any particular measurements of wave guide dimensions. This procedure should allow good comparison with results of other workers if they are standardized in a similar way.

MOLECULES WITH QUADRUPOLE COUPLING

The CH_3Cl^{35} and CH_3Br^{79} transitions observed were $J=0\rightarrow 1$ and $K=0\rightarrow 0$. These lines exhibit only second-order Stark effects and since the nuclear spins of Cl^{35} and Br^{79} are 3/2, the theoretical treatments are similar. The CH_3I and AsF_3 transitions observed were $J=1+2$ and $K=1\rightarrow 1$. These lines show first-order Stark effects and are treated similarly.

Since line widths limited the accuracy of frequency measurement, large splittings were measured in order to obtain good fractional accuracy. In order to evaluate the dipole moment the measured frequency splittings were compared with those calculated from known molecular parameters and various values of the parameter μE, the product of molecular dipole moment and electric field strength E. For these calculations the methods of Low and Townes[2] (I of this series) and of Fano[3] were used. For all four molecules of this group the electric fields were in the intermediate region where

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[1] R. G. Shulman and C. H. Townes, Phys. Rev. **77**, 500 (1950).

[2] W. Low and C. H. Townes, Phys. Rev. **76**, 1295 (1949).

[3] U. Fano, J. Research Nat. Bur. of Stand. **40**, 215 (1948).

TABLE I. Dipole moment of AsF_3. $\Delta\nu$ is the Stark displacement of the $J=1\rightarrow 2$, $F=5/2\rightarrow 7/2$, $K=1$, $M=5/2$ transition.

$\Delta\nu$(mc)	E(e.s.u./cm)	μ(Debye)
15.7	0.1394	2.737
18.1	0.1658	2.669
21.3	0.1897	2.707
51.2	0.4043	2.865
60.5	0.4730	2.863
93.5	0.7317	2.787
110.0	0.8644	2.774
59.3	0.4532	2.934
67.5	0.5127	2.927
80.6	0.6145	2.886
98.2	0.7562	2.828
	Average 2.815±0.025 debye	

the molecular couplings to the field and to the nuclear quadrupole moment are comparable in magnitude.

Arsenic Trifluoride

The intermediate field solution[2] of the AsF_3 $J=1\rightarrow 2$, $K=1\rightarrow 1$, $F=5/2\rightarrow 7/2$, $M=5/2\rightarrow 5/2$ is

$$\Delta\nu=-14.70+\mu E/4+[(6.29+\mu E/4)^2+2.800\mu E +(\mu E)^2/18+176.0]^{\frac{1}{2}}, \quad (1)$$

where μE is the product of dipole moment and electric field in megacycles/sec. and $\Delta\nu$ is the displacement in megacycles/sec. from the unperturbed frequency of this transition at 23,532.1 mc.[4] A theoretical plot of $\Delta\nu$ *vs.* μE yields values of μE for the observed $\Delta\nu$. Since E had been measured, μ was found to be 2.815±0.025 Debye units (see Table I).

Methyl Iodide

The methyl iodide moment was determined from the splitting of the $J=1\rightarrow 2$, $K=1\rightarrow 1$, $F=7/2\rightarrow 9/2$, $M=7/2\rightarrow 7/2$ transition at 30,123.64 mc.[5] The calculations are identical with those for AsF_3 except that the coefficients and molecular parameters have different numerical values. They are, in the notation of Low and Townes[2]

$$\begin{gathered} a_1=(5)^{\frac{1}{2}}/3, \quad a_2=2/3, \\ \langle\psi_1|H_E|\psi_1\rangle=-(7/27)\mu E, \\ \langle\psi_2|H_E|\psi_2\rangle=(-13/54)\mu E, \\ \langle\psi_1|H_E|\psi_2\rangle=-[(5)^{\frac{1}{2}}/27]\mu E, \\ eqQ=-1934 \text{ mc.} \end{gathered} \quad (2)$$

Substituting these values

$$\Delta\nu=-93.51+0.2500\mu E+[8743.43-1.729\mu E +69.45\times 10^{-4}(\mu E)^2]^{\frac{1}{2}}, \quad (3)$$

where $\Delta\nu$ is the displacement from 30, 123.64 mc. The value of μ is 1.647±0.014 Debye units (see Table II).

TABLE II. Dipole moment of CH_3I. $\Delta\nu$ is the Stark displacement of the $J=1\rightarrow 2$, $F=7/2\rightarrow 9/2$, $K=1$, $M=7/2$ transition.

$\Delta\nu$(mc)	E(e.s.u./cm)	μ(Debye)
28.82	0.4651	1.677
30.02	0.4841	1.676
35.18	0.5644	1.676
63.10	1.0565	1.581
65.70	1.0849	1.601
77.67	1.2458	1.638
84.03	1.3084	1.682
	Average 1.647±0.014 debye	

Methyl Chloride

Since some deviations from theory had been indicated by earlier measurements[6] of Stark effects in this molecule, all Stark components of each of the three lines of the $J=0\rightarrow 1$ transition were measured and compared with theoretical expectations over a wide range of field strengths (see Fig. 1). The general procedure in calculating Stark effects in this molecule is similar to that for the first-order case. Choosing particular values for F and M, wave functions are constructed and the energy matrix diagonalized. The allowed values of F and hence the order of the secular equation depend upon the value of M. When $|M|=J+I-1$, F can only have the two values, $J+I$ and $J+I-1$. In CH_3Cl^{35} when $J=1$, $I=3/2$ and $|M|=3/2$, F can be 3/2 or 5/2. However when $|M|=1/2$, F can be 1/2, 3/2 or 5/2 and the secular equation is of the third order. The splittings for the two possible $|M|=3/2$ components are

$$\Delta\nu=\pm 9.39+0.3286(\mu E)^2\mp 1.878[25-0.1369(\mu E)^2 +46.87\times 10^{-4}(\mu E)^4]^{\frac{1}{2}} \text{ mc}, \quad (4)$$

where the upper sign refers to the splitting of the $|M|=3/2$ component of the $F=3/2\rightarrow 3/2$, $J=0\rightarrow 1$ transition from 25,570.77 mc[5] and the lower sign to the difference between the $|M|=3/2$ component of the $F=3/2\rightarrow 5/2$, $J=0\rightarrow 1$ transition and 26,589.49 mc. The expressions can be checked against the weak field case.[2, 3] For μE sufficiently small, they reduce to

$$\Delta\nu_{F=3/2\rightarrow 5/2}=0.3029(\mu E)^2$$

and

$$\Delta\nu_{F=3/2\rightarrow 3/2}=0.3543(\mu E)^2 \quad (5)$$

which are identical with the weak field expressions. The third-order equation for $|M|=1/2$ was solved* and Fig.

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[4] Dailey, Rusinow, Shulman, and Townes, Phys. Rev. **74** 2451, (1948).

[5] Gordy, Simmons, and Smith, Phys. Rev. **74**, 243 (1948).

[6] R. Karplus and A. H. Sharbaugh, Phys. Rev. **75**, 889, 1449 (1949).

* Fano, reference 3, solves in detail the case where $J=1$. He expresses the energy as

$$\Delta W=eqQy/4(2J-1)(2J+3)I(2I-1),$$

where y is the solution of a secular equation. However, his expressions (14b) and (15) for y contained typographical errors. The corrected expressions, which Dr. Fano has very kindly

1 is a plot of experimental results *vs.* the theoretical splitting assuming $\mu = 1.869$ Debye units. This compares well with Karplus and Sharbaugh's value[6] of 1.86±0.01, also found by microwave methods. In addition there seem to be no significant differences between the theoretical curves and experimental points.

Methyl Bromide

It is difficult to predict in advance which components will be most widely split for a particular value of the field. However by using the observed intensity ratios and the theoretical values of intensities in the limiting cases the components are readily identified. [For weak field and $\Delta F = +1$, the intensities are proportional to $(F^2 - M^2)$ and for strong fields when $\Delta J = +1$ intensities are proportional to $(J^2 - M_J{}^2)$]. The CH_3Br^{79} transition measured was $J = 0 \rightarrow 1$, $F = 3/2 \rightarrow 5/2$ and $|M| = 1/2$ at 19,107 mc. Table III shows that $\mu = 1.797 \pm 0.015$ Debye units.

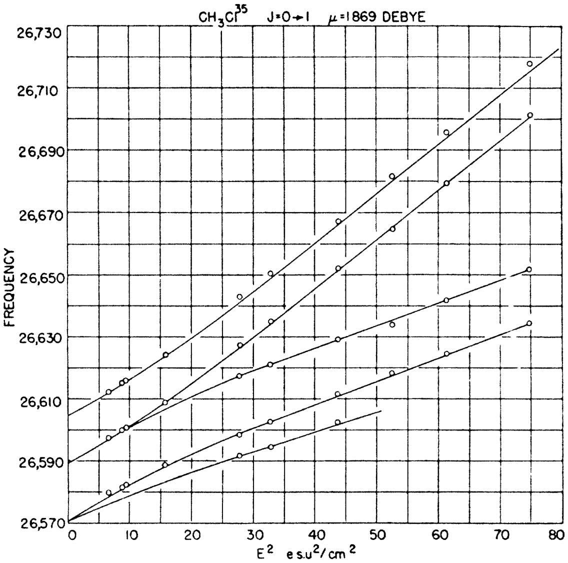

FIG. 1. Frequency of all components of CH_3Cl^{35} $J = 0 \rightarrow 1$ transition as a function of electric field strength. Curves are computed using $\mu = 1.869$ Debye.

checked, are

$$y = -\tfrac{1}{2}\left([I+3][2I-1]+x \pm 3\{[(I-1)(2I-1)+x]^2+4I[2I-1]^2\}^{\frac{1}{2}}\right) \text{ for } |M| = I.$$

For $|M| < I$,

$$y = K_1 + 2K_2^{\frac{1}{2}} \cos[\alpha + 2p\pi/3],$$

where $\rho = 0, 1, 2$

$$\cos\alpha = (-K_3/K_2^{\frac{3}{2}})$$

and

$$\begin{aligned}
K_1 &= 2,\\
K_2 &= 4I^2(I+1)^2 + I(I+1) + 1 + 2[3M^2 - I(I+1) + 1]x + x^2,\\
K_3 &= 8I^3(I+1)^3 - 24I^2(I+1)^2 + \tfrac{3}{2}I(I+1) + 1\\
&\quad + 3\{3M^2[2I(I+1) - 7/2] - \tfrac{1}{2}I(I+1)[4I(I+1)+1] + 1\}x\\
&\quad + 3[3M^2 - I(I+1) + 1]x^2 + x^3.
\end{aligned}$$

TABLE III. Dipole moment of CH_3Br. $\Delta\nu$ is the Stark displacement of the $J = 0 \rightarrow 1$, $F = 3/2 \rightarrow 5/2$, $|M| = 1/2$ transition.

$\Delta\nu$(mc)	E(e.s.u./cm)	μ(debye)
31.21	19.073	1.803
39.29	24.004	1.794
43.52	26.420	1.797
58.80	35.761	1.795
71.61	43.270	1.796
	Average 1.797±0.015 debye	

TABLE IV. Dipole moment of CH_3CF_3. $\Delta\nu$ is the Stark displacement of the $J = 1 \rightarrow 2$, $K = 0$, $|M| = 1$ transition.

$\Delta\nu$(mc)	E^2(e.s.u./cm)^2	μ(debye)
8.13	5.430	2.341
11.31	7.813	2.302
16.13	11.001	2.317
17.37	11.651	2.336
32.66	21.862	2.338
41.21	28.230	2.311
41.28	28.174	2.316
55.03	37.270	2.324
57.68	39.475	2.312
70.88	48.322	2.317
	Average 2.321±0.034 debye	

MOLECULES WITHOUT QUADRUPOLE COUPLING

Methyl Fluoroform

The $J = 1 \rightarrow 2$ transition of the symmetric top molecule CH_3CF_3 has been reported [7, 8] at 20,741 mc. Since every nucleus in this molecule has zero quadrupole moment, the spectrum shows no hyperfine structure. Although both first- and second-order Stark effects are observed, only the second-order effects were measured, giving the displacement $\Delta\nu$ of the component $K = 0$, $|M| = 1$ from its undisturbed position. From this the dipole moment can be simply calculated as 2.321±0.034 Debye units (see Table IV).

Phosphorous Trifluoride

Measurements on the displacement of the $J = 1 \rightarrow 2$, $K = 0$, $|M| = 1$ transition of PF_3 from 31,279.60 mc[9] determine its dipole moment as 1.025±0.005 Debye (see Table V).

Nitrous Oxide

Three quadrupole components of the $J = 0 \rightarrow 1$ transition of the linear molecule $N^{15}N^{14}O^{16}$ have been reported.[10] They are

$F = 1 \rightarrow 1$ 24,274.53 mc
$F = 1 \rightarrow 2$ 24,274.61 mc
$F = 1 \rightarrow 0$ 24,274.73 mc.

Since the lines were not resolved on our apparatus, this

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[7] W. F. Edgell and A. Roberts, J. Chem. Phys. 16, 1002 (1948).
[8] Dailey, Minden, and Shulman, Phys. Rev. 75, 1319(A) (1949).
[9] Gilliam, Edwards, and Gordy, Phys. Rev. 75, 1014 (1949).
[10] Coles, Elyash, and Gorman, Phys. Rev. 72, 973 (1947).

TABLE V. Dipole moment of PF_3. $\Delta\nu$ is the Stark displacement of the $K=0$, $|M|=1$ component of the $J=1\rightarrow 2$ transition.

$\Delta\nu$(mc)	E^2(e.s.u./cm)^2	μ(debye)
22.15	115.97	1.028
29.95	157.95	1.024
36.95	195.85	1.022
	Average 1.025±0.009 Debye	

TABLE VI. Dipole moment of $N^{15}N^{14}O^{16}$. $\Delta\nu$ is the Stark displacement of the $J=0\rightarrow 1$ transition.

$\Delta\nu$(mc)	E^2(e.s.u./cm)^2	μ(debye)
0.86	55.175	0.176
0.97	66.048	0.171
1.62	119.75	0.164
1.66	101.53	0.180
2.33	161.32	0.170
2.38	154.70	0.162
2.55	199.85	0.159
3.03	225.21	0.164
3.71	287.40	0.161
4.28	315.63	0.164
4.58	350.10	0.161
5.89	440.92	0.163
7.51	565.30	0.163
	Average 0.166±0.002 debye	

was an example of the strong field case and the Stark splitting was considered independent of the quadrupole coupling. Table VI shows that the dipole moment is 0.166±0.002 Debye units. This molecule affords a good example of a small dipole moment which was not accurately determinable by other methods. Previous methods had given values ranging from 0 to 0.25 Debye.

Cyanogen Cloride

The Cl^{36} nucleus has been shown[11] to have a rather small quadrupole coupling constant of -19 mc in the molecule ClCN. Since hyperfine structure in the $J=1\rightarrow 2$ transition of ClCN due to Cl^{36} and N^{14} is no wider than 5 mc, it may be ignored if wide lines and large Stark splittings are measured. Treating the $Cl^{36}C^{12}N^{14}$ molecule as a linear molecule in the strong field approximation, the dipole moment was found to be 2.802±0.014 debye units (see Table VII).

TABLE VII. Dipole moment of ClCN. $\Delta\nu$ is the separation between the $M=0$ and $|M|=1$ components of the $J=1\rightarrow 2$ transitions.

$\Delta\nu$(mc)	E^2(e.s.u./cm)^2	μ(debye)
39.03	9.318	2.804
72.6	17.486	2.792
81.8	19.467	2.809
	Average 2.802±0.020 Debye	

TABLE VIII. Comparison of present result and previous measurements of dipole moments.

Molecule	Present result, debye units	Previous values
AsF_3	2.815±0.025	2.65[12]
CH_3I	1.647±0.014	1.62[12]
CH_3Cl^{35}	1.869±0.010	1.86[12,5]
CH_3Br^{79}	1.797±0.015	1.79[12]
CH_3CF_3	2.321±0.034	
PF_3	1.025±0.009	
N_2O	0.166±0.002	0.0[12]
ClCN	2.802±0.020	2.66[13]

SUMMARY

Measurement of dipole moments by Stark effects in a wide variety of molecules appear to give satisfactory results. In the cases of the methyl halides which have been rather accurately measured by other techniques, agreement with previous results is very good, as shown by Table VIII.

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[11] C. H. Townes and L. G. Aamodt, Phys. Rev. **76**, 691 (1949).

[12] T. G. Wesson, "Tables of electric dipole moments," Technical Report No. 11, Laboratory for Insulation Research, M.I.T.

[13] Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948).