Zeeman Effect of Some Linear and Symmetric-Top Molecules*

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(Received November 14, 1955)

The Zeeman effect in the microwave rotational spectra of some linear molecules and symmetric-top molecules has been investigated. The rotational g factors obtained are in nuclear magnetons: $|g|=0.0295 \pm 0.005$ for OCS; $|g|=0.268\pm0.005$ for CO. In the symmetric-top molecules the components of the rotational g factor along the symmetry axis, g_K, and perpendicular to this axis, $g_\perp$, were measured as follows: $|g_\perp|=0.0624\pm0.005$ and $(g_\perp-g_K)=0.549$ for CH_3F; $|g_\perp|=0.03$ for CF_3H; $g_\perp\approx0$ and $g_K=0.298\pm0.006$ for CH_3CCH; $g_\perp\approx0$ and $g_K=0.31\pm0.01$ for CH_3CCD; $|g_\perp|=0.065\pm0.01$ for PF_3; $|g_\perp|=0.03$ for POF_3. The rotational g factor for OCS was measured with several different transitions up to $J=13\rightarrow14$ and was found to be a constant, independent of J within the accuracy of the measurements.

MOLECULAR and nuclear g factors can be measured with the Zeeman splitting of microwave rotational lines of molecules.[1,2] Furthermore, Zeeman patterns can often be employed for identification of spectral transitions. Measurements of molecular rotational g factors of some linear and symmetric-top molecules are described in the present work. The molecules chosen for study have only very small nuclear couplings, and hence the strong-field case (nuclear coupling completely broken down) could be easily achieved. The molecules included are nonmagnetic in the usual sense, i.e., they have singlet electronic ground states and no unbalanced electronic momentum. The molecular magnetism which causes the Zeeman splitting is therefore generated by the molecular rotation and is in all cases very small.

EXPERIMENTAL METHODS

The method of observation in principle was like that employed by Gordy, Gilliam, and Livingston[3] in their measurements on CH_3I^{129}. A coiled wave-guide cell was inserted between the poles of an electromagnet. Cells of different lengths and cross sections were employed for different regions of the spectrum. Some were coiled in the E and some in the H plane so that both the $\Delta M=0$ and the $\Delta M=\pm1$ components could be observed. The magnetic fields were measured with a proton reasonance probe.

LINEAR MOLECULES

In a linear molecule without nuclear coupling, the rotational magnetic moment is directed along the total rotational momentum vector **J** but does not necessarily point in the same direction as **J**, i.e., g_J may be positive or negative with respect to **J**. From the present experiments we cannot learn the sign of g_J but only its magnitude.

It is reasonable to assume the magnitude of the rotational magnetic moment, μ_J, to be proportional to the magnitude of the total angular momentum of the molecule. With this assumption, the magnetic moment is

$$\mu_J=\mu_0[J(J+1)]^{\frac{1}{2}}, \tag{1}$$

where μ_0 is the proportionality constant. The rotational g-factor in nuclear magneton units is then

$$g=\frac{\mu_J/\beta_I}{[J(J+1)]^{\frac{1}{2}}}=\mu_0/\beta_I, \tag{2}$$

which is a constant, independent of the rotational state. In this equation β_I represents the nuclear magneton.

By making measurements for relatively high, as well as for low, J values we have sought to test for the molecule OCS the assumption that the rotational magnetic mement is proportional to $[J(J+1)]^{\frac{1}{2}}$ or that g is a constant independent of J. Although Zeeman measurements on a few linear molecules have been previously made,[1,2] the earlier measurements have been made for low J values only and thus provide no critical test of the dependence of μ on J.

The first-order Zeeman splitting of a rotational line is readily shown to be

$$E_H=g_J\beta_IMH, \tag{3}$$

where H is the magnetic field and M_J is the magnetic quantum number,

$$M=J,\ J-1,\ \cdots -J+1,\ -J. \tag{4}$$

When M changes by ΔM, the splitting of any given rotational line $(J\rightarrow J+1)$ is

$$\Delta\nu=\beta_I\Delta MH(g_J-g_{J+1})/h. \tag{5}$$

If g is independent of J, then $g_J=g_{J+1}=g$ and

$$\Delta\nu=g\beta_IH\Delta M/h. \tag{6}$$

The π component ($\Delta M=0$) will not then be split, and the σ component ($\Delta M=\pm1$) will be a doublet with separation $2g\beta_IH/h$. With our wavelength arrangement we could observe the σ doublet without the π component.

* This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Preliminary results were described in Duke Microwave Laboratory Report No. 6 (May 1, 1954–August 1, 1954).

[1] C. K. Jen, Phys. Rev. 74, 1396 (1948); Physica 17, 379 (1951).

[2] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), Chap. 3.

[3] Gordy, Gilliam, and Livingston, Phys. Rev. 76, 443 (1949).

Figure 1 shows the doublet splitting (σ components) for four rotational transitions of OCS displayed with the same cathode-ray trace. This simultaneous display of rotational lines is made possible by the harmonic generator and broad-banded detector earlier developed in this laboratory.[4] With this harmonic method the frequency scale on the scope is condensed in proportion to the harmonic number. The harmonic number and hence the rotational quantum number increase from right to left in the figure. The doublet splitting, which is actually equal for each line, appears to decrease from left to right because of the more condensed frequency scale for the higher harmonics. To compare the splittings, one must multiply the separations on the picture by the klystron harmonic, four for the transition on the right, five for the next, and so on. When this is done, the splitting is found to be equal, within experimental error, for all lines. Table I compares the g factor for the $J=1\rightarrow2$, $7\rightarrow8$, $9\rightarrow10$, $11\rightarrow12$, and $13\rightarrow14$ transitions of OCS. They are seen to be equal within the experimental error.

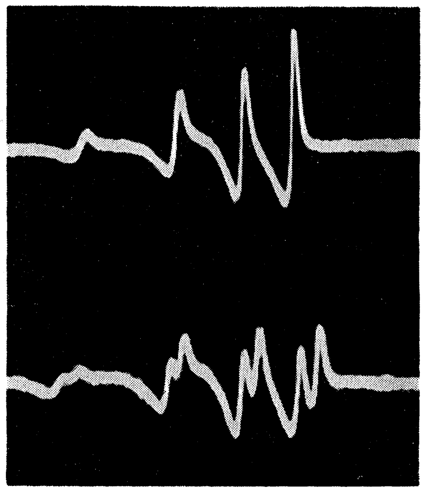


FIG. 1. Zeeman splitting ($\Delta M=\pm1$ components) of the $J=13\rightarrow14$, $11\rightarrow12$, $9\rightarrow10$, and $7\rightarrow8$ rotational lines of OCS at wavelengths of 1.76, 2.06, 2.47, and 3.09 mm from left to right respectively, as displayed by a common cathode-ray trace with the 7th, 6th, 5th, and 4th harmonics of a K-band klystron. The upper curve is for $H=0$, the lower for $H=9800$ gauss. The splitting of each component is the same, 0.44 Mc/sec, within the accuracy of the measurement. The apparent difference is caused by the fact that the scale is condensed with increase of harmonic number.

Figure 2 shows the $\Delta M=\pm1$ Zeeman components of the $J=0\rightarrow1$ rotational line of CO. The resulting g factor is 0.268 in nuclear magneton units. Interestingly, it is larger than the g factor of OCS by a factor equal approximately to the ratio of the B value of CO to that of OCS. This suggests that the larger g value of CO over that of OCS results primarily from its greater rate of rotation for a given J value.

[4] W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953); **93**, 407 (1954).

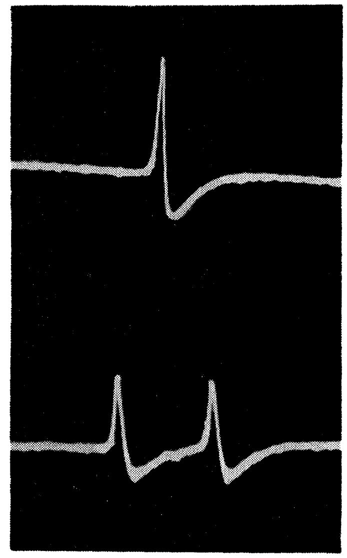


FIG. 2. Zeeman splitting ($\Delta M=\pm1$ components) of the $J=0\rightarrow1$ transition of CO at 2.69 mm wavelength. Upper curve is for $H=0$, lower for $H=10\,000$ gauss. Separation of lower components is 4.08 Mc/sec.

SYMMETRIC-TOP MOLECULES

The symmetric-top molecule has a quantized component of its total angular momentum along its symmetry axis. It likewise has a component of its rotational magnetic moment along the axis. This component is generated by the rotation about the symmetry axis and should therefore be proportional to the component of internal angular momentum $Kh/2\pi$. In nuclear magnetons we express this component as

$$\mu_K=g_K\beta_I K, \tag{7}$$

where g_K is the component of the rotational g factor with reference to the symmetry axis. We similarly designate the component of μ perpendicular to the symmetry axis by

$$\mu_N=g_\perp\beta_I[J(J+1)-K^2]^{\frac{1}{2}}, \tag{8}$$

where $g_\perp$ is the component of the rotational g factor with reference to an axis normal to the symmetry axes. The total rotational moment can then be expressed as

$$\mu_J=\beta_I\frac{g_\perp J(J+1)+(g_K-g_\perp)K^2}{[J(J+1)]^{\frac{1}{2}}}. \tag{9}$$

TABLE I. Zeeman constants of some linear molecules.

Molecule	$J\rightarrow J'$	ΔM	H(gauss)	Doublet splitting $2\Delta\nu$(Mc/sec)	Magnitude of g in mm units
CO	$0\rightarrow1$	±1	8111	3.31	0.268 ± 0.005
OCS	$1\rightarrow2$				0.029 ± 0.006[a]
	$7\rightarrow8$	±1	9812	0.442	0.0295 ± 0.005
	$9\rightarrow10$	±1	9812	0.442	0.0295
	$11\rightarrow12$	±1	9812	0.442	0.0295
	$13\rightarrow14$	±1	9812	0.43	0.030

[a] From C. K. Jen, Physica **17**, 379 (1951).

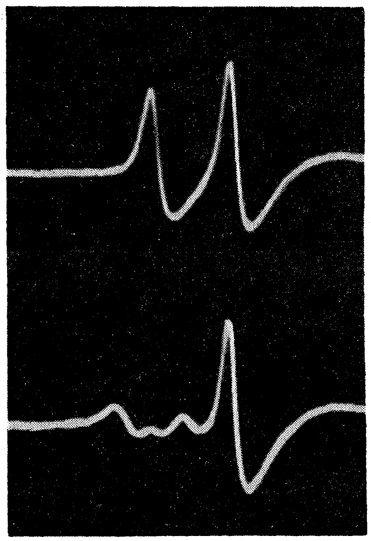


FIG. 3. Zeeman effect ($\Delta M=0$ components) of the $J=1\rightarrow2$ transition of CH_3F at 2.94 mm wavelength. The upper curve is for $H=0$, the lower for $H=10\,000$ gauss. The $K=0$ line is unsplit.

The first-order Zeeman energy is

$$E_H=\boldsymbol{\mu}_J\cdot\mathbf{H}=\frac{\mu_J MH}{[J(J+1)]^{\frac{1}{2}}} \tag{10}$$

$$=\left[g_\perp+(g_K-g_\perp)\left(\frac{K^2}{J(J+1)}\right)\right]\beta_I MH. \tag{11}$$

This expression applies to molecules without nuclear coupling. For a rotational transition $J\rightarrow J+1$, $K\rightarrow K$, the displacement of the $M\rightarrow M'$ Zeeman component from the unsplit zero field line is

$$\Delta\nu=\left[g_\perp(M'-M)+(g_K-g_\perp)\times\left\{\frac{M'K^2}{(J+1)(J+2)}-\frac{MK^2}{J(J+1)}\right\}\right]\frac{\beta_I H}{h}. \tag{12}$$

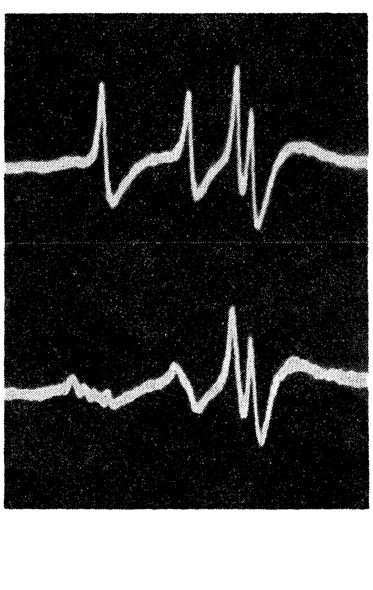


FIG. 4. Zeeman effect ($\Delta M=\pm1$ components) of the $J=3\rightarrow4$ transitions of CH_3CCH at 5.03 mm wavelength. The upper curve is for $H=0$, the lower for $H=10\,000$ gauss. The $K=0$, 1, 2, 3 components are from right to left respectively. The splitting increases with K.

When $K=0$, Eq. (12) reduces to that for linear molecules (Eq. (6)). As for linear molecules, one observes a doublet for the σ components ($M\rightarrow M\pm1$) and a single undisplaced line for $M\rightarrow M$, π component. By measurements on the $K=0$ line of a given transition, $g_\perp$ can be obtained without a knowledge of g_K. One can obtain $(g_K-g_\perp)$ from measurements on lines for which $K\neq0$ and hence with the $g_\perp$ obtained from the $K=0$ lines can obtain g_K. In our experiments, however, we could not learn the sign of $g_\perp$, only its magnitude. Hence, our values for g_K are not unabiguous except when $g_\perp$ is negligibly small.

Figure 3 shows the pattern obtained for the $\Delta M=0$ components of the $J=1\rightarrow2$ transition of methyl fluoride. Note that the $K=0$ line is unsplit and undisplaced, whereas the $K=1$ line is split into a triplet as would be expected from Eq. (12). Figure 4 shows the $\Delta M=\pm1$ components of the $3\rightarrow4$ transition of methyl acetylene. In general, the $\Delta M=\pm1$ patterns for lines with $K\neq0$ are complex. For methyl acetylene $g_\perp$ is negligibly small, and the pattern is the one obtained by

TABLE II. Zeeman constants of some symmetric-top molecules.

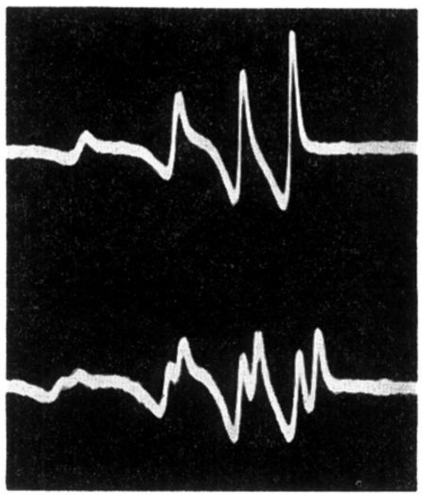
Molecule	Transition employed $J\rightarrow J'$	K	ΔM	Magnitude of g factor $\lvert g_\perp\rvert$	g_K
CH_3F	$0\rightarrow1$	0	±1		0.487
	$1\rightarrow2$	0	±1	0.0624 ± 0.005	or
	$1\rightarrow2$	1	0		0.612
					$(g_\perp - g_K=0.549)$
CF_3H	$4\rightarrow5$	4	±1	0.03	
CH_3CCH	$2\rightarrow3$	2	$0,\pm1$	≈0	0.298 ± 0.006
	$3\rightarrow4$	3	±1		
CH_3CCD	$2\rightarrow3$	2	$0,\pm1$	≈0	$0.31\ \pm0.01$
PF_3	$2\rightarrow3$	0	±1	$0.065\ \pm0.01$	
POF_3	$10\rightarrow11$		±1	0.03	

putting $g_\perp=0$ in Eq. (12). The splitting decreases rapidly with K, and only the pattern for the highest K line is resolved. Relative intensity formulas are given elsewhere.[2]

The $g_\perp$ and g_K values obtained for various symmetric-top molecules with the rotational lines used in their measurement are listed in Table II. For brevity, the magnetic field values and frequencies are omitted. The fields employed were always near 10 000 gauss, and the most widely spaced components of a given pattern were employed for the calculationof the g values.

No attempts will be made here to relate the molecular rotational magnetic moment to the electronic structure of the molecule. Treatments of this interesting subject are given by Esbach and Strandberg[5] and by Jen.[6]

[5] J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. 85, 24 (1952).
[6] C. K. Jen, Am. J. Phys. 22, 553 (1954).



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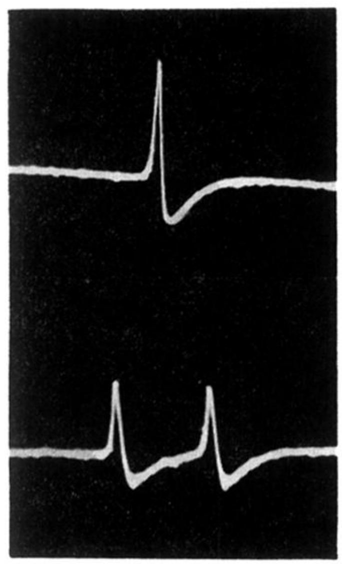

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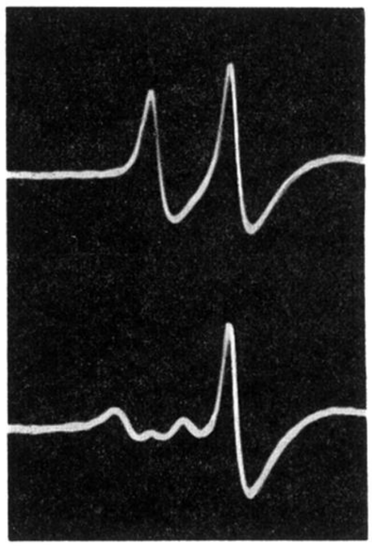
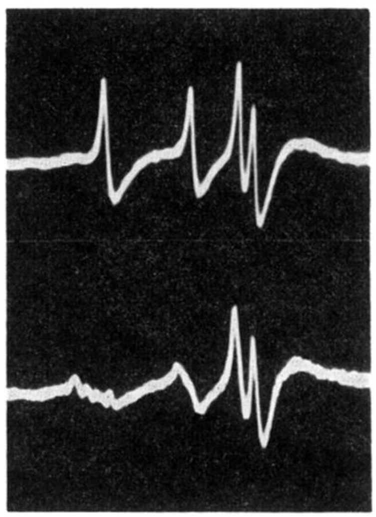


FIG. 3. Zeeman effect ($\Delta M=0$ components) of the $J=1\rightarrow 2$ transition of CH_3F at 2.94 mm wavelength. The upper curve is for $H=0$, the lower for $H=10\,000$ gauss. The $K=0$ line is unsplit.



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