Resolution of a Rotational Line of the OCS Molecule and Its Stark Effect

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WITH the method described by W. E. Good,[1] the absorption line due to the transition from the $J=1$ to the $J=2$ molecular rotational level has been resolved and shown on an oscilloscope. This line appears at the frequency of 24,320 megacycles or 0.8107 (cm^{-1}) wave numbers. The line was resolved at pressures of less than 10^{-1} mm of Hg. At pressures greater than this, the pressure broadening of the line was so great that the line was hardly observable by the oscilloscope method. The gas was introduced for the measurements, into a rectangular wave guide through which the microwaves were transmitted. Further details concerning the method can be found in the paper cited.

Carbon oxy-sulphide, OCS, is a linear molecule with the carbon atom between the oxygen and sulphur. Its moment of inertia calculated from the above frequency is 1.379×10^{-38} g cm^2.

The value (1.38×10^{-38} g cm^2) calculated using the interatomic distances observed by Cross and Brockway,[2] agrees well with this.

A linear molecule of this sort should show a Stark effect shift and splitting proportional to the square of the electric field strength and the square of the dipole moment.[3] When a d.c. electric field was applied to the carbon oxy-sulphide in the wave guide with the d.c. field parallel to the direction of the polarized electric vector of the traveling microwave, the rotational line split into two lines. One of these lines moved to a lower frequency than the unperturbed transition line and the other moved to a higher frequency. This effect was instantly (and to the authors, spectacularly) observed on the oscilloscope screen as the d.c. voltage was gradually increased. The single peak observed on the oscilloscope divided into two peaks, one of which was twice as high as the other. Figures 1–3.

The line which showed the least shift appeared twice as high (intense) as the other, in agreement with the theory. The energy level for the positive external (spatial) quantum number is the same as for the negative. Therefore, the $2(J+1)$ states become only $(J+1)$ levels. The frequency shift was found to be proportional to the square of the electric field strength, agreeing with the theory. Because the d.c. electric field is in the direction of the electric vector of the traveling microwave, no transition in the external quantum number occurs here when the rotational quantum number changes. Therefore, the frequency separation of the two lines from each other should be:

$$\Delta f=\left(\frac{3}{20}-\frac{1}{84}\right)\frac{8\pi^2 I}{\eta^3}\mu^2\cdot E^2 \text{ cycles/sec.},$$

where μ is the dipole moment and E the d.c. field strength. From the above equation the observed value of Δf and I, the moment of inertia, the dipole moment can be calculated. It was found to be 0.72×10^{-18} e.s.u. The principal uncertainty in the measurement is the separation of the electrodes (only 0.092 inch), which determines the field strength. Values of Δf as great as 5 megacycles were observed. Zahn and Miles[4] report a value of 0.65×10^{-18} for μ from dielectric constant data.

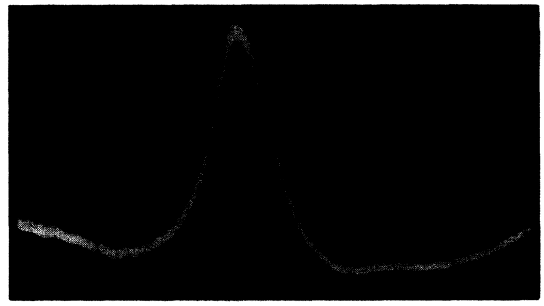


FIG. 1.

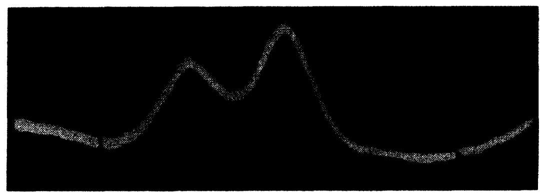


FIG. 2.

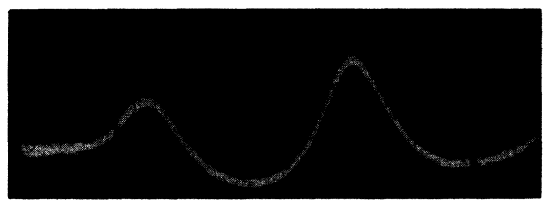


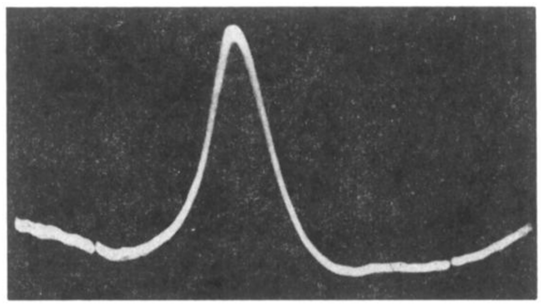
FIG. 3.

FIGS. 1–3. Oscilloscope pictures of absorption *versus* frequency for the OCS rotational line at 24,320 megacycles. The applied d.c. volts is 0 volt/cm in Fig. 1, 750 volts/cm in Fig. 2, 1070 volts/cm in Fig. 3. The frequency markers in the oscilloscope pictures are 6 megacycles apart in each case and appear as points of different intensity at each side of the oscilloscope trace. The base line is distorted so that the pictures give a somewhat inaccurate impression of the correct relative heights of the two peaks.

The d.c. field was applied by placing a thin strip of metal down the center of the wave guide and insulating it at the edges from the wave guide. This strip was in an equipotential plane with respect to the electric field of the traveling microwave. The d.c. field was then applied between this insulated strip and the wave guide.

Further measurements of the intensity of absorption, pressure broadening of the line, and more accurate measurements of the Stark effect are continuing. It is believed that this is the first time the Stark effect of a pure rotational line of a linear molecule has been observed, although it has been predicted theoretically.

[1] W. E. Good, Phys. Rev. **70**, 213 (1946).
[2] Cross and Brockway, J. Chem. Phys. **3**, 821 (1935).
[3] Cf. P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).
[4] Zahn and Miles, Phys. Rev. **32**, 497 (1928).



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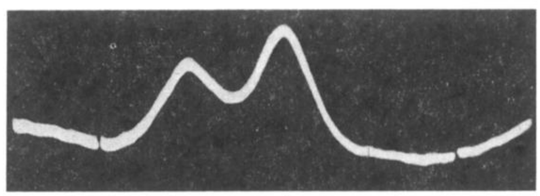
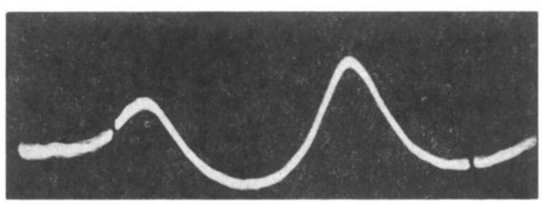


FIG. 2.



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