

Molecular Dipole Moments and Stark Effects.* II. Stark Effects in OCS†

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The dipole moments of OCS for several isotopic species and vibrational states have been determined from the Stark splitting of the $J=1 \rightarrow 2$ rotational transition. The value of the $O^{16}C^{12}S^{32}$ moment is 0.7085 ± 0.004 debye units. The $O^{16}C^{12}S^{34}$ and $O^{16}C^{13}S^{32}$ moments differ from this by less than 0.2 percent. The $O^{16}C^{12}S^{32}$ molecule in the excited bending mode ($v_2=1$) is treated formally as a slightly asymmetric top which produces a doublet. Measurement of Stark effect for these lines gives a dipole moment of 0.700 ± 0.004 debye. Upon introduction of a Stark voltage, two weak lines appear on either side of the doublet $v_2=1$. They are explained as transitions involving the doublet levels which are forbidden in zero field, but allowed upon the introduction of a perturbing field.

INTRODUCTION

THE dipole moments of various vibrational states and isotopic species of OCS were determined as the first step in the investigation of the dipole moments of a number of other molecules. The dipole moments of OCS were measured partly because they could be compared with previous measurements^{1,2} and because OCS is a linear molecule uncomplicated by nuclear quadrupole effects. It is hoped that the OCS dipole moment can conveniently be used as a standard for future dipole moment determinations.

The method employed was the splitting into components of the pure rotational transitions in the microwave region by the application of an external electric field. Upon applying the external field, the total angular momentum vector of the molecule is oriented at various discrete angles with respect to the field. The potential energy differences of the allowed orientations split the rotational energy levels and transitions.

This splitting for a linear molecule is:³

$$\Delta\nu = \frac{3M^2(16J^2 + 32J + 10) - 8J(J+1)^2(J+2)\mu^2 E^2}{J(J+2)(2J-1)(2J+1)(2J+3)(2J+5)h^2\nu_0}, \quad (1)$$

where the transition is from $J \rightarrow J+1$, M is the magnetic quantum number, μ is the permanent dipole moment of the molecule, ν_0 is the frequency of the pure rotational transition, E is the applied electric field, and $\Delta\nu$ is the difference in frequency between ν_0 and the frequency of the Stark component. Expression (1) assumes that $\Delta M=0$ for the transition, which is true in the convenient case where the applied electric field

and the electric vector of the microwave radiation are parallel.

APPARATUS

The apparatus was a Stark modulation-type microwave spectroscope⁴ of which Fig. 1 is a block diagram. The sweep from scope No. 1 is the controlling sweep of the equipment, being fed into scope No. 2 and the signal klystron repeller. The absorption cell is a 10-ft. section of wave guide immersed in a trough for temperature control. After passing through the absorption cell the signal is detected by the crystal detector, which can be biased by a small d.c. voltage to improve its performance, and from there fed into a transformer turned to the frequency of the modulating square wave, i.e., 50–200 kc. The signal is then amplified by a wide band Hewlett Packard amplifier followed by a narrow band amplifier consisting of the r-f stage of a CWQ-46161-A TRF Navy receiver into the phase detector with a band width variable from 5 c.p.s. to about 200 c.p.s. The phase detector output is displayed on an oscilloscope.

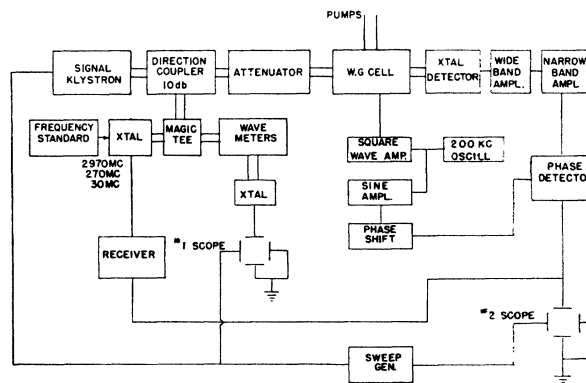


Fig. 1. Block schematic diagram of spectrometer system for measuring Stark effects.

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¹ Strandberg, Wentink, and Kyhl, *Phys. Rev.* **75**, 270 (1949).

² Dakin, Good, and Coles, *Phys. Rev.* **71**, 640 (1947).

³ R. De E. Kronig, *Proc. Nat. Acad. Sci.* **12**, 488 (1926).

⁴ R. H. Hughes and E. B. Wilson, *Phys. Rev.* **71**, 562 (1947).

Frequencies were measured at first by beating the output of a d.c. Pound stabilizer⁵ with the source klystron.⁶ Subsequently, the stabilized frequency was replaced by the harmonic output of a 2K47 frequency multiplier klystron supplied by 270 Mc multiplied up from a 7.5-Mc crystal.

The modulating Stark voltage is connected to an electrode in the guide so that the electric field is parallel to the electric field of the radiation being transmitted through the guide in the prevailing TE₀₁ mode (see Fig. 2).

EXPERIMENTAL METHOD

Examination of Eq. (1) shows that in order to determine μ for a rotational transition where J and ν_0 are known, it is necessary to measure $\Delta\nu$ and E .

The field strength, E , in volts/cm, is a function of the applied voltage and the spacing between the electrode and the walls of the guide. A cross section of the wave guide absorption cell is shown in Fig. 2.

A variable d.c. voltage with a superimposed 50-kc square wave of variable amplitude was applied to the guide electrode. The resulting scope presentation is shown in Fig. 3. The components above the line correspond in phase to the lower half of the 50-kc square wave and the components below correspond to the upper half of the square wave. When the lower half of the square wave is at zero volts with respect to the wave guide walls, then the upward deflection on the oscilloscope corresponds to the undisplaced frequency, ν_0 , of the transition.

When the d.c. was increased, the separation was increased until it was possible to measure the frequency of the top and bottom components. The average of the top displacement and the bottom displacement was considered as a first and usually good approximation to be the displacement corresponding to the d.c. voltage.

The O¹⁶C¹²S³² $J=1\rightarrow 2$ rotational transition of the ground vibrational state had been measured at 24,325.92 Mc.² The dipole moment for this transition was determined by measuring the frequency difference between the $M=0$ component which splits to lower frequencies and the $M=\pm 1$ component which splits to higher frequencies. This difference is called $\Delta\nu$ in Table I.

A weighted average of the dipole moment is $\mu=0.7119$ debye units and applying corrections for field inhomogeneities, voltage measurement, and electrode slippage, as noted below, $\mu=0.7085$ debye units.

A change of dipole moment of OCS with change of isotopic species has previously been reported.¹ O¹⁶C¹²S³⁴ has an abundance of four percent and its $J=1\rightarrow 2$ transition occurs at 23,731.33 Mc.² The splitting of this line relative to the splitting of the O¹⁶C¹²S³² line was measured at several fixed values of Stark voltage. If the dipole moments for both transitions were equal

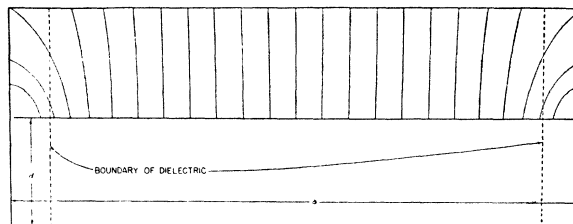


FIG. 2. Cross section of Stark wave guide and applied electric field.

then for the same voltage from Eq. (1),

$$\frac{\Delta\nu_{\text{O}^{16}\text{C}^{12}\text{S}^{34}}}{\Delta\nu_{\text{O}^{16}\text{C}^{12}\text{S}^{32}}} = \frac{\nu_{\text{O}^{16}\text{C}^{12}\text{S}^{32}}}{\nu_{\text{O}^{16}\text{C}^{12}\text{S}^{34}}} = 1.0251. \quad (2)$$

The experimental results of Table II indicate that within 0.2 percent (the accuracy of these measurements), the dipole moments are equal.

The isotopic species O¹⁶C¹³S³² has a natural abundance of 1.1 percent and its $J=1\rightarrow 2$ transition occurs⁵ at 24,247.76 Mc. If the dipole moment of this transition equals the dipole moment of the O¹⁶C¹²S³² transition, then from (1),

$$(\Delta\nu_{\text{O}^{16}\text{C}^{13}\text{S}^{32}})/(\Delta\nu_{\text{O}^{16}\text{C}^{12}\text{S}^{32}}) = 1.0032. \quad (3)$$

The experimental results of Table III show that the dipole moments are equal to within 0.2 percent.

Strandberg, Wentink, and Kyhl,¹ using a similar method, have reported that $\mu_{\text{O}^{16}\text{C}^{12}\text{S}^{32}}=0.732$ and $\mu_{\text{O}^{16}\text{C}^{13}\text{S}^{32}}=0.722$. This rather large (1.4 percent) change of dipole moment with change of isotopic species is hence in disagreement with the present experiments. Variations of several percent in dipole moment values have been reported by Strandberg *et al.* for changes of vibrational state in OCSe⁷ and for OCS as discussed below. The variation of dipole moment with nuclear mass can be attributed to different amplitudes of

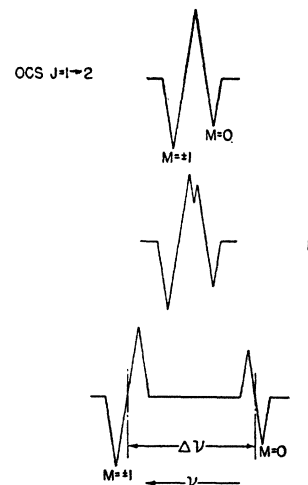


FIG. 3. Appearance on oscilloscope of microwave absorption line split into two Stark components.

⁵ R. V. Pound, M.I.T. Rad. Lab. Report No. 837 (October, 1945).

⁶ Townes, Holden, and Merritt, Phys. Rev. 74, 1113 (1948).

⁷ Strandberg, Wentink, and Hill, Phys. Rev. 75, 827 (1949).

TABLE I. Stark splitting $\Delta\nu$ between $M=0$ and $M=\pm 1$ components of $J=1\rightarrow 2$ transition as a function of field strength.

$\Delta\nu$ (Mc)	Guide No.	Volts applied (practical units)	Volts e.s.u./cm	Debye units
5.13	1	251.2	4.398	0.7160
8.14	1	317.5	5.558	0.7135
19.23	1	487.6	8.536	0.7140
19.98	1	493.2	8.634	0.7195
20.49	1	501.4	8.778	0.7167
27.09	1	576.8	10.098	0.7163
32.10	1	630.1	11.031	0.7137
Average=0.7157				
4.01	2	503.9	3.947	0.7061
12.54	2	885.0	6.932	0.7123
15.05	2	958.5	7.508	0.7201
15.60	2	994.9	7.793	0.7067
18.02	2	1071.4	8.393	0.7054
Average=0.7101				
12.34	3	363.9	6.920	0.7065
23.55	3	503.1	9.567	0.7049
23.60	3	503.0	9.565	0.7060
24.56	3	509.1	9.681	0.7113
29.88	3	564.4	10.733	0.7077
36.27	3	618.3	11.758	0.7120
Average=0.7079				

vibration in the ground state. Since the change of dipole moment with vibrational excitation and also the change with different isotopic species are both caused by the same type of distortion of the molecule, it seems reasonable to expect the more violent changes of vibrational state to have considerably more effect than a 10 percent difference of nuclear mass.

DISCUSSION OF ERRORS

Five possible sources of error were considered. Two of these sources produce only negligible errors, but the other three required the introduction of small corrections. The errors considered are listed.

First, the measurement of the d.c. voltage. The a.c. component of the Stark voltage was by-passed to ground by an L-C filter. The d.c. was then led to a voltage divider network, and thence into a Leeds and Northrup Type K potentiometer. The accuracy of this measurement was better than 0.01 percent and errors from this source are negligible.

Second were errors in the determination of the spacing between the electrode and the walls of the wave guide. Three different wave guides with different electrode spacings were used in order to minimize this error. Two X-band guides with internal dimensions 1.016×2.286 cm and one K-band guide with dimensions 0.4318×1.067 cm were used. The electrode thicknesses were 0.6350 cm, 0.1651 cm, and 0.0813 cm, respectively, and the average distances between the electrodes and the walls were 0.1904 ± 0.0005 cm, 0.4255 ± 0.0005 cm, and 0.1753 ± 0.0005 cm (see Table IV). The internal dimensions of guides were only measured at the ends. However, the dimensions at the ends of various sections

TABLE II. Stark splitting of $O^{16}C^{12}S^{32}$ and $O^{16}C^{12}S^{34}$ lines for identical fields.

$\Delta\nu_{O^{16}C^{12}S^{32}}$	$\Delta\nu_{O^{16}C^{12}S^{34}}$	Ratio
30.81	31.76	1.0308
49.98	51.12	1.0228
57.45	58.79	1.0233
83.13	85.13	1.0241
Average=1.0252		

TABLE III. Stark splitting of $O^{16}C^{12}S^{32}$ and $O^{16}C^{13}S^{32}$ lines for identical fields.

$\Delta\nu_{O^{16}C^{12}S^{32}}$	$\Delta\nu_{O^{16}C^{13}S^{32}}$	Ratio
24.56	24.59	1.0012
33.33	33.48	1.0045
44.13	44.15	1.0005
43.33	43.51	1.0042
52.69	53.11	1.0080
56.21	56.49	1.0050
Average=1.0047		

of guides from the same lot were also measured and in all cases the average dimensions were within 0.07 percent of the values given above.

The third source of error considered was unequal spacing between the electrode and the top and bottom walls of the wave guide. This would arise if the polystyrene runners supporting the electrode in the guide were not centered (see Fig. 2). If the polystyrene were at all points snug along the bottom of the guide, the difference between the top and bottom septum to guide spacings would be 0.01 cm. For an average difference of displacement which is two percent of the spacing, the true value of the dipole moment is 0.12 percent smaller than the measured value. A correction of -0.08 percent was made to the measured value of the dipole moment to allow for a possible error from this source.

The fourth source of error was the assumption that by averaging the displacements caused by the top and bottom of the applied square wave, a splitting corresponding to the d.c. voltage was measured. Since the displacement is proportional to the square of the voltage, this introduces a consistent second-order error which can be corrected. Let the d.c. volts = E_0 and the peak-to-peak square wave voltage equal $2E$. We have measured a displacement which equals

$$\frac{1}{2}K[(E_0+E)^2+(E_0-E)^2]$$

and called this = KE_0^2 . The difference in displacement is KE^2 and the fractional difference is E^2/E_0^2 . Since experimentally, $E/E_0 \approx 1/30$, then the average correction applied to the dipole moment is 0.11 percent with the true value smaller than the measured by this amount.

The fifth error was due to field inhomogeneities in the wave guides. A first look at Fig. 2, showing the variation of electric field in the guide, may give the

impression that an accurate determination of dipole moments in such an inhomogeneous field is impractical. However, since the microwave intensity is greatest in the center of the guide and decreases to zero at the outer walls, a large majority of the absorption processes take place in the more homogeneous central region of the field. In addition, it will be shown that the primary effect of inhomogeneities is to broaden the Stark component lines but not to shift their centers of gravity. As long as the absorption line is nearly symmetric in shape, only changes of the centers of gravity will produce errors in the dipole moments. Corrections to dipole moments due to field inhomogeneities were calculated and applied but were less than one percent for each of the three guides used.

In order to find the field strength of the applied Stark voltages, conformal transformations were used which give an exact solution for the field in a wave guide of the same general construction as that used, but without the thin strips of supporting dielectric, and with the wide dimension of the wave guide cross section infinitely large compared with the narrow dimension ($a \gg d$).

Figure 4 shows the nature of the transformations and the configuration actually solved.

If $c_1 = \exp[\frac{1}{2}\pi(U+iV)]$, where V is the potential and U the stream function, then the positive x_1 axis is at unit potential and the positive y_1 axis is at unit potential. The z_1 plane is transformed into the z_2 plane by the Schwarz transformation⁸ $z_2 = 2\pi \sin^{-1}z_1$ which gives

$$E_x = -\partial V/\partial x = 1/[\coth\pi y/2 \sin^2\pi x/2 + \tanh\pi y/2 \cos^2\pi x/2] \quad (4)$$

$$E_y = -\partial V/\partial y = -1/[\tan\pi x/2 \cosh^2\pi y/2 + \cot\pi x/2 \sinh^2\pi y/2]. \quad (5)$$

E_x approaches the constant value one, and E_y approaches zero, when y is large. If the large cross-sectional dimension of the wave guide (along the y axis of z_2) is much greater than the small dimension ($a \gg d$), then Eqs. (4) and (5) give good approximations to the field from the edge of the wave guide to the center. In the case of the actual wave guide, E_y must be zero and E_x equal to one at the center. For the wave guides used $a > 5d$ and the above equations give $|E_y| < 0.003$ and $1.000 > E_x > 0.993$ at the center of the guide

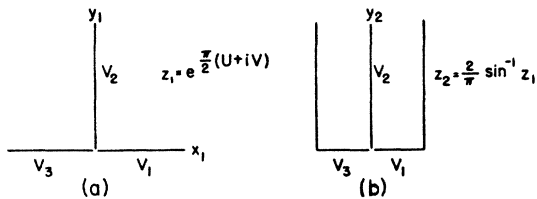


FIG. 4. (a) Configuration for which the electric field distribution is solved and (b) conformal transformation used.

⁸ W. R. Smythe, *Static and Dynamic Electricity* (McGraw-Hill Book Company, Inc., New York, 1939), p. 80.

TABLE IV. Dimensions of wave guides used.

Guide	Int. dimensions	Electrode thickness	Electrode spacing	1/electrode spacing
1	1.016 × 2.286 cm	0.6350 cm	0.1904 ± 0.0005	5.252
2	1.016 × 2.286 cm	0.1651 cm	0.4255 ± 0.0005	2.350
3	0.4318 × 1.067 cm	0.0813 cm	0.1753 ± 0.0005	5.705

($y = 1/2a$), so that they represent a very good approximation to the case of a wave guide without supporting dielectric material.

Now consider the effect on the center of a Stark component of the deviations from a uniform field ($E_x = 1, E_y = 0$). For a second-order Stark displacement, the frequency shift, $\Delta\nu$, produced by a field E , is $\Delta\nu = CE^2$, where C is some constant. The intensity of the microwave energy in the TE_{01} mode varies with y as $\sin^2\pi y/a$. The transitions of primary importance are those which the angular momentum about the x axis does not change ($\Delta M = 0$). The number of such transitions is proportional to the microwave intensity and the square of the cosine of the angle between the microwave electric field (always parallel to the x axis) and the Stark electric field, or proportional to $(\sin^2\pi y/a)(E_x^2/E^2)$. Hence, the average displacement of a Stark component of this type is

$$\langle \Delta\nu \rangle_{av} = \frac{\int CE^2 \sin^2\pi y/a (E_x^2/E^2) dx dy}{\int \sin^2\pi y/a (E_x^2/E^2) dx dy}, \quad (6)$$

where the integration need be taken only over one-quarter of the cross-sectional area of the guide, on one side of the septum and between the center and one wall.

Setting $E_x = E_{x0} + \delta E_x$ where E_{x0} is the field strength in the center of the guide, $(\delta E_x)/(E_{x0}) \ll 1$ and $(E_y)/(E_{x0}) \ll 1$, Eq. (6) may be approximated as

$$\langle \Delta\nu \rangle_{av} = CE_{x0}^2 \left[1 + 2E_{x0} \int \delta E_x dx + \frac{4}{aE_{x0}^2} \left\{ \int \sin^2\pi y/a \delta E_x^2 dx dy + \int \sin^2\pi y/a E_y^2 dx dy \right\} \right]. \quad (7)$$

Since the potential between the septum and the wave guide is fixed, $\int (E_{x0} + \delta E_x) dx = \text{constant}$ and hence $\int \delta E_x dx = 0$, and the fractional error in $\langle \Delta\nu \rangle_{av}$ produced by field inhomogeneities is

$$\frac{4}{aE_{x0}^2} \left\{ \int \sin^2\pi y/a \delta E_x^2 dx dy + \int \sin^2\pi y/a E_y^2 dx dy \right\}. \quad (8)$$

The dimension d of the wave guide is taken to be one in these expressions. It should be noted that the field

TABLE V. Stark splitting and resulting dipole moment of OCS excited state $v_2=1$.

$\Delta\nu$ meas. Mc	μ debye units
- 6.98	0.6984
- 18.60	0.7037
- 28.08	0.7033
- 28.52	0.6974

Average = 0.7007 ± 0.0014 debye units and the corrected value is 0.7000 ± 0.004 debye. This agrees with the value of 0.701 ± 0.007 debye found by Hill *et al.*⁹ for this vibrational state.

⁹ A. G. Hill, M.I.T. Research Lab. of Electronics Quarterly Progress Report (October 15, 1948).

variation qE_x produces a broadening of the Stark line, but according to (8) does not in first-order approximation shift the line's center. E_y and δE_x may be obtained from (4) and (5) and the integrals of (8) evaluated numerically. δE_x can be expressed in the rather simple form

$$\delta E_x = \frac{e^{-\pi y} - \cos \pi x}{\cosh \pi y - \cos \pi x}. \quad (9)$$

Similarly, for a first-order Stark component where $\Delta\nu = C'E$, the fractional error in $\langle \Delta\nu \rangle_w$ may be found to be

$$\frac{2}{aE_x a^2} \int \sin^2 \pi y / a E_y^2 dx dy. \quad (10)$$

As confirmation that these integrals are not large, it may be observed that the relative intensity of Stark components with change of M ($\Delta M = \pm 1$) to those with no change of M ($\Delta M = 0$) is given by the same type of integral. Since no components associated with a change in M have been observed in the guides used, their intensities are small.

The presence of the thin strip of supporting dielectric material at the wave guide walls was partially allowed for by solving exactly for the microwave intensity instead of using the simple form $\sin^2 \pi y / a$ of the above formulas. The effect of the dielectric on the Stark field, which was not considered, is probably small.

Numerical integration of the two terms of (8) over y shows that for each value of x the integrals are almost exactly equal. No general proof of this could be found, however.

For second-order Stark components, the fractional correction to the dipole moments is just one-half of that for the displacement $\Delta\nu$. The dipole moment correction was found to be -0.1 percent for guide No. 3 and -0.6 percent for guide No. 2. For guide No. 1 a correction of -0.1 percent was estimated.

VIBRATIONAL-ROTATION INTERACTION

The rotational transitions discussed above are due to changes of rotational level where both initial and final levels are in the ground vibrational state. At room temperature, about eight percent of the OCS molecules

are in the first excited state of the perpendicular vibration ν_2 . The spectrum due to the $J=1 \rightarrow 2$ rotational transition of $O^{16}C^{12}S^{32}$ in this state consists of two lines at 24,355.50 Mc and 24,380.84 Mc.² These lines, the so-called l -type doublets, are not at the same frequency as the ground state line because of vibration rotation interaction.

The frequency of a rotational transition $J-1 \rightarrow J$ of a linear molecule is

$$\nu = 2B_v J, \quad (11)$$

where

$$B_v = B_e - \sum_i \alpha_i (v_i + d_i/2), \quad (12)$$

and B_e = rotational constant if the nuclei were stationary at their equilibrium positions. α_i is a coefficient of the change of rotational constant per quantum of excitation of the i th vibrational state and v_i and d_i are the corresponding quantum number and degree of degeneracy of the vibration.

The change in vibrational state therefore produces a shift in frequency of the line. However, for the explanation of the doublet structure, the vibration-rotation interaction Hamiltonian of this type of degenerate vibration must be considered.

The total wave function, to a first order of approximation, which is a solution of the rotation-vibration interaction Hamiltonian is, according to Nielsen⁹

$$\psi = \Pi_S \exp(-q_s^2/2) H_{v_s}(q_s) \Pi_R \times \exp(-\rho_r^2/2) F_{\rho_r}{}^{l_r}(\rho_r) \exp(\pm il_r \phi_r) \psi_R^0, \quad (13)$$

where $\Pi_S \exp(-q_s^2/2) H_{v_s}(q_s)$ and $\Pi_R \exp(-\rho_r^2/2) \times F_{\rho_r}{}^{l_r}(\rho_r)$ are the contributions of the normal vibrations, $l_r \hbar/2\pi$ is the angular momentum about the symmetry axis due to vibration and ψ_R^0 is the pure rotational part of the wave function.

The angular dependence or what may be considered the rotational part of this wave function is identical with the rotational wave function for the slightly asymmetric top. This may be expected since the degenerate vibration introduces an angular momentum around the molecular symmetry axis similar to the angular momentum K for a symmetric top. In addition, the vibration-rotation interaction splits the degenerate bending modes in a way similar to the splitting of symmetric top levels by a slight asymmetry.

If the amount of splitting is calculated from the rotation-vibration interaction, or empirically evaluated, a linear molecule in an excited bending mode may thus be treated as a slightly asymmetric rotor.

Since notation, matrix elements, and Stark effects have been well established for the asymmetric top, we shall treat the OCS molecule as a slightly asymmetric prolate rotor. Using the asymmetric rotor notation $J_{\tau M}$, where τ is a pseudo-quantum number, the l -type doublets correspond to the transitions $1_{0M} \rightarrow 2_{-1M}$ and $1_{1M} \rightarrow 2_{0M}$.

⁹ H. H. Nielsen, Phys. Rev. **60**, 794 (1941).

EXCITED STATE DIPOLE MOMENT

The Stark effect for the slightly asymmetric top has been derived¹⁰ as a function of the energy difference between the near degenerate levels, the matrix element of transition between these levels, and the dipole moment of the molecule. Using the $J\tau M$ notation, upon the application of an external field E , the energy levels are

$$W = \frac{1}{2} [H(J\tau M) + H(J\tau' M) \pm ([H(J\tau M) - H(J\tau' M)]^2 + 4\mu^2 E^2 \Phi^2)^{\frac{1}{2}}], \quad (14)$$

where

$$H_{(J\tau M)} = W_{J\tau^0} + E^2 \sum_{J\tau^0} \frac{\mu_0^2 [(\Phi_{20})_{J\tau M, J'\tau' M}]^2}{W_{J\tau^0} - W_{J'\tau'^0}}.$$

The summation is over all levels where $W_{J\tau^0} \neq W_{J'\tau'^0}$ and Φ_{20} is the matrix element of direction cosine.

If we let ν_0 be the frequency of the hypothetical transition between the center of the doublet levels for $J=1$ and the center for $J=2$, then for any value of E

$$\nu_0 = \frac{\frac{1}{2} [H(20M) + H(2-1M) - H(11M) - H(10M)]}{h}. \quad (15)$$

The separation between the two doublet lines is

$$\Delta\nu = \{ (H(20M) - H(2-1M))^2 + 4\mu^2 E^2 \Phi_{22}^2 \}^{\frac{1}{2}} - \{ (H(11M) - H(10M))^2 + 4\mu^2 E^2 \Phi_{11}^2 \}^{\frac{1}{2}}. \quad (16)$$

Using this formula, Table V shows the values of dipole moment measured for this transition.

In measuring $\Delta\nu$, the interval between the components was measured. In this way the second-order shifting of the levels is negligible.

ANOMALOUS LINES

Two weak lines symmetrically situated on either side of the l -type doublets were observed upon the application of a Stark field. The lines first appear, with very weak fields, separated by about twice the separation of the doublets themselves. With increasing voltage these lines move apart in frequency and increase in intensity, passing through a maximum intensity and eventually fading out.

These lines are explained by considering them as corresponding to the transitions of the perturbed $1_{0M} \rightarrow 2_{0M}$ and $1_{1M} \rightarrow 2_{-1M}$ levels, forbidden in the absence of a field but allowed in the presence of a field.

Consider the unperturbed wave functions to be A_{20}^0 , A_{2-1}^0 , A_{11}^0 , and A_{10}^0 and the perturbed functions

$$\begin{aligned} \psi_1 &= a_1 A_{20}^0 + b_1 A_{2-1}^0 \\ \psi_2 &= a_2 A_{20}^0 - b_2 A_{2-1}^0 \\ \psi_3 &= a_3 A_{11}^0 + b_3 A_{10}^0 \\ \psi_4 &= a_4 A_{11}^0 - b_4 A_{10}^0. \end{aligned} \quad (17)$$

The Hamiltonian including the field is $H_0 - E \sum \Phi_{20} \mu_0$ ignoring the contribution of polarization by the field.

¹⁰ S. Golden and E. B. Wilson, J. Chem. Phys. 16, 669 (1948).

Since the wave function of the original level can be considered as comprising two complete orthonormal sets of two members each then

$$\begin{aligned} b_1 &= a_2 & a_1 &= b_2 \\ b_3 &= a_4 & a_3 &= b_4 \end{aligned} \quad (18)$$

and the complete solution yields

$$\begin{aligned} a_1 &= \left[\frac{(W_1 - W_{2-1}^0)^2}{(\mu^2 E^2 / 36) + (W_1 - W_{2-1}^0)^2} \right]^{\frac{1}{2}} \\ b_1 &= \left[\frac{\mu^2 E^2 / 36}{(\mu^2 E^2 / 36) + (W_1 - W_{2-1}^0)^2} \right]^{\frac{1}{2}} \\ a_3 &= \left[\frac{(W_3 - W_{10}^0)^2}{(\mu^2 E^2 / 4) + (W_3 - W_{10}^0)^2} \right]^{\frac{1}{2}} \\ b_3 &= \left[\frac{\mu^2 E^2 / 4}{(\mu^2 E^2 / 4) + (W_3 - W_{10}^0)^2} \right]^{\frac{1}{2}} \end{aligned}$$

where

$$\begin{aligned} W_1 &= \frac{1}{2} [W_{20}^0 + W_{2-1}^0 + \{ (W_{20}^0 - W_{2-1}^0)^2 \\ &\quad + 4\mu^2 E^2 \Phi_{20M, 2-1M}^2 \}^{\frac{1}{2}}] \\ W_3 &= \frac{1}{2} [W_{11}^0 + W_{10}^0 + \{ (W_{11}^0 - W_{10}^0)^2 \\ &\quad + 4\mu^2 E^2 \Phi_{11M, 10M}^2 \}^{\frac{1}{2}}] \end{aligned} \quad (19)$$

and where

$$\Phi_{20M=1, 2-1M=1}^2 = 1/36, \quad \Phi_{11M=1, 10M=1}^2 = \frac{1}{4}.$$

The separation of these anomalous lines from each other then is

$$\Delta\nu = \{ (W_{20}^0 - W_{2-1}^0)^2 + (\mu^2 E^2 / 9) \}^{\frac{1}{2}} + \{ (W_{11}^0 - W_{10}^0)^2 + \mu^2 E^2 \}^{\frac{1}{2}}, \quad (20)$$

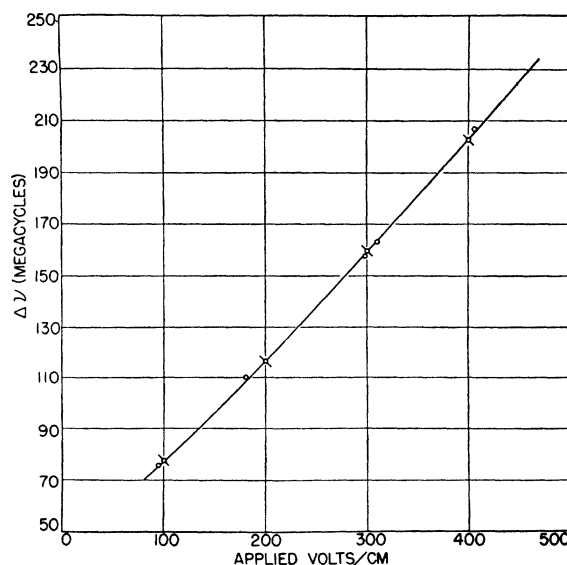


FIG. 5. Frequency difference between anomalous lines as a function of field strength.

where $W_{20}^0 - W_{2-1}^0 = 37.82$ mc, $W_{11}^0 - W_{10}^0 = 12.60$ mc, and $\mu = 0.700$ debye units.

The plot of theoretical separation *vs.* field strength (see Fig. 5) agrees with the plot of experimental separation *vs.* field strength to within 0.5 percent. The intensities of both components are the same and are proportional to $[a_1^2 a_4^2 - 2a_1 a_4 b_1 b_4 + b_1^2 b_4^2]$. This expression varies from zero when the field is zero through a maximum as the field increases and decreases to zero

again for large fields. Rough intensity measurements showed that the intensity followed the theoretical expectations.

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Some General Properties of Nuclear Reaction and Scattering Cross Sections*

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This paper deals with some general properties of nuclear reaction and scattering cross sections which can be derived from the dispersion-theoretic treatment of nuclear reactions as given, for example, by Wigner and Eisenbud. The form of the cross section near the resonances is found to satisfy the Breit-Wigner formula with corrections of the order Γ^2/D^2 , Γ =level width, D =level spacing. In the region between the resonances, the behavior is found to be of three types. In the first two types, simple minima occur differing in order of magnitude in the two cases by a factor Γ^2/D^2 . In the third type, a flat non-resonance maximum occurs between the resonances considered, accompanied by two minima. This type of behavior may be associated with a large fluctuation of Γ or D at some of the neighboring levels. The cross sections are explicitly calculated for some special choices of the Γ and D , and the averages compared with those of the statistical theory. The effect of the potential scattering on the scattering cross sections is briefly discussed.

I. INTRODUCTORY REMARKS

IT is the purpose of this paper to investigate in a more or less quantitative manner the behavior of nuclear reaction and scattering cross sections both near and between the resonances, using as a basis the results of the formal (dispersion) theory of nuclear reactions.¹⁻⁵

These results are concerned first with the estimation of the maxima and minima of the cross sections (corresponding to the behavior near and between the resonances), both of which may be derived from the general theory, even when the explicit form of the cross section as a function of energy cannot be easily calculated, provided only that it is assumed that $\Gamma/D \ll 1$, Γ being the width of the resonance lines and D their spacing.

On the basis of more far-reaching assumptions about the nuclear parameters, it is possible to calculate the cross sections explicitly as functions of the energy; the results so obtained serve to indicate what may happen if the assumption $\Gamma/D < 1$ is relaxed. It is then also possible to calculate the average cross sections, and to

compare the results thus obtained with those obtained from the statistical theory,⁶ which serves to clarify the connection between the quantities occurring in the latter and the parameters of nuclear dispersion theory.

II. NOTATION

The following results or definitions are used in the remaining sections:

σ_{st} denotes the cross section for the reaction in which the pair of particles denoted by "s" collide to form the pair "t." In particular, σ_{ss} denotes the scattering cross section for the collision of the pair "s." As is usual in this work, "s," "t," etc., denote not only the type of particles, but also their internal states, their spin orientation, and their relative angular momentum. If there are n such possible reactions "st" associated with the same compound nucleus in a given energy range, then σ_{st} may be expressed, in this energy range, in terms of the n -dimensional, symmetric, unitary collision matrix U by the formula

$$\sigma_{st} = (\pi/k_s^2) |(U-1)_{st}|^2. \quad (2.1)$$

k_s is the relative (reduced) wave number of the pair "s" in their center-of-mass system. U itself may be expressed in terms of the diagonal "potential" matrices B , C , and ω , and the real symmetric "derivative"

⁶ V. F. Weisskopf, Phys. Rev. **52**, 295 (1937).

* This paper contains some results of a Ph.D. dissertation submitted to Princeton University (1949).

¹ E. P. Wigner and L. Eisenbud, Phys. Rev. **72**, 29 (1947).

² E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

³ E. P. Wigner, Am. J. Phys. **17**, 99 (1949).

⁴ E. P. Wigner and T. Teichmann (unpublished).

⁵ T. Teichmann, Ph.D. dissertation, Princeton (1949). This reference contains further details of the methods described in this paper.