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Abstract

Extended measurements in the microwave rotational spectrum of carbonylsulfide (OCS) are presented and correlated with the data obtained by other investigators. Precision measurements of rotational transitions for $J_{1\rightarrow 2}$, $J_{2\rightarrow 3}$, $J_{3\rightarrow 4}$, $J_{4\rightarrow 5}$ allow the evaluation of precise reciprocal moments of inertia in the ground vibrational state, and the centrifugal distortion coefficient. From frequencies observed for $O^{16}C^{12}S^{32}$, $O^{16}C^{13}S^{32}$, and $O^{16}C^{12}S^{34}$, internuclear distances have been calculated. Equilibrium moments of inertia and internuclear distances cannot as yet be given, since thus far only one of the three vibrational-rotational interaction coefficients (α_2) has been reported. Theoretical considerations involving such equilibrium data are discussed. Data on ℓ-doubling in $O^{16}C^{12}S^{32}$, $O^{16}C^{13}S^{32}$, and $O^{16}C^{14}S^{32}$ are presented. The Stark effect of carbonylsulfide has been measured in $O^{16}C^{12}S^{32}$ and $O^{16}C^{13}S^{32}$. These measurements lead to the evaluation of the dipole moment and indicate the effect of isotopic changes on the dipole moment.

ROTATIONAL ABSORPTION SPECTRUM OF OCS

Carbonyl sulfide (OCS) is known to be a linear molecule. In this paper we have attempted to correlate existing information regarding the structure of this molecule which may be deduced from the rotational absorption spectrum, and to give extended measurements in order to allow a unified presentation. We wish to point out that several other investigators have been instrumental in obtaining much of the experimental and theoretical data considered below.

1. General Theory

The rotational contribution to the energy levels of an unperturbed linear rotor in any vibrational state can be shown to be[1]

$$W = \left[J(J+1) - \ell^2\right] hcB_v - \left[J(J+1) - \ell^2\right]^2 hcD_v \qquad (1)$$

where W is in ergs,

J = total orbital angular momentum quantum number

ℓ = quantum number of angular momentum parallel to figure axis due to a degenerate bending vibration

h = Planck's constant

c = speed of light

B_v = "reciprocal moment of inertia" in cm^{-1}.

D_v = centrifugal distortion coefficient in cm^{-1}.

Thus, from the Bohr frequency condition and the selection rule $\Delta J = +1$, rotational transitions are induced in a molecule with an electric dipole moment by radiation with frequencies in cycles/sec given by

$$\nu_{J \rightarrow J+1} = 2cB_v(J+1) - 4cD_v\left[(J+1)^3 - \ell^2(J+1)\right] . \qquad (2)$$

The "reciprocal moment of inertia" of the molecule in any vibrational state is related to the moment of inertia with the atoms in the minima of the vibrational potentials through the relation[1]

$$B_v = B_e - \sum_i \alpha_i\left(v_i + \frac{d_i}{2}\right) \qquad (3)$$

where $B_e = \frac{h}{8\pi^2 I_e c}$ cm^{-1}

I_e = equilibrium moment of inertia

i = index over all vibrational states

v_i = vibrational quantum number

d_i = degeneracy of vibration: 1,2, ...

α_i = coefficient measuring vibration-rotation interaction in cm^{-1}.

It should be noted that this representation is the usual one; in view of present knowledge it would be better, perhaps, to sum over all vibrational states separately instead of grouping the degenerate ones. For example, in a linear triatomic molecule it is known that the bending vibration is doubly degenerate since two orthogonal planes may be passed through the figure axis. Yet the vibration-rotation interaction is different for the two degenerate vibrations, so that the rotational absorption has a doublet structure when the molecule is in the bending vibrational state ($v_1 = v_3 = 0$; $v_2 = 1$). This splitting is referred to as ℓ-doubling. The difference of the displaced rotational energy levels in the two bending modes is given by

$$\Delta W_J = hqJ(J+1) \text{ ergs,} \tag{4}$$

and the two absorption lines ($J \rightarrow J+1$) are detected at frequencies different by

$$\Delta\nu = 2cq(J+1)$$

where $\Delta\nu$ is in cycles/sec, and q is a measure of the difference of vibrational-rotational interactions, in cm^{-1}.

In other words, the two bending vibrational modes have different interaction coefficients (α_2); if the average is used in the standard form for B_v the same results are obtained as if, more correctly, every mode were summed over independently. The theory of ℓ-type doubling has been discussed by Herzberg[2] and calculations have been made by H. H. Nielson and W. H. Shaffer[3].

The term values may also be perturbed by external fields. In the presence of an electric field the energy levels of a molecule with an electric dipole moment are perturbed because of the interaction of the rotating dipole with the static electric field, i.e., the Stark effect. This perturbation energy for linear molecules in the ground vibrational state is of second order and has been shown to be[4]

$$W^{(2)}_{J,m} = \frac{4\pi^2\mu^2E^2I}{h^2}\;\frac{J(J+1) - 3m^2}{J(J+1)(2J-1)(2J+3)} \qquad (5)$$

where m = magnetic quantum number and $|m| \leq J$
μ = electric dipole moment
E = electric field strength.

Thus, the original transition has the spatial degeneracy partly removed and the frequencies for induced transitions are now given by

$$\left(\nu_{\text{Stark}}\right)_{J\rightarrow J+1} = \left(\nu_o\right)_{J\rightarrow J+1} + \Delta\nu\ . \qquad (6)$$

The selection rule $\Delta J = +1$, $\Delta m = 0$ applies when the Stark field is parallel to the electric vector of the incident radiation, and this is the case in these experiments. This is called a π-type transition and is the only case which will be considered in this paper. When $\Delta m = 0$,

$$\Delta\nu = \frac{6m^2(16J^2 + 32J+10) - 8J(J+1)^2(J+2)}{J(J+2)(2J-1)(2J+1)(2J+3)(2J+5)}\left(\frac{\mu^2E^2}{h^2\nu_o}\right)\ .$$

The perturbation of the energy levels given by Eq. (5) are indicated in Fig. 1. The absorption spectrum for a given isotopic configuration with and without a Stark field is indicated in Fig. 2.

For the transition $J \rightarrow J+1$, $\Delta m = 0$, the square of the dipole direction cosine matrix element has a $\left[(J+1)^2 - m^2\right]$ dependence. Therefore, the intensity of each component follows a $\epsilon\left[(J+1)^2 - m^2\right]$ law; $\epsilon = 1$ when $m = 0$ and $\epsilon = 2$ for $0 < |m| \leq J$, because of the spatial degeneracy of the $+$ and $-m$ levels.

The study of the rotational absorption spectra of a molecule with various isotopic compositions with and without known electric fields can be used to deduce certain physical quantities.[5] First, if the vibrational interaction energies are ignored for zero-point vibrations, i.e., with a rigid rotor approximation, interatomic distances may be calculated if as many isotopic forms of the molecule are studied as there are structural parameters. Thus, in a linear unsymmetrical triatomic molecule with known atomic masses m_1, m_2, m_3, the moment of inertia is a function of the two interatomic distances, r_{12}, r_{23}. One may then solve the following set of equations for the interatomic distances r_{12} and r_{23}.

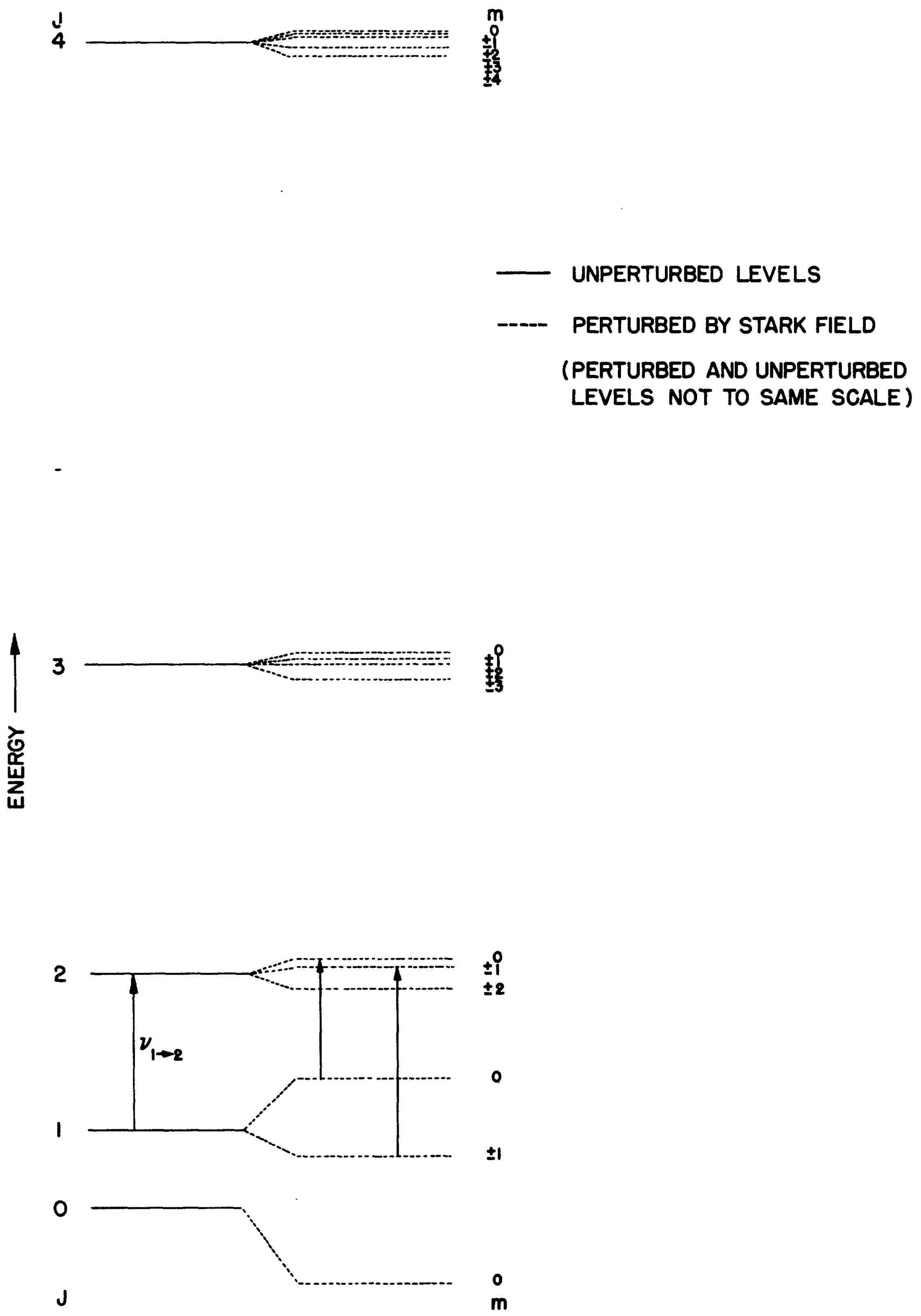
J
4
m
0
±1
±2
±3
±4
UNPERTURBED LEVELS
PERTURBED BY STARK FIELD
(PERTURBED AND UNPERTURBED LEVELS NOT TO SAME SCALE)
3
0
±1
±2
±3
ENERGY
2
0
±1
±2
$\nu_{1\rightarrow 2}$
0
1
±1
0
0
J
m

Fig. 1. Energy levels in a rigid linear rotor.

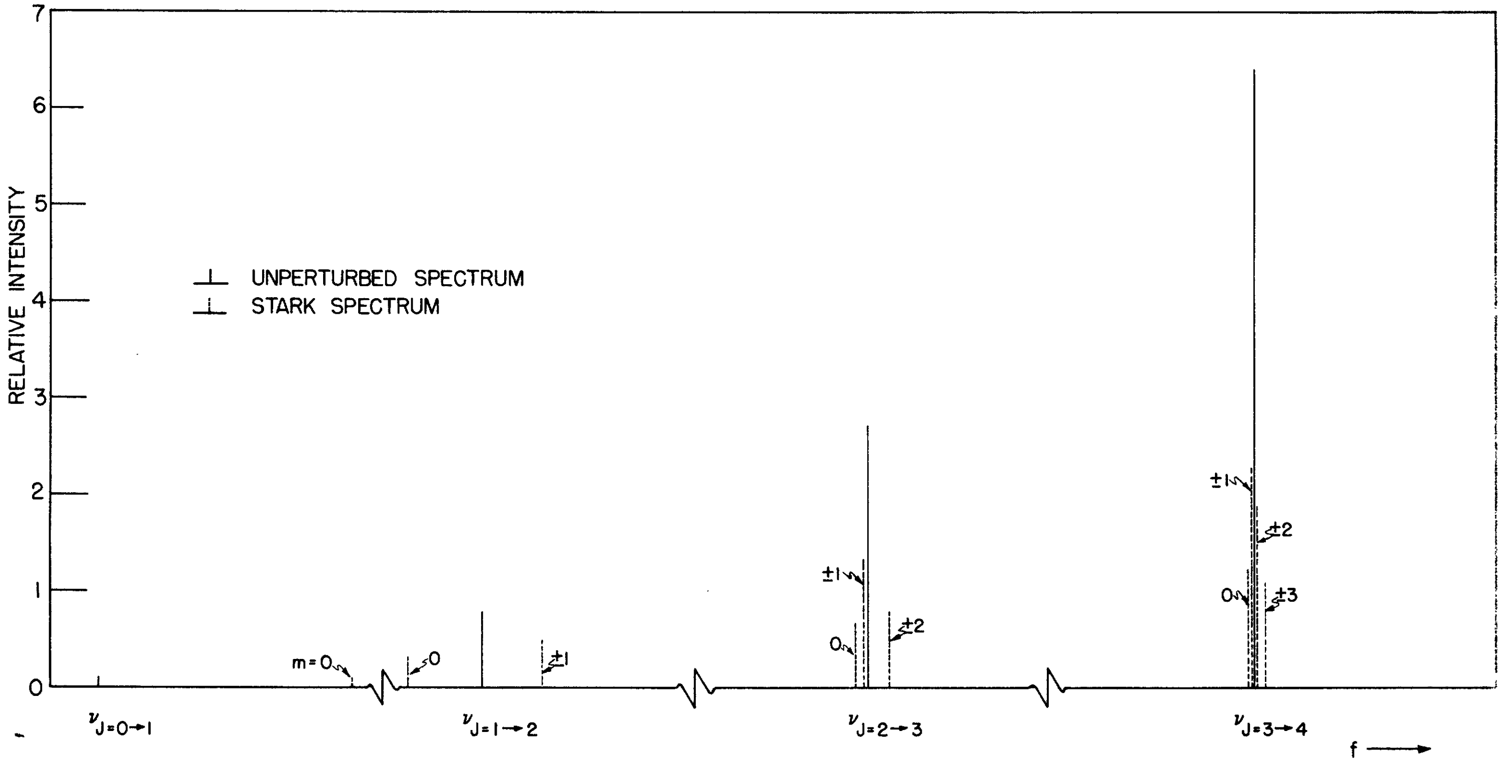

Fig. 2. Theoretical spectrum of a rigid linear rotor. Separation of unperturbed lines = $2B_v$. Frequency scale about unperturbed lines expanded to show relative shifts in Stark effect.

$$I_{(m_1 m_2 m_3 r_{12} r_{23})} = \frac{2(J+1)h}{8\pi^2 \nu_0}$$

$$I_{(m_1' m_2 m_3 r_{12} r_{23})} = \frac{2(J+1)h}{8\pi^2 \nu_0'} .$$

The primes refer to the isotopically different molecule.

If absorptions are detected for the isotopic molecules in the ground vibrational state for two different J transitions, the centrifugal distortion energy can be evaluated (see Eq. (1)). Also if one J transition for each of the excited vibrational states is observed, the zero-point vibrational energy can be eliminated and the equilibrium moment of inertia can be evaluated. In this way the true equilibrium interatomic distances can be computed. The vibrational-rotational interaction energies must be used in the precise evaluation of the interatomic distances, since only the equilibrium distances may be assumed to be independent of nuclear mass changes.[6]

Secondly, the dipole moment of the molecule may be calculated for the molecule in any given vibrational state, and for any isotopic form, by measuring the Stark effect in that vibrational state in a known, homogeneous electric field. The dipole moment may also be inferred from the line intensities, since the absorption coefficient α_{max} in cm^{-1} can be shown to be

$$\frac{4\pi^2 N_o h\nu^3\mu^2}{3k^2T^2\Delta\nu c} e^{-hcB_vJ(J+1)/kT}$$

where N_o = molecular density (molecules/unit volume)

h = Planck's constant

ν = resonant frequency

μ = dipole moment

k = Boltzmann constant

T = gas temperature in ^oK

$\Delta\nu$ = half breadth of absorption at half intensity.

However, the dipole moment may not be evaluated by this method with facility or accuracy since the measurement of absolute absorption depends upon so many things; e.g., the purity of the sample, the calibration of the measuring system, etc.

2. Experimental Method

Some knowledge of the structure of OCS is available from electron-diffraction data.[7] Such information is useful in calculating the reciprocal moment to an accuracy sufficient for a preliminary prediction of the spectral line frequencies to be expected in the microwave region. Alternatively, the bond distances may be calculated from the resonant bond model of Pauling.[8] A number of investigators have studied the absorption of OCS in the 24000-Mc/sec region[9,10,11,12,13,14] and Dakin, Good, and Coles[9] have reported some preliminary Stark measurements.

The absorption lines studied by us were detected with an apparatus which has come to be known as a sweep spectroscope. The frequencies were measured with a secondary frequency standard calibrated with the National

Bureau of Standards frequency signals transmitted by WWV. We will outline only briefly both of these instruments.

The sweep spectroscope is roughly of the type in general use in the field of microwave spectroscopy.[15] Figure 3 is a block diagram of the apparatus. The absorption cell used for these measurements consists of 9.75 meters of 3-cm brass waveguide equipped with an electrode for the application of the Stark field. Figure 3a shows the electrode orientation.

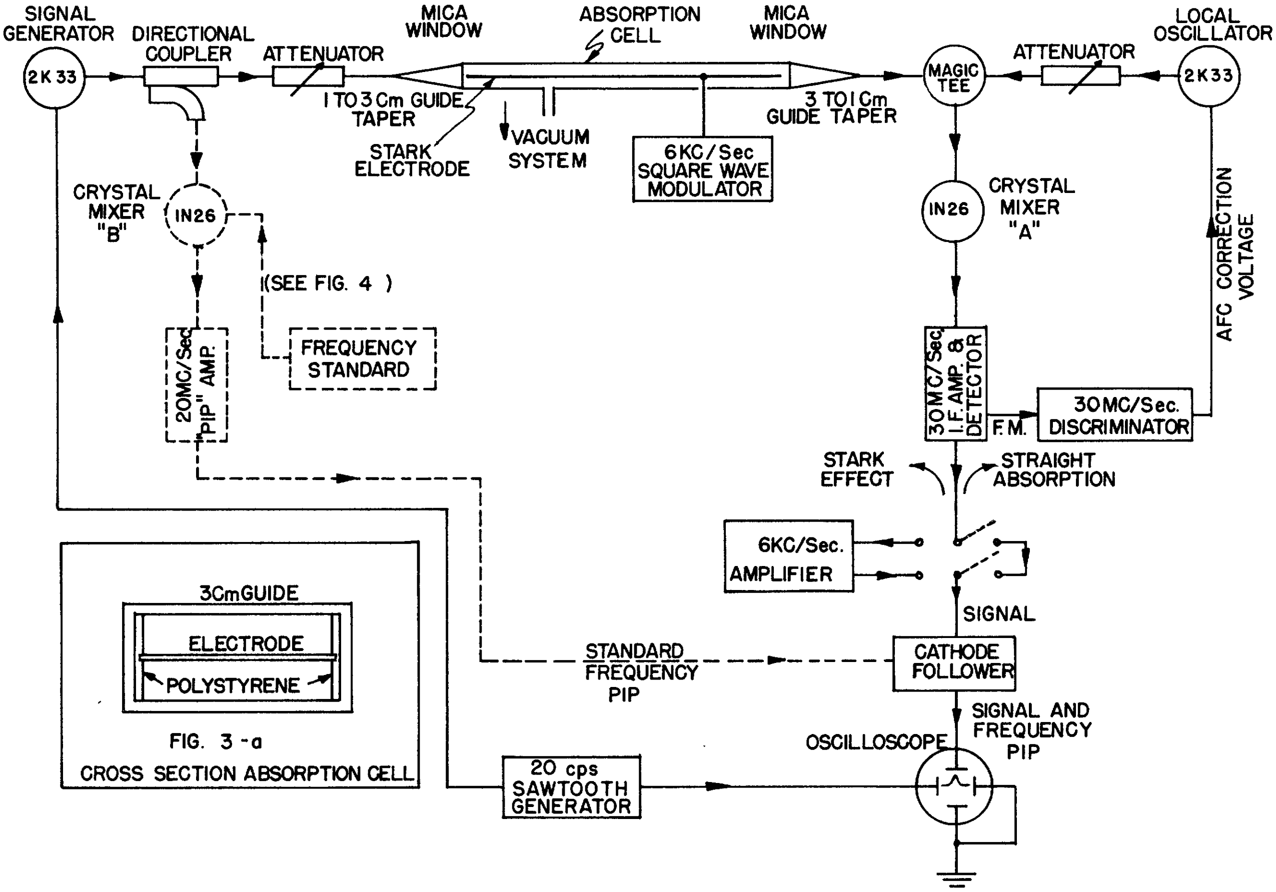
SIGNAL GENERATOR
2K33
DIRECTIONAL COUPLER
ATTENUATOR
MICA WINDOW
ABSORPTION CELL
MICA WINDOW
1 TO 3 Cm GUIDE TAPER
STARK ELECTRODE
VACUUM SYSTEM
6 KC/Sec SQUARE WAVE MODULATOR
3 TO 1 Cm GUIDE TAPER
MAGIC TEE
ATTENUATOR
LOCAL OSCILLATOR
2K33
CRYSTAL MIXER "B"
IN26
(SEE FIG. 4)
FREQUENCY STANDARD
20MC/Sec "PIP" AMP.
CRYSTAL MIXER "A"
IN26
AFC CORRECTION VOLTAGE
30 MC/Sec I.F. AMP. & DETECTOR
F.M.
30MC/Sec. DISCRIMINATOR
STARK EFFECT
STRAIGHT ABSORPTION
6KC/Sec. AMPLIFIER
SIGNAL
3CmGUIDE
ELECTRODE
POLYSTYRENE
FIG. 3 -a
CROSS SECTION ABSORPTION CELL
STANDARD FREQUENCY PIP
CATHODE FOLLOWER
SIGNAL AND FREQUENCY PIP
OSCILLOSCOPE
20 cps SAWTOOTH GENERATOR

Fig. 3. Block diagram of microwave spectroscope.

Figure 4 is a picture of the $O^{16}C^{12}S^{32}$ absorption $J = 1 \rightarrow 2$. The line is square-wave Stark-modulated at a low frequency so that the unperturbed and perturbed absorptions appear in alternate time intervals. Figure 5 shows the same absorption as it appears thru a 6-kc/sec amplifier. The sweep of Fig. 4 has been expanded considerably compared with that of Fig. 5. The $m = 0$ line is on the right; $m = \pm 1$ line is on the left. It is apparent that the sum of the individual absorptions equals the unperturbed absorption (center) and that their intensities obey the expected $\epsilon(2^2-m^2)$ relation.

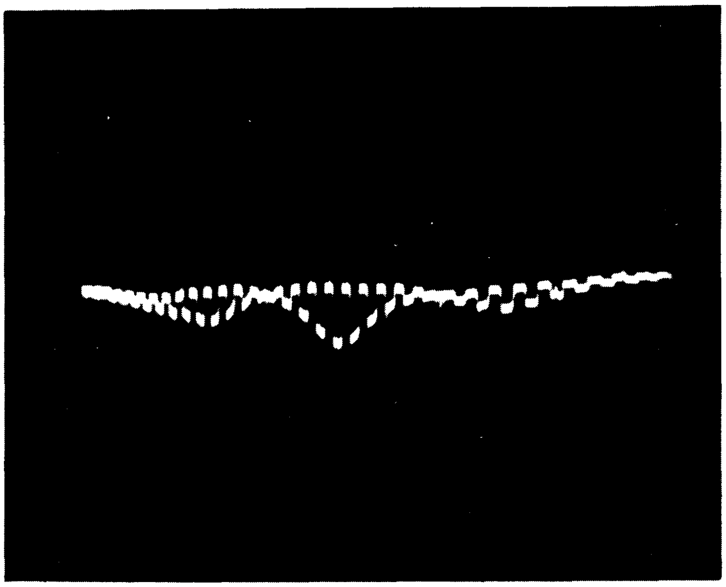

Fig. 4. Stark effect in COS $J_{1\rightarrow 2}$.

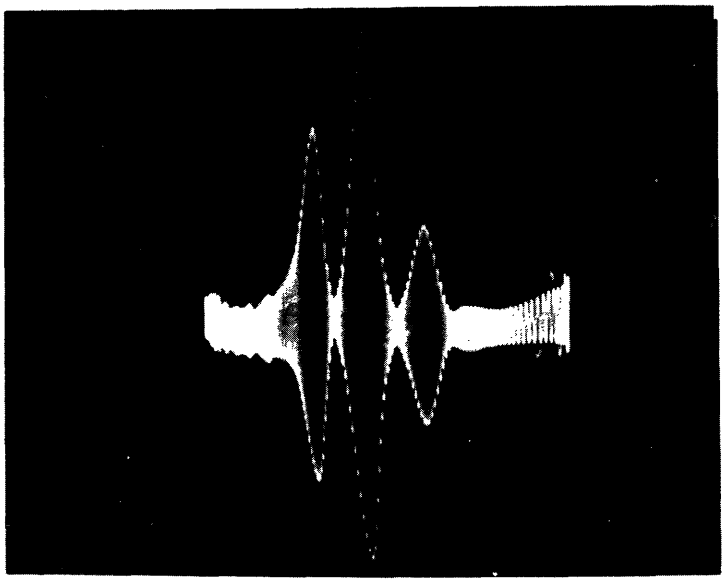

Fig. 5. Stark effect in COS $J_{1\rightarrow 2}$ (Signal through narrowband 6-kc/sec amplifier).

The type of frequency standard used is described in Vol. 11 of the M.I.T. Radiation Laboratory Series[16] and is shown schematically in Fig. 6. The frequency standard "pip" is generated by the beating of the frequency-swept signal generator of the spectroscope with the frequency standard signal. If this "pip" is made to coincide in time with an absorption line, the standard frequency will be set at the line frequency plus or minus the pip amplifier i-f frequency. Therefore, the standard is set higher and lower than the line frequency, by an amount equal to the pip amplifier i-f frequency,

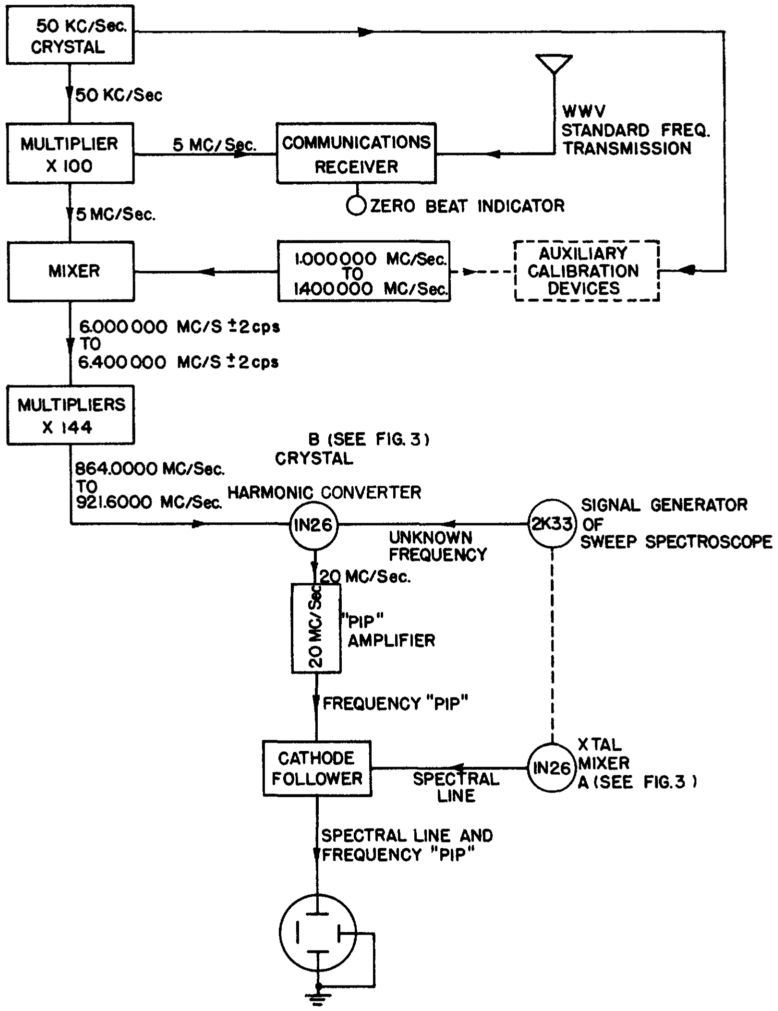
50 KC/Sec. CRYSTAL
50 KC/Sec
MULTIPLIER X 100
5 MC/Sec.
COMMUNICATIONS RECEIVER
WWV STANDARD FREQ. TRANSMISSION
ZERO BEAT INDICATOR
5 MC/Sec.
MIXER
1.000000 MC/Sec. TO 1.400000 MC/Sec.
AUXILIARY CALIBRATION DEVICES
6.000000 MC/S ±2cps TO 6.400000 MC/S ±2cps
MULTIPLIERS X 144
864.0000 MC/Sec. TO 921.6000 MC/Sec.
B (SEE FIG. 3) CRYSTAL HARMONIC CONVERTER
IN26
UNKNOWN FREQUENCY
2K33
SIGNAL GENERATOR OF SWEEP SPECTROSCOPE
20 MC/Sec.
20 MC/Sec
"PIP" AMPLIFIER
FREQUENCY "PIP"
CATHODE FOLLOWER
SPECTRAL LINE
IN26
XTAL MIXER A (SEE FIG.3)
SPECTRAL LINE AND FREQUENCY "PIP"

Fig. 6. Block diagram of frequency measurement scheme.

and these two readings are made. The average of these two readings is the actual molecular absorption frequency.

3. Experimental Data

Measurements of the OCS spectrum are given in Table I. The $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ transitions were measured with 2K33-type klystron generators. The $J = 3 \rightarrow 4$ and $J = 4 \rightarrow 5$ transitions were measured with this same type of oscillator by using the second-harmonic energy generated when the fundamental radiation is applied to a non-linear silicon crystal.

It should be noted that the error quoted is not a probable error. The standard is adjusted to WWV to at least 2 parts in 10^7. Doppler shift in transmissions from WWV due to fading appears to be less than one part in 10^7 and WWV itself is claimed to be accurate to two parts in 10^8. The absorption lines are generally less than 200 kc/sec wide when measured

TABLE I. Observed Absorption Frequencies

Molecule	Transition J→J + 1	v_1 v_2 v_3	Frequency Mc/sec.	Reference
$O^{16}C^{12}S^{32}$	1→2	0 0 0	24325.92 ± .01	
	1→2	0 1 0	24380.70 ± .2	
	1→2	0 1 0	24355.49 ± .2	
	2→3	0 0 0	36488.82 ± .03	
	3→4	0 0 0	48651.64 ± .05	
	4→5	0 0 0	60814.08 ± .05	
$O^{16}C^{12}S^{33}$	1→2	0 0 0	24020.3 ± .1	(12)
$O^{16}C^{12}S^{34}$	1→2	0 0 0	23731.33 ± .03	(13)
	3→4	0 0 0	47462.40 ± .05	
$O^{16}C^{13}S^{32}$	1→2	0 0 0	24247.82 ± .03	
	1→2	0 1 0	24301.05 ± .2	
	1→2	0 1 0	24275.25 ± .2	
$O^{16}C^{14}S^{32}$	1→2	0 0 0	24173.0 ± 1.	(14)
	1→2	0 1 0	24224.0 ± 1.	(14)
	1→2	0 1 0	24197.0 ± 1.	(14)

TABLE II. Derived Constants for OCS

Term Value Parameters

Molecule	B_o cm^{-1}	I_{000}x10^{-40}gm^2	cD_v cycles/sec	cq Mc/sec	$c\alpha_2$ Mc/sec	Reference
$O^{16}C^{12}S^{32}$	.202864	138.0	1600 ± 50	6.31 ± .03	-10.54 ± .1	
$O^{16}C^{12}S^{33}$	.200319	139.7				(12)
$O^{16}C^{12}S^{34}$	.197910	141.4	1400 ± 100			
$O^{16}C^{13}S^{32}$	.202216	138.4		6.45 ± .03	-10.08 ± .12	
$O^{16}C^{14}S^{32}$	.20159	138.8		6.7 ± .1	-9.4 ± .3	(14)

Internuclear Distances

	r_o(C=O)	r_e(C=O)	r_o(C=O)	r_e(C=S)	r_o(S=C=O)	Ref.
Covalent Radii	1.17 A.		1.54 A.		3.71 A.	(8)
OCO	1.1632	1.1615 A.				(1)
SCS			1.554			(1)
OCS	1.1637 ± .0013*		1.5586 ± .0010*		3.7223 ± .0003*	
OCS	1.16 ± .02		1.56 ± .03		3.72 ± .05	(4)

* Error determined from internal consistency of distances calculated from various isotopic forms; see text.

and readings are made to 4 parts in 10^7. The J = 1→2 line of $O^{16}C^{12}S^{32}$ has been measured many times over a period of 3 months giving results which are constant within ± 10 kc/sec. The error quoted is thus large enough to insure reproducibility of the lines measured.

These data may be immediately reduced to yield the centrifugal stretching coefficient, the moments of inertia of the molecules in the ground vibrational state, and, to a rigid rotor approximation, the interatomic distances. These reduced data are given in Table II. We have used $h = 6.6242 \times 10^{-27}$ erg-sec, $H^1 = 1.65990 \times 10^{-24}$ gm, and in atomic mass units $C^{12} = 12.00386$, $C^{13} = 13.00754$, $S^{32} = 31.98089$, and $S^{34} = 33.97711$.

The J = 1→2 transition frequencies agree, within the experimental error, with those measured by Townes,[12] and Dakin, Good and Coles.[13] Townes has also published values of the rotational absorption frequency of $O^{16}C^{12}S^{33}$ in the ground vibrational state and of $O^{16}C^{12}S^{32}$ in the doubly degenerate bending vibrational state.[12] We have measured the ℓ-doubling in $O^{16}C^{13}S^{32}$ and Roberts[14] has measured the ℓ-doubling for $O^{16}C^{14}S^{32}$. This measurement of the reciprocal moment of inertia in an excited vibrational state allows the evaluation of the α_2 coefficient in the expression for vibration-rotation interaction (Eq. (3)). Values of α_2 and q obtained are given in Table II. Since the similar coefficients for the interaction coefficients of the symmetric and antisymmetric stretching vibrations are not also known, this additional information is of no use at present in evaluating the equilibrium interatomic distances. Expressions due to Adel,[17] A. H. Nielsen,[18] and H. H. Nielsen[19] are available to calculate these unknown coefficients, but unfortunately the vibrational potential function of OCS is not well enough known to allow the coefficients to be computed with any accuracy. Of course the inverse process could be performed; i.e., that of solving for the two unknown cubic force constants, by using the known α_2's determined from isotopic molecules. We have investigated this problem and feel that present precision of the necessary data, the α_2's and the contrifugal distortion coefficients, is not great enough to yield significant values for these force constants.

Dakin,[13] Townes,[12] and their collaborators have analysed some of the factors limiting the accuracy of the determination of the dimensions of OCS. We consider the most important corrections are those due to zero-point vibrations.

Spectroscopic determination of molecular structure parameters is certainly not a new endeavor. Rotation, and vibration-rotation spectra in the infra-red have long been used for such purposes. In fact, the dimensions of OCO, a molecule chemically and structurally similar to OCS, have been obtained from rotation-vibration spectra with corrections made for zero-point vibration. This is of course possible only in a linear, symmetrical, triatomic molecule, since then only one distance must be determined from the one equilibrium moment of inertia. Only unsymmetrical linear molecules possess the permanent dipole moments necessary for pure rotational absorption. However, isotopic variations are readily observed, and though corrections for vibration-rotation interaction is very difficult, useful information is still obtained by making the rigid rotor approximation.

In the case of OCS the rigid rotor approximation is not a bad one, since it is the shift in frequency of the absorption due to an isotopic substitution upon which the interatomic distances are dependent. This may be seen roughly as follows.

Since the α_i themselves are a small correction, and the change of the α_i with isotope will be a much smaller correction, we may assume α_i/B_v to be constant to a zero order of approximation. The equilibrium moments of inertia may then be written as:

$$B_e = B_v + \sum_i \frac{\alpha_i d_i}{2} = \beta^2 B_v$$

$$B_e' = B_v' + \sum_i \frac{\alpha_i' d_i}{2} = \beta^2 B_v'$$

$$\text{where } \beta^2 = \left(1 + \frac{\sum \alpha_i d_i}{2B_v}\right) .$$

Ignoring the vibration interaction is thus roughly equivalent to changing the interatomic distances by the factor β. In OCS the correction term $\sum_i \alpha_i d_i/2$ can be as large as 60 Mc/sec; this will make β^2 about 1.01. Hence the calculated interatomic distances may be high by approximately $\frac{1}{2}$ per cent. The assumption that β is essentially constant is apparantly good to a rather high order, since calculations of interatomic distances from $O^{16}C^{12}S^{32}$ and $O^{16}C^{12}S^{34}$, from $O^{16}C^{13}S^{32}$ and $O^{16}C^{12}S^{32}$ and from $O^{16}C^{13}S^{32}$, $O^{16}C^{12}S^{34}$ yield identical results to about 0.1 per cent, the error listed in Table II.

It might be thought that a better approximation may be made to the interatomic distances by considering three isotopic molecules and solving for the interatomic distances in terms of frequency shifts alone. The purpose here would be to use the data to yield equilibrium distances to a higher accuracy since to zero order the vibration-rotation interaction might cancel. However, this is not the case. This is easily shown by solving for the interatomic distance in terms of the equilibrium moment of inertia of the original molecule I_e^{o}, and the equilibrium moment of inertia with a center and end atom changed, I_e^c and I_e^e. The equilibrium distances then turn out to be:

$$r_{12} = \frac{\frac{m_3^o}{m_1^o + m_2^o}\delta_e - \delta_c}{m_1^o\left(\frac{m_3^o}{m_1^o + m_2^o} - 1\right)}$$

$$r_{23} = \frac{\delta_e - \delta_c}{\Sigma m^o}$$

where

$$\delta_e^2 = \frac{\Sigma m^o \Sigma m^e (I_e^o - I_e^e)}{(m_3^o - m_3^e)}$$

and

$$\delta_c^2 = \frac{\Sigma m^o \Sigma m^c (I_e^o - I_e^c)}{(m_2^o - m_2^c)} .$$

By definition:

$$I_e - I_e' = \frac{h}{8\pi^2 c}\left(\frac{1}{B_v + \Sigma\frac{\alpha_i d_i}{2}} - \frac{1}{B_v' + \Sigma\frac{\alpha_i' d_i}{2}}\right)$$

$$= \frac{h}{8\pi^2 c}\left(\frac{1}{B_v} - \frac{1}{B_v'} + \frac{\Sigma\alpha_i' d_i}{2B_v'^2} - \frac{\Sigma\alpha_i d_i}{2B_v^2}\right) .$$

Again to zero order the α_i's are proportional to B_e or to B_v for the reasons stated above. Thus we may write

$$(r_{12})_e = (r_{12})_v(1 - \frac{\Sigma \alpha_i d_i}{2B_v})^{\frac{1}{2}}$$

$$(r_{23})_e = (r_{12})_v(1 - \frac{\Sigma \alpha_i d_i}{2B_v})^{\frac{1}{2}}$$

which are the identical expressions for the distances solved with only two isotopic molecules.

It is interesting to note the similarity of the O-C and C-S distances in the related molecules OCO and SCS. This is to be expected from the simple resonant bond model of Pauling. These comparison distances are given in Table II.

4. Stark Measurements

Stark measurements of the permanent electric dipole moment of OCS are interesting in that they give the order of magnitude of the dependence of the dipole moment on isotopic substitutions. Figures 7 and 8 show the experimental data for the Stark effect of the $J = 1 \rightarrow 2$ transition in $O^{16}C^{12}S^{32}$ and $O^{16}C^{13}S^{32}$ as a function of electric field strength. The dipole moments so determined in Debye units are 0.732 ± 1 per cent for $O^{16}C^{12}S^{32}$ and 0.722 ± 1 per cent for $O^{16}C^{13}S^{32}$. The probable statistical error is so low (.25 per cent) that the main error in the determination of the dipole moment is due to the error in the measurement of the field strength. This is essentially a matter of reading the voltage applied by the square-wave generator, since it can be shown that field inhomogeneities over the cross section of the waveguide slightly broaden the observed line without shifting it. The orientation of the central Stark electrode is critical in that errors in centering can cause appreciable shift of the Stark components, as well as line broadening. The septum centering in our apparatus is better than 0.5 per cent. The applied voltage can be determined to better than 1 per cent so that this is the limit of error of the measurement. However, the relative magnitudes are good to the probable error of fit or to 2.5 parts in 10^3. The indicated variation in dipole moment probably is due to the different zero-point vibration amplitudes in the isotopic molecules.

Good, Dakin, and Coles[9] have previously reported a preliminary value of .72 Debye units for the dipole moment of $O^{16}C^{12}S^{32}$ based on Stark effect measurements. The dipole moment of OCS has also been measured by the Debye method of observing the temperature dependence of the polarization

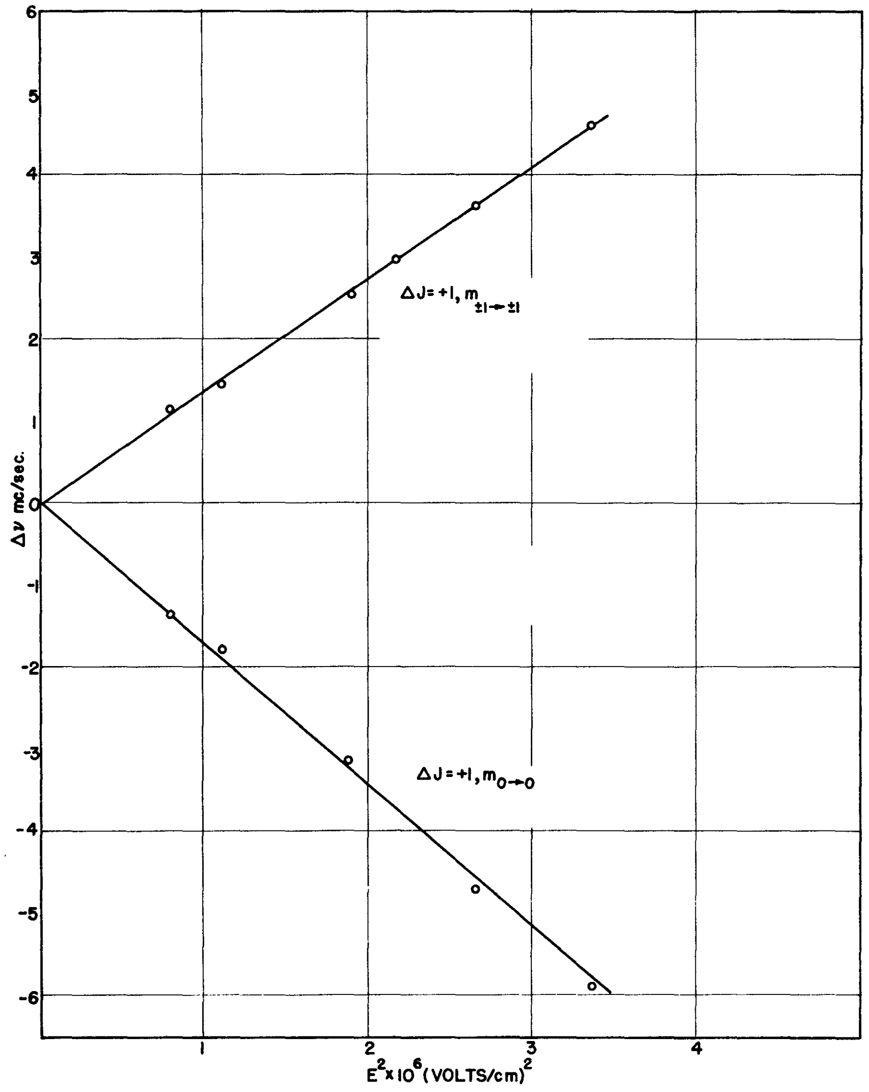

Fig. 7. Stark effect in $O^{16}C^{12}S^{32}$.

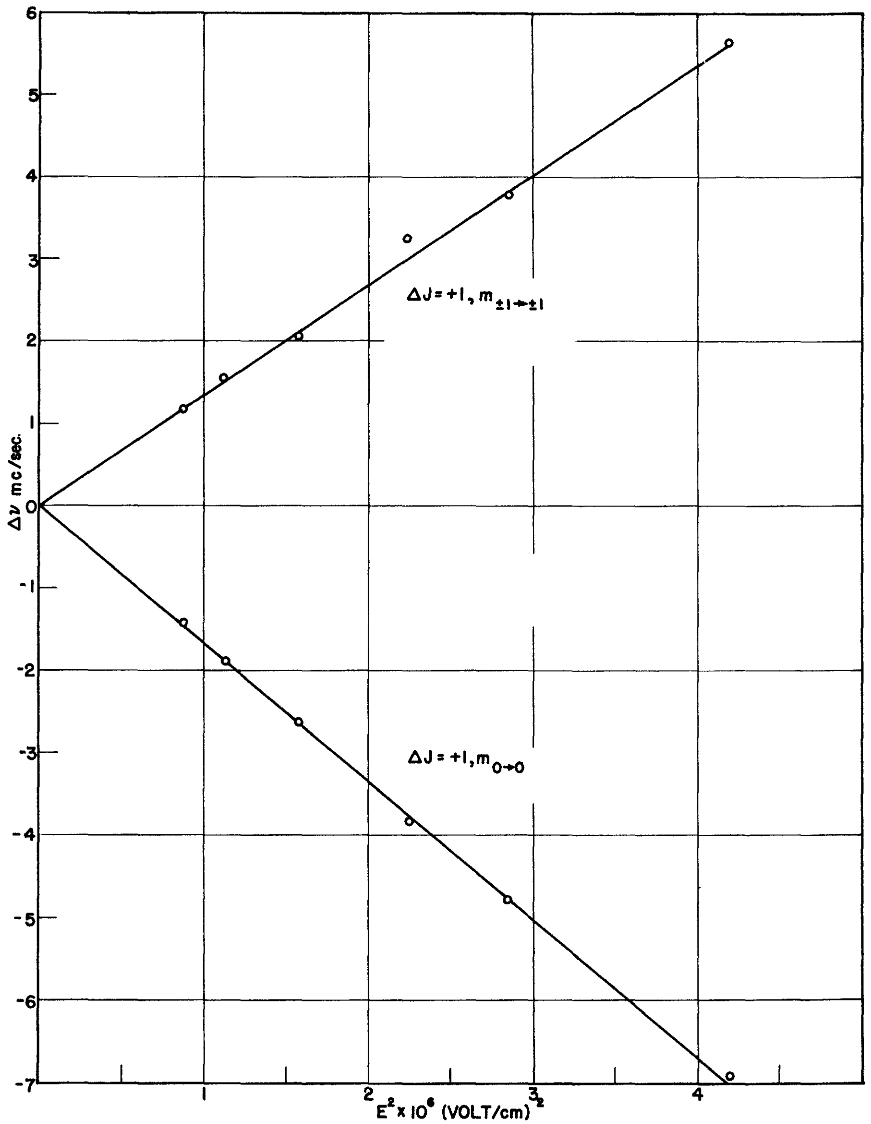

Fig. 8. Stark effect in $O^{16}C^{13}S^{32}$.

of the gas. Zahn and Miles[20] reported a value of .68 Debye units and Jelatis[21] has recently repeated the measurement and arrived at a value of .720 ± .005 Debye units for the electric dipole moment. The latter measurement checks well with our determination. The value of the dipole moment measured spectroscopically is independent of chemical impurities, as opposed to the Debye method in which the presence of impurities, especially those of a polar nature, may cause appreciable error. It should be pointed out that the spectroscopic value is determined for a given vibrational state (zero vibrational here), while the Debye method yields a statistical average of the dipole moment over all of the vibrational states of the molecule excited at the temperature of measurement.

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