Microwave Spectrum of Carbon Monsulfide*

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CS was produced by an electrical discharge through CS_2 and continuously flowed through a conventional Stark spectrometer. The $J=0\rightarrow1$ transitions of the isotopic species $C^{12}S^{32}$, $C^{12}S^{33}$, $C^{12}S^{34}$, and $C^{13}S^{32}$ were observed in their vibrational ground states. $C^{12}S^{32}$ was also observed in its first excited vibrational state. The spectra yield the following molecular constants: In Mc/sec,

$$B_e(C^{12}S^{32}) = 24\ 584.352\ \pm0.015,$$
$$B_e(C^{12}S^{33}) = 24\ 381.011\ \pm0.027,$$
$$B_e(C^{12}S^{34}) = 24\ 190.198\ \pm0.014,$$
$$B_e(C^{13}S^{32}) = 23\ 205.215\ \pm0.020,$$
$$\alpha(C^{12}S^{32}) = +\ 177.544\ \pm0.026,$$

$$eqQ(C^{12}S^{33}) = +\ 12.835\ \pm0.026,$$

Dipole moment = 1.97 ±0.02 Debye units,

Equilibrium bond distance = 1.5349±0.0002 A,

where B_e=equilibrium rotational constant, α=vibration-rotation interaction constant, and eqQ=electric quadrupole coupling constant.

The mass ratios calculated from the above B_e values are: S^{32}/S^{34} =0.941246±22, S^{32}/S^{33}=0.9696909±32, and C^{12}/C^{13}=0.9228447 ±20.

Nuclear magnetic interactions of S^{33} were also detected. The coefficient C of the $CI\cdot J$ coupling term was found to have the value 0.019±0.015 Mc/sec.

INTRODUCTION

THE present investigation was undertaken primarily as a wedge to develop techniques that would facilitate microwave absorption studies of rather short-lived molecules and free radicals. CS was considered a suitable first choice since it exhibits rather long lifetimes[1] at least in glass and quartz apparatus. In the experiment described here, CS was produced by an electrical discharge in CS_2. The CS was flowed through a Stark spectrometer, and its pure rotation spectrum was observed in the 6-mm region.

The $J=0\rightarrow1$ transitions of a number of isotopic species were measured (Table I) in their ground vibrational state. The $J=0\rightarrow1$ transition in the first excited vibrational state was also observed for the most abundant species $C^{12}-S^{32}$. From these measured transitions the molecular constants B_e, r_e, and α were calculated and tabulated in Table II. From the values of B_e for the various isotopic species, certain mass ratios of sulfur and carbon isotopes were calculated (Table III). The dipole moment was determined (Table II) from the second-order Stark effect of the $J=0\rightarrow1$ transition of $C^{12}-S^{32}$ in its ground vibrational state.

The hfs resulting from the S^{33} nuclear quadrupole interaction was completely resolved. The quadrupole coupling constant determined from this hfs together with the coupling coefficients of other sulfur compounds permitted a reasonable structure for CS to be proposed. The measured spacings in the hfs required the introduction into the interaction Hamiltonian of a term in-

volving the interaction of the magnetic moment of S^3 with the magnetic field produced by the rotation of the molecule as a whole (an $I\cdot J$ interaction term).

The OH free radical has been observed by Sanders, Schawlow, Dousmanis, and Townes[2] at microwave frequencies by use of a technique similar to that described here. However, in the case of OH, Zeeman modulation was used for detection purposes instead of Stark modulation (Zeeman modulation being suitable for free radicals). The electronic ground state of CS has been shown to be a $^1\Sigma^+$ state from its ultraviolet spectrum.[3] Consequently, it should probably be classified as a molecule and not as a free radical. Because CS was observed in the nonmagnetic ground state, Stark modulation was most suitable.

EXPERIMENTAL PROCEDURE

The small moment of inertia of CS requires that the lowest rotational transition, $J=0\rightarrow1$, fall in the 6-mm microwave region. Although klystrons are available in this region, it was found most convenient to use the second harmonic of a K-band klystron for all of the measurements. The frequency multiplication and de-

[1] P. J. Dyne and D. A. Ramsay, J. Chem. Phys. **20**, 1055 (1952).

TABLE I. Frequencies of the observed transitions of CS.

Molecule	Transition	Frequency, Mc/sec
$C^{12}S^{32}$	$J=0\rightarrow1$, $v=0$	48 991.000±0.006
$C^{12}S^{32}$	$J=0\rightarrow1$, $v=1$	48 635.912±0.040
$C^{12}S^{34}$	$J=0\rightarrow1$, $v=0$	48 206.948±0.006
$C^{13}S^{32}$	$J=0\rightarrow1$, $v=0$	46 247.472±0.020
	$J=0\rightarrow1$, $v=0$	
	$F=3/2\rightarrow3/2$	48 589.068±0.010
$C^{12}S^{33}$	$F=3/2\rightarrow5/2$	48 585.906±0.010
	$F=3/2\rightarrow1/2$	48 583.264±0.010

[2] Sanders, Schawlow, Dousmanis, and Townes, Phys. Rev. **89**, 1158 (1953). Also the OD spectrum has recently been reported by G. C. Dousmanis, Phys. Rev. **94**, 789(A) (1954).
[3] For references see G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 523.

TABLE II. Molecular constants.

$$B_e(\mathrm{C^{12}S^{32}}) = 24\ 584.352\ \pm 0.015\ \mathrm{Mc/sec}$$
$$\alpha_e(\mathrm{C^{12}S^{32}}) =\qquad 177.544\ \pm 0.026\ \mathrm{Mc/sec}$$
$$B_e(\mathrm{C^{12}S^{33}}) = 24\ 381.011\ \pm 0.027\ \mathrm{Mc/sec}$$
$$B_e(\mathrm{C^{12}S^{34}}) = 24\ 190.198\ \pm 0.014\ \mathrm{Mc/sec}$$
$$B_e(\mathrm{C^{13}S^{32}}) = 23\ 205.215\ \pm 0.020\ \mathrm{Mc/sec}$$
$$eqQ = +\qquad 12.835\ \pm 0.026\ \mathrm{Mc/sec}$$
$$\mathrm{I \cdot J\ coefficient,}\ C = +\quad 0.019\ \pm 0.015\ \mathrm{Mc/sec}$$
$$\mathrm{Dipole\ moment} =\qquad 1.97\ \pm 0.02\ \mathrm{Debye\ units}$$
$$\mathrm{Equilibrium\ bond\ distance,^a}\ r_e =\qquad 1.5349 \pm 0.0002\ \mathrm{A}$$

ᵃ $h = (6.62363 \pm 0.0016) \times 10^{-27}$ erg sec.

tection techniques were according to usual procedures.[4] Stark modulation was used.

A 60-cycle discharge of about 1100 v and about 30 ma was used for the production of CS. The discharge was in CS_2 at a pressure of approximately 0.7 mm, the vapor pressure of CS_2 at the temperature of a dry ice-acetone mixture. The separation of the aluminum electrodes was about two feet and the diameter of the discharge tube one inch. A considerable amount of free sulfur is formed in the discharge and condenses on the walls of the tube. CS polymerizes on the walls of the apparatus including the absorption cell as a black solid. Thin films appear dark red. This polymer gives a convenient indication of the existence of CS.

CS_2 was prevented from entering the absorption cell by interposing a cold trap between the discharge tube and the cell. The trap was maintained at $-122°C$ by an acetone-solid ether mixture. At this temperature CS_2 has no measurable vapor pressure and the CS itself is not condensed. The CS was pumped continuously through the six-foot X-band Stark cell throughout the final observations. The remaining CS that went completely through the cell without polymerizing was trapped in a liquid nitrogen trap. It was found that CS would be accumulated for several hours at liquid nitrogen temperatures. The CS polymerizes explosively when the temperature is raised above $-195°C$ (and sometimes without a deliberate increase in temperature), a rather annoying feature of the substance. The glass trap was usually shattered by one of these explosions.

Although the accumulation of CS polymer in the absorption cell does effect microwave transmission and the behavior of the Stark modulation system, spectroscopy may be done for periods of about thirty hours or more. The polymer is a fairly good insulator and only after many hours of use was the resistance across the Stark voltage input observed to be low. The polymer formed on the mica cell windows had no noticeable effect on microwave transmission.

After long periods of use, a corona discharge occurs between the Stark septum and the walls of the cell at Stark voltages above about 200 v. It is believed that this corona discharge is initiated by flakes of CS polymer

that scale off of the cell walls. If the temperature of the intermediate trap is then raised to about $-100°C$ to permit CS_2 to enter the cell under these conditions of breakdown the CS spectrum may be observed even after turning off the discharge tube. Apparently CS is formed in the corona. Under the proper conditions, the CS spectrum is more intense than when using the discharge tube without breakdown. The ions and free electrons produced in the discharge provide a considerable noise source and a continuous absorption modulated at the frequency to which the phase sensitive detector is tuned. The breakdown is usually detected in the receiving system in addition to the superposed spectrum. For this reason the original technique using the discharge tube was used in making the quoted measurements.

The cell was kept at dry ice temperatures for all of the measurements in the ground vibrational state. Line breadths were about 300 kc/sec. Room temperatures were used for the excited vibrational state measurements, higher temperatures favoring a higher population in the excited state.

From observation of the persistence of the spectral lines after discharge was turned off, the lifetime of the CS in the brass absorption cell was about 2 or 3 seconds at the longest. The lifetime depended upon the conditions of the cell.

The technique employed here for the study of the CS spectrum could probably be used for a number of other molecules and free radicals with lifetimes of the order of one-half second. Variations of the technique, in particular methods by which the desired molecule or fragment could be produced inside the absorption cell, would probably permit investigation of molecules of even shorter lifetimes. Such a possibility was suggested by the observation of the CS spectrum during Stark break down in the current experiment.

RESULTS

The rotational transition frequencies of a diatomic molecule for the selection rule $J = +1$ are given to good approximation by

$$\nu = 2[B_e - \alpha_e(v + \tfrac{1}{2})](J+1) - 4D_e(J+1)^3 \qquad (1)$$

neglecting hyperfine structure. Here $B_e = h/8\pi^2 I_e$ is the equilibrium rotational constant, α_e is the vibrational-rotational interaction constant, $D_e = 4B_e^3/\omega_e^2$ is the

TABLE III. Mass ratio comparisons.ᵃ

Mass ratio	Result from present data	Result from mass spectrographic and nuclear data
S^{32}/S^{34}	0.9412462 ± 22	$0.9412446 \pm\ 6$
S^{32}/S^{33}	0.9696909 ± 32	0.9696905 ± 10
C^{12}/C^{13}	0.9228447 ± 20	0.9228395 ± 11

ᵃ These and other comparisons are made in some detail in the article by Geschwind, Gunther-Mohr, and Townes, Revs. Modern Phys. 26, 444 (1954).

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

centrifugal distortion constant, and v is the vibrational quantum number. The measured frequencies of the $J=0\rightarrow1$ transitions of several isotopic combinations are recorded in Table I.

The values of D_e necessary for the calculation of the B_e and α_e values were determined from the vibrational frequency ω_e obtained from the ultraviolet data[3] for $C^{12}S^{32}$. The various molecular constants obtained from the spectra are included in Table II. The masses used in the calculations are from the mass spectrographic data of Ogata and Matsuda.[5] The B_e and α_e values for $C^{12}S^{32}$ compare nicely with the ultraviolet results.[3]

Comparison of the mass ratios calculated from the CS spectra with the best present values obtained from mass spectrographic and nuclear reaction data are made in Table III.

Comparison of the sulfur ratios is satisfactory but comparison of the C^{12}/C^{13} ratio is not within the supposed experimental errors. Additional data from the spectra of diatomic molecules would be useful. Perhaps the spectrum of CO would be suitable for another determination of the C^{12}/C^{13} ratio.

The nuclear spin of S^{33} is $\frac{3}{2}$. The $J=1$ state is split into a triplet. An analysis of the data for $C^{12}S^{33}$ indicates that the hyperfine structure of the $J=0\rightarrow1$ transition does not arise entirely from the interaction of the nuclear quadrupole moment with the rest of the molecule. There is a measurable $\mathbf{I}\cdot\mathbf{J}$ interaction between the spin of S^{33} and the rotational angular momentum. Equation (1) must then be modified by the addition of two interaction terms. The interaction energy then has the form

$$E = -eqQ(\text{Casimir function})$$
$$+\tfrac{1}{2}C[F(F+1)-I(I+1)-J(J+1)]. \quad (2)$$

The quadrupole coupling constant eqQ and the $\mathbf{I}\cdot\mathbf{J}$ coupling coefficient C are given in Table II together with the other calculated molecular constants. The positive value for C is in keeping with the positive nuclear magnetic moment of S^{33}. The small separations of the hfs lines made intensity comparison and assignment particularly easy since all three lines could be observed together on the oscilloscope.

The dipole moment of $C^{12}S^{32}$ in its ground vibrational state was determined from its Stark effect. The Stark cell was calibrated with the known Stark effect of OCS in the usual way. The result is included in Table II.

DISCUSSION

A reasonable bond structure for CS may be deduced from the measured quadrupole coupling constant[6] of

$C^{12}S^{33}$ and from consideration of other sulfur-containing molecules for which the quadrupole coupling has been measured. This has already been done by one of us (G.R.B.) and C. H. Townes.[7] For completeness we shall consider this problem again here.

First suppose that the nonhybridized structures,

$$C^+-S^-, \quad C=S, \quad \text{and} \quad C^-\equiv S^+,$$
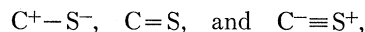
are plausible structures. The measured bond distance favors a combination of the latter two structures. Furthermore the eqQ of C^+-S^- is negative, whereas the observed value is positive. Therefore we assume that C^+-S^- does not contribute significantly. A combination of the remaining two structures with appropriate hybridization can be shown to give a suitable set of structures.

The dipole moment and bond distance of CS indicate that the unhybridized $C^-\equiv S^+$ structure would contribute about 27 percent. But the unhybridized $C=S$ structure contributes a negative eqQ and $C^-\equiv S^+$ has a zero eqQ value. Then to attain the measured eqQ for the molecule hybridization is necessary. Fifty percent s-hybridization gives consistent results. With this hybridization $C=S$ gives a zero eqQ value and $C^-\equiv S^+$ the value 34.4 Mc/sec if one assumes that the coupling per unbalanced p electron is -55 Mc/sec.[7] Now with hybridization, instead of $C^-\equiv S^+$ contributing 27 percent it contributes 40 percent. This gives an eqQ for the molecule of $+13.8$ Mc/sec which compares satisfactorily with the measured value $+12.84$ Mc/sec.

Thus for the structure of CS we choose $C=S$ to have 60 percent importance and $C^-\equiv S^+$ to have 40 percent importance, each with 50 percent s-hybridization of the p_σ bonds.

[5] K. Ogata and H. Matsuda, Phys. Rev. **89**, 27 (1953).
[6] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

[7] G. R. Bird and C. H. Townes, Phys. Rev. **94**, 1203 (1954).