V. MICROWAVE SPECTROSCOPY

Prof. M. W. P. Strandberg   Dr. R. B. Lawrance   J. G. Ingersoll
Dr. R. E. Hillger   B. F. Burke   H. R. Johnson
Dr. G. W. King   J. R. Eshbach   M. T. Weiss
                             B. V. Gokhale

A. ORGANIC MOLECULES

Experimental work on microwave absorption spectra of organic compounds has begun. The following compounds have been studied:

Methyl Mercaptan	$H_3C - SH$
Ethyl Mercaptan	$H_3C - CH_2 - SH$
Dimethyl Sulphide	$H_3C - S - CH_3$

Absorption lines have thus far been located only in the case of methyl mercaptan. These are:

A close doublet with frequencies   Estimated intensity

25,290.9 Mc/sec
and $\left\{ \alpha \sim 10^{-6}/cm \right.$
25,291.8

Two more lines
25,246.6 Mc/sec $\left\{ \alpha \sim 10^{-7}/cm \right.$
25,259.9

Each of these latter lines might again be a close doublet; but it was not possible to resolve them on account of insufficient intensity.

The measurement of Stark-shift gives, from each of these lines, a dipole moment μ of about 1.06 Debye units (parallel to "a" axis). The intensity indicates that 1 percent abundance is just detectable on a sensitive system.

The frequencies of the close doublet are very nearly equal to the frequency for the $0_{00} \rightarrow 1_{01}$ transition predicted by simple rigid-rotor theory based on the model described below. CH_3 forms the usual tetrahedral structure.

$$r_{CH} = 1.09 \text{ A,}$$
$$r_{SH} = 1.34 \text{ A,}$$
$$r_{CS} = 1.82 \text{ A,}$$
$$\angle HSC = 100°$$

The spectrum studied so far is indicative of internal rotation of SH group about the CS axis. However, application of internal rotation theory must await further investigation.

No absorption lines have been found for either of the other two compounds. Such a negative conclusion must, of necessity, be of a provisional character.

Both the compounds mentioned above possess large moments of inertia and hence small "rotational constants". Strong absorption lines therefore result from transitions out of states which have large angular momenta. Such lines generally fall far outside the microwave region that can be investigated at present. These absorption lines which result from transitions out of states of small angular momenta have frequencies in a suitable range, but their intensities are quite small on account of the low statistical weights of states with small angular momenta.

It is not impossible for a strong absorption line to occur within a suitable frequency range, but its prediction would require extremely laborious calculations based on available molecular-structure data, and they are usually inadequate.

For these reasons the only course open to us is a thorough search of the available frequency range. The observation of lines requires a narrow band amplifier used in conjunction with a microwave generator swept slowly through a small frequency range. The search over the available 8, 000. Mc/sec interval is therefore a painfully slow process.

The interval from 19, 000 Mc/sec to 25, 000 Mc/sec was searched in this manner for absorption lines of ethyl mercaptan with no success. However, there is some ground for fear that the sample was contaminated in the process of introduction into the absorption cell. It is therefore intended to examine this compound once more.

For methyl sulphide the interval searched has been 27,000 Mc/sec, to 19,000 Mc/sec. No absorption lines have been found.   B. V. Gokhale

B.   DEUTERO-AMMONIAS

Measurements of the inversion-rotation spectra of the deutero-ammonias have been made in the 7, 000 Mc/sec to 80, 000 Mc/sec region. Thirty-five lines of NH_2D and NHD_2 have been measured and identified by means of the Stark effect. As expected, our results show that for these molecules only simultaneous rotational and inversion transitions can be observed. Thus, corresponding to each $J_\tau \to J_{\tau'}$ transition, two absorption lines can be observed separated by either twice the rotational energy separation or twice the inversion splitting of the levels involved.

From our observations, the inversion splittings of the partially deuterated molecules can be calculated, and are found to be in good agreement with the Dennison and Uhlenbeck (1) inversion doubling theory. Thus the inversion splittings for the ammonia molecules are approximately as follows: 24, 000 Mc/sec for NH_3; 12, 000 Mc/sec for NH_2D; 5, 000 Mc/sec for NHD_2; 2, 000 Mc/sec for ND_3. Our results are also in agreement with the structural parameters of ammonia as given by Herzberg (2). The sign of the nuclear quadrupole coupling constant was also measured and found to be negative,

as expected.

A technical report is now being prepared giving a complete list of our observed lines and our interpretation of these spectra.   K. Sawyer is also investigating the frequency region below 7, 000 Mc/sec.

References

1. D. M. Dennison, G. E. Uhlenbeck: Phys. Rev. 41, 313 (1932).

2. G. Herzberg: Infrared and Raman Spectra, p. 439 (D. Van Nostrand, New York, 1945).

M. T. Weiss

C.   KETENE

1. Synthesis

Since the Quarterly Progress Report, July 15, 1950, a new system for ketene synthesis has been built. Figure V-1 is a diagram of this system. It is closed, mainly so that small quantities (3 cc is typical) of isotopic acetones may be used with very little waste. Although slow in operation, requiring several hours per cc of ketene, it appears to give a yield of about 70 percent. This compares favorably with previous methods. Acetone is circulated around the path ABCDE by heat applied at A(50° C water bath) and tap water cooled condenser at D.   B contains a nichrome wire (see J. Org. Chem. 5, 122, 1940) electrically heated to a dull red, which causes pyrolysis of the acetone; one of the main products formed is ketene.

Ketene vapor passes through the water-cooled condenser F and the capillary G (1 m long, 0. 4 mm bore) and is condensed in traps H and I which are liquid nitrogen cooled. The ketene in trap H is then distilled at $-78°$ C (dry ice and acetone bath) to trap I, which is liquid nitrogen cooled. The liquid remaining in H is mainly acetone, and is distilled back into A for another run.

Further purification of the ketene is accomplished by two more distillations at $-78°$ C, which seems to remove compounds less volatile than ketene. Those more volatile were originally removed by slowly raising the sample temperature, while pumping on it, until about one-third of it had vaporized. Now, this process is monitered by a spectroscope, set, for example, on the frequency of the $J = 0 \rightarrow J = 1$ line. Considerably less than the upper third of the sample appears to be an impurity (possibly CO). The sample is kept at liquid nitrogen temperatures since slow deterioration, over a period of weeks, was noticed when it was kept at $-78°$ C. Slow decrease of absorption intensity of the lines is observed; the lines drop to half their initial intensity after about half an hour when a sample is held for that long in a brass waveguide at room temperature. This decrease is considerably less when the waveguide is cooled with dry ice.
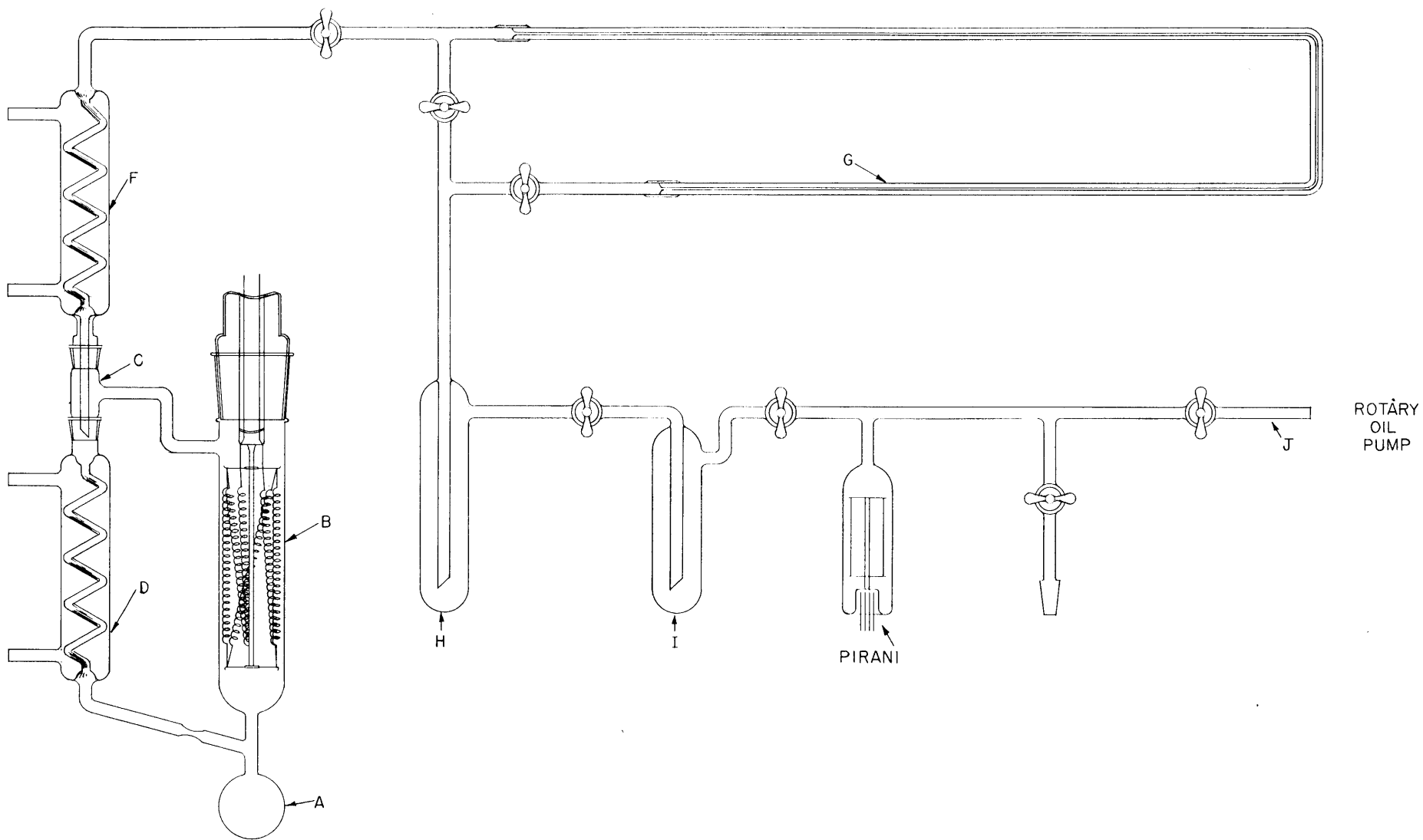
Fig. V-1 System for ketene synthesis.

2. $H_2^1C_2^{12}O^{16}$

Fifteen new absorption transitions of this molecule have been observed since the last report. They are summarized in Table I. The lines, frequencies, intensities and Stark patterns are well-fitted by asymmetric rotor theory using Lawrance's correction for centrifugal distortion (forthcoming technical report). The constants used are listed in Table II.

A check of the calculations of dipole moment has indicated an error which changes the values reported in the October Progress Report. In addition, an error in the frequency measurement of the $J = 0 \rightarrow J = 1$ transition of the molecule in the ground vibrational state has been found; this eliminated the discrepancy mentioned in the July Progress Report.

3. $D_2^2C_2^{12}O^{16}$

This isotopic ketene was synthesized with a sample of 3 cc of 97 percent pure heavy acetone kindly supplied us by Prof. Lord of the M.I.T. department of physical chemistry.

Fifteen transition frequencies of this molecule have been measured, and are listed in Table III. The molecular parameters which fit these line frequencies are listed in Table II.

4. $D^2H^1C_2^{12}O^{16}$

This isotopic ketene was synthesized from acetone containing roughly 50 percent light and 50 percent heavy acetone. Three lines have been found and identified so far, and are listed in Table IV. Table II contains the constants which fit these observations. Theoretical intensities will be halved because the purest obtainable sample of this molecule will be only 50 percent pure.
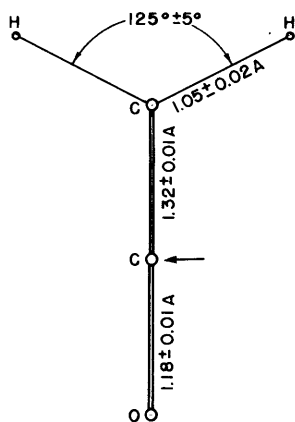
5. Structure

Provided the usual plane-molecule, symmetrical representation is adopted, the structure of ketene involves four parameters. Unfortunately, the position of the center of gravity of the molecule is extremely close to the location of the carbon atom marked with an arrow in Fig. V-2, for all reasonable isotopic modifications. Consequently, it seems very difficult to determine the position of this nucleus to any accuracy. We have tentatively assumed that 0.9 $r_0(C = C) = r_0 (C = O)$. Actually, we have only measured the angle HCH, $r_0(C - H)$, and $r_0(C = O)$ $+r_0 (C = C)$.

Fig. V-2 Structure of ketene.

Table I. $H_2^1C_2^{12}O^{16}$

1) Ground vibrational state

Initial State	Final State	Frequency	Calc. Intens. $\times 10^{-7}$
$0_{0,0}$	$1_{0,1}$	20,209.20	36
$1_{0,1}$	$2_{0,2}$	40,417.90	280
$1_{1,0}$	$2_{1,1}$	40,793.62	650
$1_{1,1}$	$2_{1,2}$	40,038.80	630
$2_{0,2}$	$3_{0,3}$	60,625.68	960
$2_{1,2}$	$3_{1,3}$	60,057.92	2500
$2_{1,1}$	$3_{1,2}$	61,190.24	2600
$2_{2,1}$	$3_{2,2}$	60,615.88	5300
$2_{2,0}$	$3_{2,1}$	60,617.30	5300
$9_{1,9}$	$9_{1,8}$	16,980.97	14
$10_{1,10}$	$10_{1,9}$	20,753.90	18
$11_{1,11}$	$11_{1,10}$	24,903.53	22
$12_{1,12}$	$12_{1,11}$	29,430.02	27
$13_{1,13}$	$13_{1,12}$	34,333.14	33
$14_{1,14}$	$14_{1,13}$	39,612.55	40

2) Excited vibrational states

Initial State	Final State	Frequency	Initial State	Final State	Frequency
0_{00}	1_{01}	20,220.64	1_{10}	2_{11}	40,809.98
0_{00}	1_{01}	20,232.33	1_{11}	2_{12}	40,926.95
0_{00}	1_{01}	20,267.17	1_{11}	2_{12}	40,087.77
1_{01}	2_{02}	40,440.17	1_{11}	2_{12}	40,110.92
1_{01}	2_{02}	40,462.26	1_{11}	2_{12}	40,135.35
1_{01}	2_{02}	40,532.78			

Table II. Molecular Constants (Ground vibrational state)

Quantity	$H_2^1C_2^{12}O^{16}$	$D_2^2C_2^{12}O^{16}$	$H^1D^2C_2^{12}O^{16}$
b + c (megacycles)	20,209.14	17,673.42	18,821.67
b − c (megacycles)	377.41	568.138	472.422
δ	0.001386	$(4.26479 \pm 0.00020) \times 10^{-3}$	0.002633
μ (Debye units)	1.417	1.423	

Table III $D_2^2 C_2^{12} O^{16}$

1) Ground vibrational state

Initial State	Final State	Frequency	Calc. Intens. $\times 10^{-7}$
$0_{0,0}$	$1_{0,1}$	17,673.44	45
$1_{0,1}$	$2_{0,2}$	35,345.13	350
$1_{1,0}$	$2_{1,1}$	35,913.66	170
$1_{1,1}$	$2_{1,2}$	34,777.36	160
$8_{1,8}$	$8_{1,7}$	20,448.71	6.4
$9_{1,9}$	$9_{1,8}$	25,558.93	8.6
$10_{1,10}$	$10_{1,9}$	31,235.60	11
$22_{2,21}$	$22_{2,20}$	18,737.62	8.5
$23_{2,22}$	$23_{2,21}$	22,181.36	11
$24_{2,23}$	$24_{2,22}$	26,050.17	13
$25_{2,24}$	$25_{2,23}$	30,368.36	16
$26_{2,25}$	$26_{2,24}$	35,159.06	21

2) Excited vibrational states

Initial State	Final State	Frequency
$0_{0,0}$	$1_{0,1}$	17,726.71
$1_{0,1}$	$2_{0,2}$	35,431.86
$1_{1,0}$	$2_{1,1}$	36,048.40
$1_{1,1}$	$2_{1,2}$	34,835.26
$1_{1,1}$	$2_{1,2}$	34,842.81

Table IV $H^1 D^2 C_2^{12} O^{16}$ (Ground vibrational state)

Initial State	Final State	Frequency
$0_{0,0}$	$1_{0,1}$	18,821.68
$9_{1,9}$	$9_{1,8}$	21,254.31
$10_{1,10}$	$10_{1,9}$	25,975.83

6. Plans for Future Work

Accurate values of δ for these molecules can only be obtained by measuring a set of Q-branch transitions between levels of $K_{-} = 2$. Because of intensity troubles, lines of this sort have been found so far only for $D_2^2 C_2^{12} O^{16}$. A more careful search for them for the other molecules is planned.

The frequency of the $J = 1 \rightarrow J = 2$ transition $D^2 H^1 C_2^{12} O^{16}$ will be measured and satellites searched for.   H. R. Johnson

D. NUCLEAR MAGNETIC MOMENT OF S^{33}

The measurement of the nuclear magnetic moment of S^{33} by the Zeeman effect of the microwave rotational spectra of OCS^{33} has been completed. Results previously reported in the literature (1, 2, 3, 4), have not been in good agreement with each other. The principal difficulties appeared to result from the low intensities of the hyperfine lines at the low natural abundance of S^{33} and the uncertainty of the sign of the OCS rotational g-factor.

The results reported here were obtained by using a slow-sweep recording spectrograph with a waveguide absorption cell and Stark modulation detection. The work was done jointly with Dr. C. K. Jen who performed similar measurements at Harvard with a cavity-type microwave spectroscope (5). A sample of OCS^{33} enriched to about 5.5 percent in the S^{33} isotope (natural abundance = 0.74 percent) was kindly loaned to us by Dr. Jen.

The hyperfine structure of the OCS^{33} $J = 1 \rightarrow 2$ rotational transition was first studied by Townes and Geschwind (6), who measured the nuclear quadrupole coupling and determined the nuclear spin, $I(S^{33})$, as $3/2$. The spin assignment has been confirmed by the present measurements, but the quadrupole coupling constant was found to be slightly different from that previously reported. The measured quadrupole pattern and coupling constant are given elsewhere in this report. The Zeeman splittings for most of the hyperfine lines were examined for both π and σ transitions.

The strongest line in the spectrum at zero field represents the two coincident transitions: $F = 3/2 \rightarrow 5/2$ and $F = 5/2 \rightarrow 7/2$. The Zeeman components of this line are too numerous to be resolved. The variation of intensity of this line as a function of the magnetic field was used in some preliminary experiments (2, 4) for the determination of $\mu(S^{33})$. The results obtained in this manner are now superseded by much more accurate results derived from the well-resolved splittings of the hyperfine lines.

The Zeeman splittings of the following hyperfine lines have been examined: $F = 1/2 \rightarrow 3/2$, $5/2 \rightarrow 5/2$, $1/2 \rightarrow 1/2$, $3/2 \rightarrow 3/2$ and $3/2 \rightarrow 1/2$. In each instance, there were at least two strong and well-resolved components. It has been found that the observed Zeeman spectra are consistent with theory (5, 7) if $|g_N| = 0.421$, $|g_{mol}| = 0.026$, and

g_{mol} and g_N have opposite signs. Here, g_N is the S^{33} nuclear g-factor and g_{mol} is the rotational g-factor for OCS. The quantity g_{mol} determined here is consistent with the value determined directly from the OCS^{32} spectrum.

The algebraic signs of the g-factors were established by observing σ transitions with circularly polarized radiation, and a magnetic field parallel to the axis of the waveguide cell. The sign of g_N was found to be positive and that of g_{mol} negative, thus in agreement with the relative sign determination from the π and σ measurements with linearly polarized radiation.

Using $g_N = +0.421$ and $I = 3/2$, the final result for the nuclear magnetic moment is $\mu(S^{33}) = +0.632 \pm 0.010$ nuclear magnetons. This result is within the Schmidt limits and is in agreement with the predictions of the single particle model of nuclear shell structure.

A more complete description of this work is being prepared as a technical report.

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<div align="right">J. R. Eshbach, R. E. Hillger</div>

E.   ELECTRIC QUADRUPOLE COUPLING OF THE S^{33} NUCLEUS IN $O^{16}C^{12}S^{33}$

The spin of the sulphur isotope S^{33} was determined by Townes and Geschwind (Phys. Rev. 74, 626, 1948) from observations on the hyperfine pattern of the $J = 1 \rightarrow 2$ transition of carbonyl sulphide ($O^{16}C^{12}S^{33}$) at about 24020 Mc/sec. Their observed frequencies were found to fit the theoretical pattern if $I(S^{33}) = 3/2$ and $eqQ(OCS^{33}) = -28.5 \pm 0.7$ Mc/sec. They did not, however, observe the complete pattern which should occur for $I = 3/2$, but the unobserved line was known to be of very low intensity. Also, two of the four measured frequencies represented an average measurement of unresolved lines.

In the present work, this hyperfine pattern was remeasured preliminary to the Zeeman-effect experiment also described in this report. Using the sample of OCS enriched in the S^{33} isotope to about 5.5 percent and a slow-sweep spectrograph, the complete pattern was observed and good resolution was obtained. The full line widths at

Table I

Transition $F_1 \rightarrow F_2$	Intensity* $(\alpha \times 10^8)$	Measured Frequency** (Mc/sec)	Townes and Geschwind's Frequency (Mc/sec)
(J = 1 → 2)			
1/2 → 3/2	3.2	24,012.23	⎰ 24,013.04
5/2 → 5/2	3.4	24,012.94	⎱
5/2 → 3/2	0.4	24,018.13	(unobserved)
1/2 → 1/2	3.2	24,019.59	⎰ 24,020.21
3/2 → 5/2, 5/2 → 7/2	23.3	24,020.23	⎱
3/2 → 3/2	4.1	24,025.42	24,025.39
3/2 → 1/2	0.7	24,032.68	24,032.75

* α is the absorption coefficient in cm^{-1} for an OCS sample with all the component atoms occuring in their natural abundance.

** The estimated accuracy for these frequencies is $\pm$ 0.02 Mc/sec.

Table II

Transition $F_1 \rightarrow F_2$	Measured Splitting* (Mc/sec)	Theoretical Splitting** (Mc/sec)	Difference (Mc/sec)
(J = 1 → 2)			
1/2 → 3/2	− 7.27	− 7.27	0.00
5/2 → 5/2	− 6.66	− 6.65	− 0.01
5/2 → 3/2	− 1.47	− 1.46	− 0.01
1/2 → 1/2	− 0.01	0.00	− 0.01
3/2 → 5/2, 5/2 → 7/2	0.63	0.62	+ 0.01
3/2 → 3/2	5.82	5.81	+ 0.01
3/2 → 1/2	13.08	13.08	0.00

* Splitting taken from the frequency which gives a least square fit with theory.

** These calculations were made taking $eqQ(OCS^{33}) = -29.07$ Mc/sec.

half intensity were 0.12 Mc/sec. The measured frequencies for these transitions are given in Table I, where they are compared with the frequencies measured by Townes and Geschwind. The relative frequency splittings are given in Table II, and these are compared with the theoretical splittings for the value of eqQ which gave the best fit. It was found that the splittings are in agreement with first order quadrupole coupling theory to within $\pm$ 0.01 Mc/sec if $I(S^{33})$ = 3/2 and $eqQ(OCS^{33})$ = $-$ 29.07 Mc/sec.

Since the fit with quadrupole coupling theory obtained in the present experiment was exact to within the capability of the experiment, it is presumed that the coupling of the S^{33} nucleus through its magnetic dipole interaction with the molecular magnetic field is less than 0.01 Mc/sec. In the analysis of the Zeeman effect data, the value $eqQ(OCS^{33})$ = $-$ 29.07 $\pm$ 0.01 Mc/sec was used.

J. R. Eshbach, R. E. Hillger