The Nuclear Magnetic Moment of S^{33} from Microwave Spectroscopy*

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The magnetic dipole moment of the S^{33} nucleus was determined by means of the Zeeman effect on the hyperfine pattern of the $J=1\rightarrow2$ rotational absorption of the molecule $O^{16}C^{12}S^{33}$ at about 24,020 Mc/sec. The result is

$$\mu(S^{33}) = +0.633\pm0.010 \text{ nuclear magneton.}$$

The sign of this moment was determined by using circularly polarized microwave radiation with σ-type Zeeman observations.

The frequencies of all of the components of the hyperfine pattern were measured. They all fit the nuclear electric quadrupole coupling theory to within ±0.01 Mc/sec. The measured value for eqQ of the S^{33} nucleus in $O^{16}C^{12}S^{33}$ is

$$eqQ(O^{16}C^{12}S^{33}) = -29.07\pm0.01 \text{ Mc/sec.}$$

I. INTRODUCTION

THE INTERACTION OF NUCLEI WITH MOLECULAR ROTATION

MOST molecules have $^1\Sigma$ electronic ground states, which means that these molecules have zero electronic orbital and spin angular momenta. Thus, the total angular momentum, which is a constant of the motion of the system of particles comprising the molecule, is instantaneously the vector sum of the angular momentum of molecular-rotation and the spin-angular-momenta of the nuclei. These component angular momenta are not constant in time, since in general there are interaction forces between them. The magnetic dipole moment of the total molecule is therefore some combination of the rotational magnetic moment, discussed elsewhere,[1,2] and the nuclear magnetic moments. Since one can observe different known combinations of the nuclear moments with the rotational moment, they can be deduced separately. The results given in reference 1 show that the rotational magnetic moments are of the same order of magnitude as nuclear moments.

Usually the interaction energies between the nuclear spins and the molecular rotation are very small compared to the rotational energy of the molecule. In the limit of no interaction the orientation of the nuclear spins with respect to molecule fixed axes cannot affect the molecular energy and the energy levels may be labeled with the rotational quantum numbers alone. For a linear molecule let J be the rotational quantum number and I the spin quantum number of one of its nuclei. Then, if there is no interaction, the rotational levels may be specified by J alone, since the various permitted combinations of I with a given value of J will all result in the same energy. In this case the rota-

tional angular momentum and the nuclear spin are separate constants of the motion as well as the total angular momentum.

If a small interaction between I and J exists, then the rotational energy level labeled by a given value of J will become a group of closely spaced levels each of which must now be labeled with a value of the total angular momentum quantum number, F. F takes on all integrally spaced values from $J+I$ to $|J-I|$. A rotational absorption, which resulted in a single line in the absence of interaction, becomes a group of closely spaced lines when the interaction is present. Such a group is called a hyperfine pattern. The allowed rotational transitions (molecular electric dipole transitions are normally observed in microwave spectroscopy) which give rise to the hyperfine pattern are given by the selection rules $\Delta F=0, \pm1$ (but $F=0\rightarrow0$ is not allowed), and $\Delta M_F=0, \pm1$. The relative spacings between the lines of a hyperfine pattern depend on the type of interaction causing the splitting, while the magnitude of the spacings depends, of course, on the strength of the interaction.

Two types of interactions between a nucleus and molecular rotation have been important in microwave spectroscopy up to now. Of greatest importance is the interaction of the nuclear electric quadrupole moment with the gradient of a component of the electric field at the nucleus due to the remainder of the molecule.[3,4] Of secondary importance is the energy of the nuclear magnetic dipole moment in the weak magnetic field due to molecular rotation. This magnetic dipole-dipole energy alone is usually too small to cause a hyperfine pattern resolvable by present-microwave spectroscopic methods, but its importance must be recognized in some cases as a small correction to the electric quadrupole type of splitting in order to account for experimental data.[5,6]

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[1] J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. 85, 24 (1952).
[2] C. K. Jen, Phys. Rev. 81, 197 (1951).

[3] Daily, Kyhl, Strandberg, Van Vleck, and Wilson, Phys. Rev. 70, 984 (1946).
[4] J. Bardeen and C. H. Townes, Phys. Rev. 73, 97 (1948).
[5] H. M. Foley, Phys. Rev. 72, 504 (1947).
[6] J. M. Jauch, Phys. Rev. 74, 1262 (1948).

A well-resolved hyperfine pattern is essential for the measurement of a nuclear magnetic moment by the Zeeman effect on a rotational absorption line. Let eqQ be the quadrupolar interactions energy, where Q is the nuclear electric quadrupole moment and $q = (\partial^2 V)/(\partial z^2)$, the second derivative along the molecular axis of the electrostatic potential at the nucleus; and let the energy of the molecule in an externally applied magnetic field be $-\mu H$, where μ is an effective magnetic dipole moment for the total molecule. Two limiting cases are evident, $|\mu H| \ll |eqQ|$ and $|\mu H| \gg |eqQ|$. In the first, or weak field case, the nuclear spin and the molecular rotation combine in the same way as when no field was present and the permitted transitions are given by the same selection rules as before. In the strong field case the nuclear moment and the rotational magnetic moment tend to orient themselves in the applied field independent of each other and the proper magnetic quantum numbers become M_I and M_J, instead of M_F. Also, the selection rules for the rotational transitions observed by the microwave absorption method become $\Delta M_J = 0$, ± 1 and $\Delta M_I = 0$. These considerations show that in order to determine the nuclear magnetic moment a resolved Zeeman pattern must be obtained under weak field conditions, since the selection rule $\Delta M_I = 0$ means that the nuclear moment does enter into the observed strong field transitions. This is the same as saying that a well-resolved quadrupole hyperfine pattern is required, since in the case of an unresolved hyperfine pattern a strong field condition is necessary to produce resolved Zeeman components. This more or less intuitive picture is substantiated by the quantitative expressions given below.

II. THEORETICAL BACKGROUND

The effect of nuclear electric quadrupole coupling in the case of atomic spectra was first investigated quantum-mechanically by Casimir.[7] Casimir's results have subsequently been applied to nuclear quadrupole interaction with molecular rotation.[3,4,8,9] For a symmetric top molecule the diagonal quadrupole energy, which must be added to the unperturbed rotational energy, is

$$E_q(I, J, K, F) = eqQ\left[\frac{3K^2}{J(J+1)} - 1\right]G(I, J, F), \quad (1)$$

where

$$G(I, J, F) = \frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2(2J+3)(2J-1)I(2I-1)},$$

$$C = F(F+1) - I(I+1) - J(J+1).$$

In the case of a linear molecule this becomes simply

$$E_q(I, J, F) = -eqQG(I, J, F). \quad (2)$$

[7] H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, De Erren F. Bohn, Haarlen, 1936).
[8] Kellogg, Rabi, Ramsey, Jr., and Zacharias, Phys. Rev. **57**, 677 (1940).
[9] J. H. Van Vleck, Phys. Rev. **71**, 468 (A) (1947).

The Zeeman effect on the resulting hyperfine pattern has been treated theoretically by Jen[10,11] and Coester[12] following the procedure used in atomic spectra.[13] If the resolved hyperfine splitting is caused by the interaction of a single nucleus of the molecule, the others having $I < 1$ or negligible interaction, then the total Hamiltonian for the rotating molecule in a magnetic field, $\mathbf{H}$, may be written

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_q + \mathcal{H}_m, \quad (3)$$

where $\mathcal{H}_0$ is the rotational energy; $\mathcal{H}_q$ is the quadrupole interaction energy; and

$$\mathcal{H}_m = -\mu_0[g_{\text{mole}}(\mathbf{J} \cdot \mathbf{H}) + g_{\text{nuc}}(\mathbf{I} \cdot \mathbf{H})], \quad (4)$$

where $\mu_0 = e\hbar/2M_p c$, the nuclear magnetron (M_p = the proton mass), g_{mole} is the molecular rotational g-factor and may depend on the rotational quantum numbers as explained in reference 1, and g_{nuc} is the nuclear g-factor.

In a weak magnetic field, $|\mathcal{H}_m| \ll |\mathcal{H}_q|$, the $IJKFM_F$ representation is suitable. The energy levels are given by

$$E = E_0(J, K) + E_q(I, J, K, F) + E_m(I, J, K, F, M_F), \quad (5)$$

where $E_0(J, K) = BJ(J+1) + (A-B)K^2$ for a symmetric top and is diagonal in this representation. (A and B are the rotational constants for the molecule.) $\mathcal{H}_q$ has the diagonal elements given in Eq. (1). There are also off-diagonal elements of $\mathcal{H}_q$ with respect to J, but these are usually negligible since they represent an interaction with levels remote with respect to $\mathcal{H}_q$; they do not affect the Zeeman splittings in this case anyway. $\mathcal{H}_m$ has the diagonal elements

$$E_m(I, J, K, F, M_F) = -M_F\mu_0 H[\alpha_J g_{\text{mole}} + \alpha_I g_{\text{nuc}}], \quad (6)$$

where

$$\alpha_J = [F(F+1) - I(I+1) + J(J+1)]/[2F(F+1)],$$

$$\alpha_I = [F(F+1) - J(J+1) + I(I+1)]/[2F(F+1)],$$

and $M_F = F, F-1, \cdots, -F$ so that each hyperfine level splits into $2F+1$ levels in the presence of a magnetic field. These expressions are identical with those of Back and Goudsmit[13] for the Zeeman effect on the hyperfine structure of atomic levels. The off-diagonal elements of $\mathcal{H}_m$ will be discussed shortly.

In the strong field case, $|\mathcal{H}_m| \gg |\mathcal{H}_q|$, the $IJKM_IM_J$ representation is proper. $\mathcal{H}_m$ is diagonal and its elements are

$$E_m = -\mu_0 H[M_J g_{\text{mole}} + M_I g_{\text{nuc}}]. \quad (7)$$

The quadrupole energy expression in the strong field is given by Coester,[12] but it is quite complicated and is not needed for the following discussion.

The selection rules are affected by the presence of a magnetic field. In the weak field case $\Delta M_F = 0$ transitions occur when the electric vector of the incident microwave radiation is parallel to the applied magnetic

[10] C. K. Jen, Phys. Rev. **74**, 1396 (1948).
[11] C. K. Jen, Phys. Rev. **76**, 1494 (1949).
[12] F. Coester, Phys. Rev. **77**, 454 (1950).
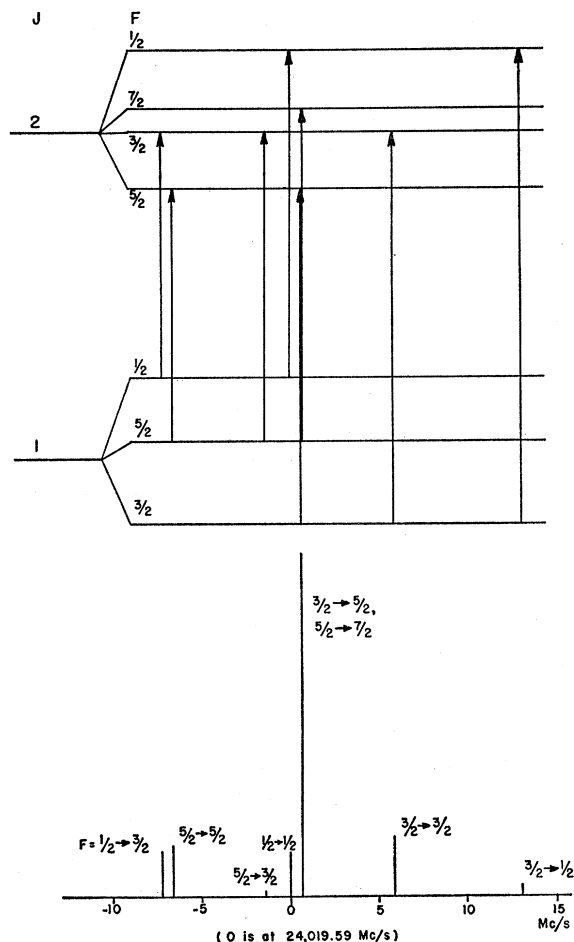[13] E. Back and S. Goudsmit, Z. Phys. **47**, 174 (1928).

FIG. 1. The $J=1\rightarrow2$ hyperfine pattern of $O^{16}C^{12}S^{33}$.

field (π-transitions) and $\Delta M_F=\pm1$ transitions occur if it is perpendicular to the applied field (σ-transitions). For a strong field condition the selection rules become $\Delta M_J=0$, $\Delta M_I=0$ for π-transitions and $\Delta M_J=\pm1$, $\Delta M_I=0$ for σ transitions.

Using these selection rules and expression for the first-order Zeeman effect, Eq. (6), the expression for the transition frequencies under weak field conditions for a linear molecule (g_{mol} is the same for both the initial and final levels) is found to be:

For π transitions ($\Delta M_F=0$)

$$\Delta\nu_m=M_F(\mu_0/h)H(g_{mol}-g_{nuc})(\alpha_{J1}-\alpha_{J2}). \qquad (8)$$

For σ transitions ($M_F\rightarrow M_F\pm1$)

$$\Delta\nu_m=(\mu_0/h)H\{g_{mol}[M_F(\alpha_{J1}-\alpha_{J2})\pm\alpha_{J2}] \\ +g_{nuc}[M_F(\alpha_{I1}-\alpha_{I2})\pm\alpha_{I2}]\}, \qquad (9)$$

where α_{J1} and α_{J2} are the α_J's of the initial and final levels respectively, and α_{I1} and α_{I2} are the α_I's of the initial and final levels.

As has been pointed out, the weak field case is of greatest interest for the purpose of measuring nuclear

moments. However, a resolved Zeeman effect under true weak field conditions, in the sense that the off-diagonal elements of $\mathcal{K}_m$ are negligibly small, is often not fully realized experimentally. In particular, for the OCS[33] experiment described below it was found that even the second order correction, as given in Coester's paper, was not always sufficient to satisfy the experimental data; but, as shown in the following, the matrix of $\mathcal{K}_m$ is sometimes simple enough to permit exact diagonalization at any given intermediate field strength rather than relying on perturbation approximations.

In the $IJKFM_F$ representation $\mathcal{K}_m$ is diagonal with respect to M_F so that only states with the same M_F can mix with each other, and for a given M_F matrix the only off-diagonal elements are between F and $F\pm1$ levels. Only the off-diagonal elements for levels of the same J need be considered since the energy difference between levels of different J is large enough to make the perturbation between J and $J\pm1$ levels truly negligible except in extremely strong fields. Thus, the energy matrix for a given M_F under consideration is of the form

$F\backslash F$	$I+J$	$I+J-1$		$\|M_F\|+1$	$\|M_F\|$
$I+J$	X	X	0	0	0
$I+J-1$	X	X	X	0	0
	0	X	X	X	0
$\|M_F\|+1$	0	0	X	X	X
$\|M_F\|$	0	0	0	X	X

where the X's indicate the nonzero elements. It is to be noted that only states for which $\|M_F\|\leqslant F$ exist. The diagonal elements of this matrix are given in Eqs. (5), (1), and (6). The off-diagonal elements are given by Coester[12] and are

$$(F, M_F\|\mathcal{K}_m\|F-1, M_F) \\ =\mu_0H(g_{nuc}-g_{mole})[(F^2-M_F^2)R(F)]^{\frac{1}{2}}, \qquad (10)$$

where

$$R(F)=[F^2-(I-J)^2][(I+J+1)^2-F^2]/ \\ [4F^2(2F-1)(2F+1)]$$

and $\mathcal{K}_m$ is given in Eq. (4).

TABLE I. Measured frequencies for the $J=1\rightarrow2$ hyperfine pattern of $O^{16}C^{12}S^{33}$.

Transition $F_1\rightarrow F_2$	Intensity[a] ($\alpha\times10^8$)	Measured frequency present Work[b] (Mc/sec)	Measured frequency Townes and Geschwind[c] (Mc/sec)
$1/2\rightarrow3/2$	3.2	24,012.33⎫	24,013.04
$5/2\rightarrow5/2$	3.4	24,012.94⎭	
$5/2\rightarrow3/2$	0.4	24,018.13	
$1/2\rightarrow1/2$	3.2	24,019.59⎫	
$3/2\rightarrow5/2,$			24,020.21
$5/2\rightarrow7/2$	23.3	24,020.23⎭	
$3/2\rightarrow3/2$	4.1	24,025.42	24,025.39
$3/2\rightarrow1/2$	0.7	24,032.68	24,032.75

[a] α is the absorption coefficient in cm^{-1} for an OCS sample with all the component atoms occurring in their natural abundance.
[b] All frequencies are measured to ±0.02 Mc/sec.
[c] See reference 15.

The exact diagonalization of these matrices was used in the analysis of the OCS^{33} experiment. A convenient method of solution for the roots of such a matrix is the continued fraction scheme described by Crawford and Cross.[14]

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

The nuclear spin of the sulfur isotope of mass number 33 was determined by Townes and Geschwind[15] by measuring the relative splittings in the hyperfine pattern of the $J=1{\rightarrow}2$ transition of carbonyl sulfide (O^{16}C^{12}S^{33}) at about 24,020 Mc/sec. Carbonyl sulfide is a linear molecule[16,17] and the spins of both O^{16} and C^{12} were known to be zero.[18] The observed frequencies were found to best fit the nuclear quadrupole coupling expression, Eq. (2), if $I(S^{33})=3/2$ and $eqQ(OCS^{33})=-28.5\pm0.7$ Mc/sec. In their experiment, because of low resolution, they did not observe the complete pattern which should occur for $I=3/2$ but the observed pattern and line shapes were compared with those for several possible values of I.

In the present work this quadrupole hyperfine pattern was remeasured preliminary to the Zeeman effect experiment [determination of the nuclear magnetic dipole moment $\mu(S^{33})$].

A sample of carbonyl sulfide, prepared from sulfur enriched in S^{33} to 5.54 percent (about 7.5 times the natural abundance), was used for this experiment.[19] This enrichment provided a corresponding increase in the absorption intensities. The increased intensities and the use of a high sensitivity spectrograph to be described in a future report afforded the opportunity of measuring the entire pattern and of completely resolving all the hyperfine components.

TABLE II. Comparison of measured and theoretical hyperfine splittings for $eqQ(OCS^{33})=-29.07$ Mc/sec.

Transition $F_1{\rightarrow}F_2$	$\Delta\nu$ measured[a] (Mc/sec)	$\Delta\nu$ calculated[a] (Mc/sec)	Discrepancy (measured-calculated) (Mc/sec)
$1/2{\rightarrow}3/2$	-7.27	-7.27	0.00
$5/2{\rightarrow}5/2$	-6.66	-6.65	-0.01
$5/2{\rightarrow}3/2$	-1.47	-1.46	-0.01
$1/2{\rightarrow}1/2$	-0.01	0.00	-0.01
$3/2{\rightarrow}5/2, 5/2{\rightarrow}7/2$	0.63	0.62	$+0.01$
$3/2{\rightarrow}3/2$	5.82	5.81	$+0.01$
$3/2{\rightarrow}1/2$	13.08	13.08	0.00

[a] The calculated $\Delta\nu$'s are taken from the $F=1/2{\rightarrow}1/2$ frequency and the measured $\Delta\nu$'s are taken so as to give a least square fit.

[14] B. L. Crawford and P. C. Cross, Jr., J. Chem. Phys. **5**, 621 (1937).
[15] C. H. Townes and S. Geschwind, Phys. Rev. **71**, 562 (1947).
[16] G. Herzberg, *Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).
[17] Strandberg, Wentink, and Kyhl, Phys. Rev. **75**, 270 (1949).
[18] H. L. Poss, Brookhaven National Laboratory Report 26 (T-10), October 1, 1949.
[19] The authors are indebted to C. K. Jen for the loan of this OCS sample. Then enhanced S^{33} was initially obtained from the Isotopes Division of the Atomic Energy Commission.
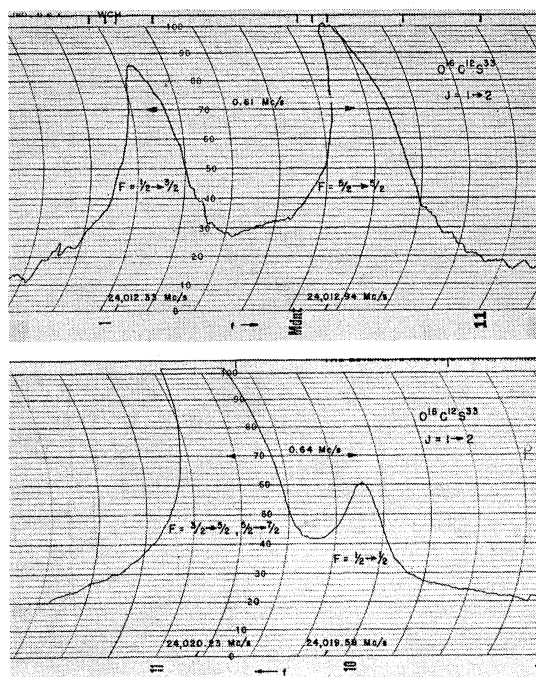

FIG. 2. Part of the O^{16}C^{12}S^{33} hyperfine pattern.

The allowed transitions and the resulting hyperfine patterns are displayed in Fig. 1.

The measured frequencies for these transitions are given in Table I. All of the relative frequency splittings are in agreement with the quadrupole coupling theory to within ±0.01 Mc/sec if $I(S^{33})=3/2$ and $eqQ(OCS^{33})=-29.07$ Mc/sec. The calculated splittings using these values are compared with the measured splittings in Table II. The frequencies reported by Townes and Geschwind are also given in Table I. Their frequency for the unresolved $F=1/2{\rightarrow}3/2$, $5/2{\rightarrow}5/2$ transitions is apparently in error since it falls outside of the frequencies of the resolved lines (which are of nearly equal intensity) as measured in the present experiment. Also their value for eqQ does not fit their measured individual relative splittings too well, although it represents an average fit of their data.

Since the fit obtained in the present experiment with the quadrupole coupling expression, Eq. (2), 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 and also that the effects of off-diagonal elements of the quadrupole energy matrix are correspondingly small, as was previously pointed out. In the analysis of the Zeeman effect data the value

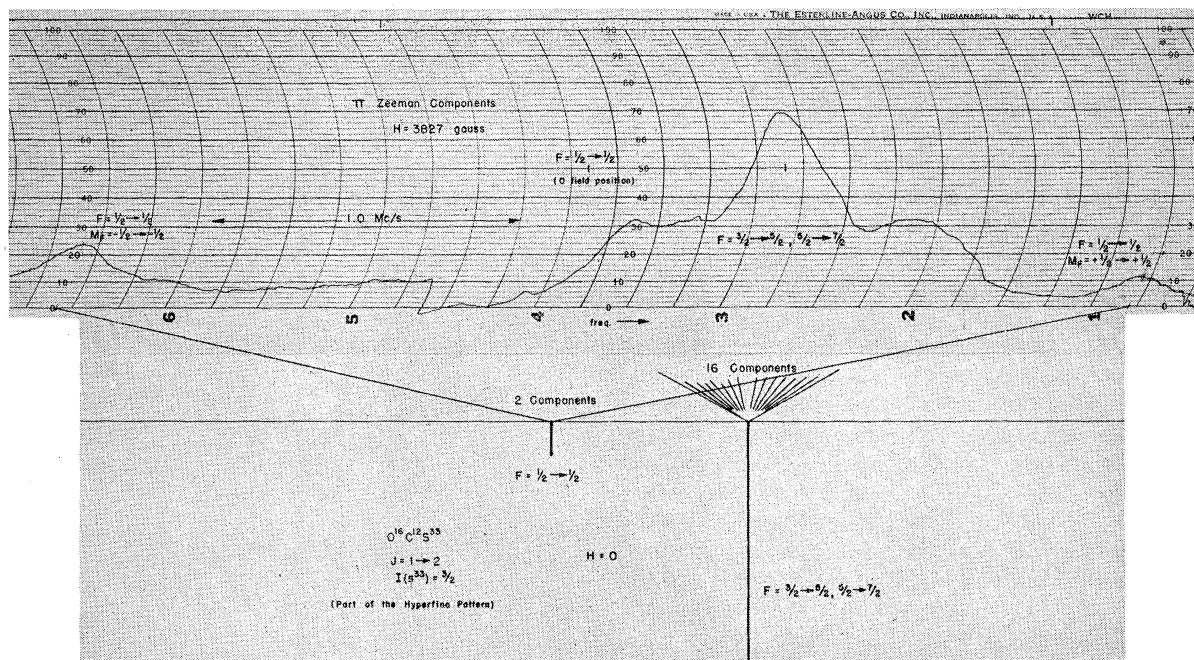$$eqQ(OCS^{33})=-29.07\pm0.01 \text{ Mc/sec}, \quad (11)$$

was therefore used.

FIG. 3. π Zeeman components of the $F=3/2{\to}5/2$, $5/2{\to}7/2$ and the $F=1/2{\to}1/2$ lines.

Spectrograms of some of the lines of this hyperfine pattern are shown in Fig. 2.[20]

IV. THE ZEEMAN EFFECT EXPERIMENT AND RESULTS

Previous attempts to measure the nuclear magnetic moment of S^{33} by means of the Zeeman effect on the $J=1{\to}2$ rotational transition of $O^{16}C^{12}S^{33}$ have not been in agreement in spite of the large uncertainties assigned.[18,21] The difficulties lay in the low intensities of these lines with the natural abundance of S^{33} (0.74 percent) and the sensitivity of the spectroscopes used. A high sensitivity spectrograph ($\alpha_{min}{\simeq}3\times10^{-9}$ cm^{-1}) and the OCS sample previously mentioned were used in the present experiments to determine $\mu(S^{33})$ by the method outlined in Part II. Both π- and σ-transitions were observed using linearly polarized microwave radiation. As is seen from the theory reviewed in Part II, the absolute values of both g_{nuc} and g_{mole} and their relative sign may be obtained from such measurements. A σ transition observation using circularly polarized radiation then served to fix the absolute sign of the

g-factors. Actually g_{mole} may be obtained from a separate experiment. $g_{mole}(O^{16}C^{12}S^{32})$ is easily obtained from σ type Zeeman measurements on the $O^{16}C^{12}S^{32}$ rotational spectrum since all the nuclear spins involved are zero. According to the theory of rotational magnetic moments, $g_{mole}(O^{16}C^{12}S^{33})$ may then be found by multiplying by the ratio of the molecular moments of inertia. Since $g_{mole}(OCS^{32})$ had been previously determined,[1,2] its value was used as a check on the analysis of the data

TABLE III. π-transition Zeeman measurements on the $J=1{\to}2$ hyperfine pattern of $O^{16}C^{12}S^{33}$. ($H=3912$ gauss.)

Transition $F_1{\to}F_2$ (M_F)	$\Delta\nu$ measured (Mc/sec)	$\Delta\nu_{calc}$ exact diagonalization (Mc/sec)	Discrepancy with measured $\Delta\nu$	$\Delta\nu_{calc}$ 1st order theory only (Mc/sec)	Discrepancy with measured $\Delta\nu$
$1/2{\to}1/2$ $(\pm1/2)$	3.530 3.530 3.515 3.509				
	3.521	3.513	+0.008	3.567	−0.046
$3/2{\to}1/2$ $(\pm1/2)$		2.286	2.275	+0.011	2.320	−0.034
$1/2{\to}3/2$ $(\pm1/2)$	2.005 2.002 1.995 1.985 2.014 2.018				
	2.003	1.999	+0.004	1.963	+0.040
$5/2{\to}5/2$ $(\pm5/2)$	1.537 1.521 1.516 1.505 1.523 1.525				
	1.521	1.528	−0.007	1.527	−0.006

[20] After completion of the present work the following frequencies have been reported by Geschwind and Gunther-Mohr [referred to by Wentink, Koski, and Cohen, Phys. Rev. 81, 948 (1951)], for some of the hyperfine components of the transition under consideration.

$F_1{\to}F_2$	Frequency (Mc/sec)
$1/2{\to}3/2$	24,012.292
$5/2{\to}5/2$	24,012.974
$1/2{\to}1/2$	24,019.641
$3/2{\to}5/2$, $5/2{\to}7/2$	24,020.264
$3/2{\to}3/2$	24,025.467

[21] J. E. Mack, Revs. Modern Phys. 22, 65 (1950).

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TABLE IV. σ-transition measurements on the $J=1\rightarrow2$ hyperfine pattern of $O^{16}C^{12}S^{33}$.

(a) $F=1/2\rightarrow1/2$	$\Delta\nu$ measured (Mc/sec)	$\Delta\nu_{calc}$ $g_{nuc}=+0.424$ $g_{mole}=-0.025$	$\Delta\nu_{calc}$ $g_{nuc}=-0.474$ $g_{mole}=-0.025$
Total splittings between $M_F=+1/2\rightarrow-1/2$ and $M_F=-1/2\rightarrow+1/2$ components ($H=1486$ gauss).	0.276 0.259 0.264 0.257 —— 0.264	0.287	0.398
Splitting of low frequency component from zero field position ($H=3019$ gauss).	0.183 0.179 —— 0.181	0.197	0.311
(b) $F=3/2\rightarrow1/2$ Total splitting between $M_F=-3/2\rightarrow-1/2$ and $M_F=+3/2\rightarrow+1/2$ components. ($H=1486$ gauss).	1.559	1.564	1.678

of the present experiment. Once g_{nuc} is established, the nuclear magnetic dipole moment in nuclear magnetons is given by

$$\mu=g_{nuc}I. \qquad (12)$$

From Eq. (8) it is seen that π-type Zeeman measurements give the quantity $|g_{nuc}-g_{mole}|$ directly. This is actually true to even better than first order since in the off-diagonal elements for the Zeeman perturbation, Eq. (10), the g-factors also appear only in the combination $|g_{nuc}-g_{mole}|$. Because of this, considerable effort was placed on the π-transition measurements. The π-measurements were made on five of the seven lines of the hyperfine pattern (Fig. 1). The coincident $F=3/2\rightarrow5/2$, $5/2\rightarrow7/2$ transitions were not used because the multitude of Zeeman components, many of which had low splitting factors, $(\alpha_{J1}-\alpha_{J2})$, [see Eq. (8)], resulted in an unresolved pattern (see Fig. 3). The $F=5/2\rightarrow3/2$ transition was not used because its components were too weak to be accurately measured. Zeeman splittings of the remaining five hyperfine lines were observed at various values of magnetic field. The measurements used in arriving at the value of $|g_{nuc}-g_{mole}|$ are given in Table III. In every case these measurements represent the total splitting between two Zeeman components; this type of measurement eliminates the second-order effect of the off-diagonal elements since it is the same for both components, and thus discrepancies with theory are actually effects of third or higher order. Actually, as mentioned in Part II, the matrices involved in the analysis can easily be diagonalized exactly; this was done and the least square discrepancy between theory and experiment was obtained if

$$|g_{nuc}-g_{mole}|=0.449\pm0.002 \text{ nuclear unit.} \qquad (13)$$

Here the error of ±0.002 is determined by the internal consistency of the measurements and does not include a possible consistent error in measuring the magnetic field. The error in magnetic field is estimated to be less than 1 percent.

Table III also gives the theoretical splittings, calculated with the value of Eq. (13), for both the exact Zeeman theory and the first-order theory only to show the magnitude of the discrepancy with experiment and

the magnitude of higher order corrections. The total spread of the measured splittings for a given transition is of the order of 0.020 Mc/sec, equally contributing factors being the limitations of the frequency measuring scheme and the reproducibility of a given value of the magnetic field.

Some of the spectrograms of the π-transitions are included in the Appendix.

$g_{mole}(OCS^{32})$ was previously measured as

$$g_{mole}(OCS^{32})=-0.025\pm0.002 \text{ nuclear unit.} \qquad (14)$$

Thus, as mentioned above, we can find $g_{mole}(OCS^{33})$ by multiplying by the ratio of an OCS^{33} rotational frequency to the corresponding OCS^{32} frequency. For the $J=1\rightarrow2$ transition this ratio is

$$\nu(OCS^{33})/\nu(OCS^{32})=24{,}019.59/24{,}325.92=0.9874. \qquad (15)$$

Thus $g_{mole}(OCS^{33})$ should be about 1 percent lower than $g_{mole}(OCS^{32})$. It is hardly necessary to apply this correction, since it is well within the error in determining $g_{mole}(OCS^{32})$, Eq. (14).

The determination of the relative sign between g_{nuc} and g_{mole} remains. On examining the theoretical splitting of the σ-type transitions for the two possibilities,

$$g_{nuc}=-0.025+0.449=+0.424,$$

and

$$g_{nuc}=-0.025-0.449=-0.474,$$

it was found that the splitting of the $F=1/2\rightarrow1/2$ line should be most critical for deciding which was correct. The σ splitting of this line was therefore measured. Table IV (a) shows the comparison between the experimental results and the expected results calculated for the two cases. It is seen that g_{nuc} and g_{mole} must be of opposite sign, although even then the agreement is not perfect for the values of g_{nuc} and g_{mole} assumed for these calculations. It should be noted that these splittings are quite small and thus the discrepancies in percent appear large; but the absolute differences are only about 0.020 Mc/sec, which is the experimental accuracy. These differences could be introduced by the proximity of the $F=1/2\rightarrow1/2$ line to the much stronger $F=3/2\rightarrow5/2$, $5/2\rightarrow7/2$ absorption. A spectrogram of this transition is shown in Fig. 4.
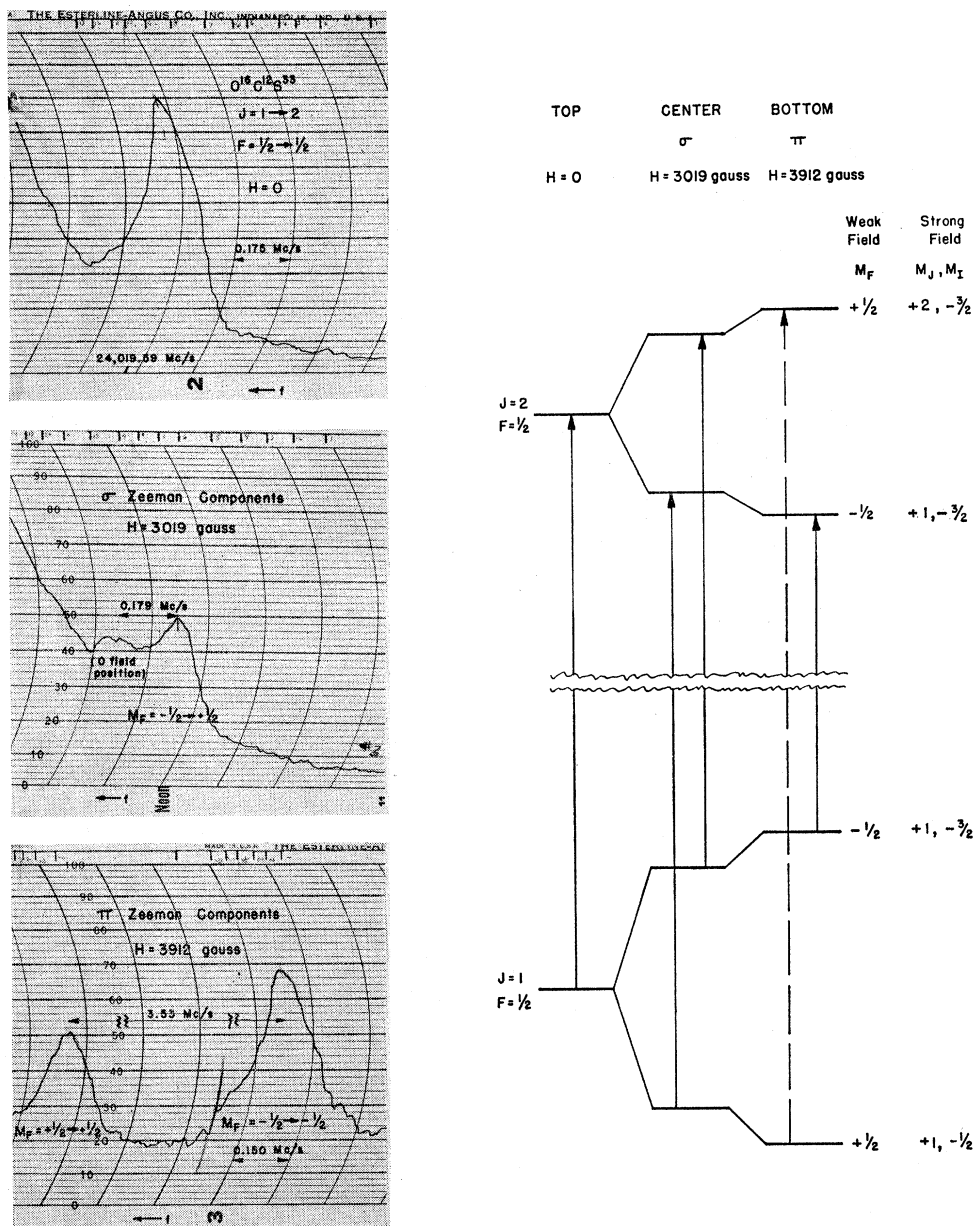
Fig. 4. σ- and π-Zeeman components of the $F=1/2\rightarrow1/2$ line.

The σ-transition Zeeman components of the $F=3/2$ $\rightarrow1/2$ line were also measured and the results again compared with calculations based on the same and opposite relative signs for g_{nuc} and g_{mole}. Table IV (b) gives the results. Again it is definitely indicated that the g-factors have opposite signs.

As a more direct check on the absolute sign of g_{nuc} an observation was made of the $F=3/2\rightarrow5/2$, $5/2\rightarrow7/2$ σ components with circularly polarized radiation. This observation required careful analysis since for $\Delta M_F=$ $+1$ (or $\Delta M_F=-1$) transitions some of the σ-components go to higher frequencies and some to lower

frequencies. (The weaker hyperfine lines with fewer components could not be detected with the apparatus used for the circular polarization experiments.) This observation again indicated that g_{nuc} was positive as expected.

Finally values of g_{nuc} and g_{mole} were found which gave the best fit for all the data taken, both for π- and σ-transitions. The result becomes

$$g_{nuc}=+0.422\pm0.004 \text{ nuclear unit,} \qquad (16)$$

where the error is that of internal consistency. Including possible consistent errors, primarily in the magnetic

field measurement, we have for the final result

$$g_{nuc} = +0.422 \pm 0.007 \text{ nuclear unit} \qquad (17)$$

and according to Eq. (12) the corresponding magnetic dipole moment for the sulfur 33 nucleus is

$$\mu(S^{33}) = +0.633 \pm 0.010 \text{ nuclear magneton.} \qquad (18)$$

This value is uncorrected for the partial shielding of the S^{33} nucleus from the externally applied field due to the electronic diamagnetic effects. This effect was studied theoretically for atoms by Lamb[22] and recently for molecules by Ramsey.[23] The exact theory in the molecular case is difficult to apply quantitatively, but Ramsey concludes that the shielding of a particular nucleus may be approximated by considering only its own electrons, so to speak, and by ignoring those tightly bound to other nuclei in the molecule. Thus, Lamb's theory applied to the sulfur atom may be used. This diamagnetic correction is about 0.11 percent[18] and is thus negligible to the accuracy of the present experiment.

Following the publication of the essential result of our experiment,[24] Dharmatti and Weaver have made a more accurate measurement of the S^{33} nuclear magnetic moment, using the nuclear induction method.[25] Their result is

$$\mu(S^{33}) = +0.64282 \pm 0.00014 \text{ nuclear magneton.}$$

APPENDIX. SPECTROGRAMS OF THE $O^{16}C^{12}S^{33}$ HYPERFINE PATTERN AND ZEEMAN EFFECT

In the spectrograms the absorption intensity is plotted vertically against the microwave frequency. The spectrograph receiver gain varies from one spectrogram to another, but, in general, relative gain settings may be estimated from the noise level. The frequency scale is different in the various figures and therefore a frequency scale is indicated on each spectrogram.

In Fig. 2, the lines can be compared for relative intensity and frequency splittings with the schematic pattern in Fig. 1. Note particularly the $F=1/2 \rightarrow 1/2$ line on the skirt of the stronger $F=3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$ absorption. This line was especially useful for the measurement of $\mu(S^{33})$ by means of the Zeeman effect since it has only two components for either π or σ transitions.

Figure 3 shows the two π-components of the $F=1/2 \rightarrow 1/2$ line split out so that one of them has passed through the $F=3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$ line and is resolved on the high frequency side. The components of the $F=3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$ line are numerous and have low splitting factors and hence are unresolved.

In Fig. 4, the upper spectrogram is another zero field observation of the $F=1/2 \rightarrow 1/2$ line. The skirt of the $F=3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$ line is again noticeable. The low splitting factor for the σ-components of this line is obvious from the center spectrogram, where at 3019 gauss one component has split only 0.179 Mc/sec from the zero field position. The high frequency component has merged with the $F=3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$ line and the small component
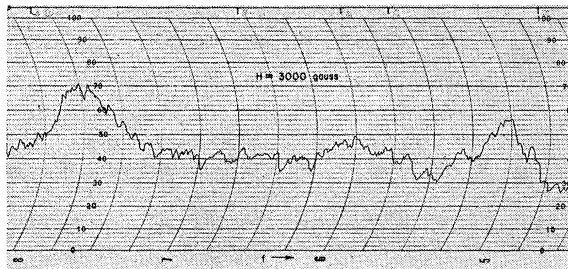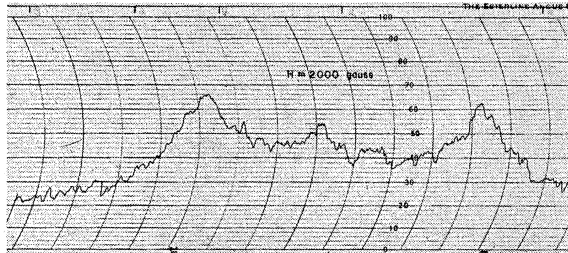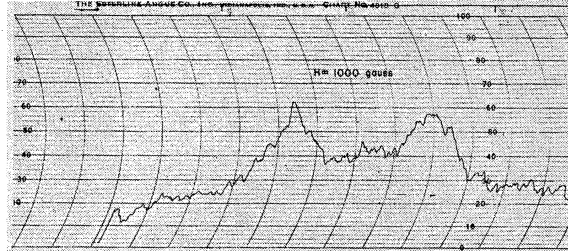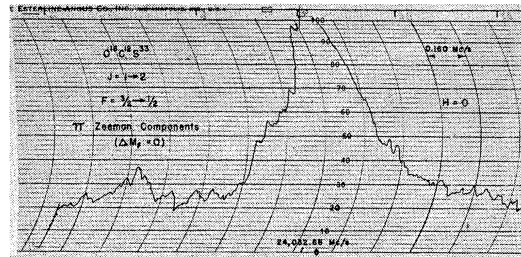
[22] W. E. Lamb, Jr., Phys. Rev. **60**, 817 (1941).
[23] N. F. Ramsey, Jr., Phys. Rev. **78**, 699 (1950).
[24] Eshbach, Hillger, and Jen, Phys. Rev. **80**, 1106 (1950).
[25] S. S. Dharmatti and H. E. Weaver, Phys. Rev. **83**, 845 (1951).

FIG. 5. π-Zeeman splitting of the $F=3/2 \rightarrow 1/2$ line.

at the zero field position is due to a short part of the absorption cell which extended beyond the magnetic field.

The π-components of this line had the largest splitting factor for any of the components in the entire hyperfine pattern and provided the most accurate measurements of the experiment. These components, shown in the lower spectrogram, are split out on either side of the $F=3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$ line as in Fig. 3. Note also that the high frequency component, which is forbidden in the strong field limit, has already started to weaken in this intermediate field compared to the low freequency component which is permitted at all field strengths.

In Fig. 5, the $F=3/2 \rightarrow 1/2$ line is one of the weakest absorptions in the hyperfine pattern and hence the noise level appears high. However, the π-transition splitting as a function of the magnetic field is clearly visible. The four spectrograms are lined up with respect to the zero field position and a second-order shift (shift of the center of gravity of the two components) is noticeable. This shift agreed very closely with the theoretical Zeeman effect.