At lower energies the simple interpolation formula

$$\sigma(E, K)dK=\frac{dK}{K}\left[\frac{4}{3}-\frac{4}{3}\frac{K}{E}+\frac{K^2}{EE_0}\right], \qquad \text{(A7)}$$

gives an extremely satisfactory approximation as can be verified by comparison with the graphs given by Rossi and Greisen.[1]

### Compton Effect

The probability for a Compton transition per unit radiation length is for $K' \gg \mathrm{mc}^2$

$$\sigma(K, K')dK'=\frac{BdK'}{KK'}\left(1+\frac{K'^2}{K^2}\right), \qquad \text{(A8)}$$

with $B=137\pi\mathrm{mc}^2/4\bar{Z}\ \lg 183Z^{-\frac{1}{3}}=0.017$ for air and 0.0265 for lead. The integrated Compton probability is

$$\sigma(K)=\frac{B}{K}\left(\lg\frac{2K}{mc^2}+\frac{1}{2}\right). \qquad \text{(A9)}$$

The average energy $\bar{E}$ of an electron produced in a Compton collision with a quantum $K$ is

$$\bar{E}=K\left[1-\frac{4}{3}\left(\lg\frac{2K}{mc^2}+\frac{1}{2}\right)^{-1}\right]. \qquad \text{(A10)}$$

The *absorption coefficient* for photons is obtained from the combination of Compton and pair production cross sections.

### Knock-on Probability

$$\sigma_k(E, E')=\frac{2BdE}{E'^2}\left(1-\frac{2E'}{E}\right), \qquad \text{(A11)}$$

where $B$ is the same as for the Compton effect.

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# Microwave Spectra of Some Linear *XYZ* Molecules

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Measurements of the pure rotational spectra of a number of isotopes and vibrational states of OCS, ClCN, BrCN, and ICN near one centimeter wave-length have been made. Experimental techniques used and interpretation of the spectra of linear *XYZ* molecules are discussed. Tables include frequencies and intensities of lines and comparison with theoretical values, rotational constants $B_0$, rotation-vibration constants $\alpha$, $l$-type doubling constants, internuclear distances, half-width parameters of lines, quadrupole coupling constants, and nuclear quadrupole moments. Agreement between experimental results and available theory is good in all cases except for the values of $l$-type doubling constants.

SINCE much of the pure rotational spectra of molecules lies in the microwave region, and since microwave techniques have been developed to give both high resolution and accurate frequency measurements, microwave spectroscopy may be expected to make a considerable contribution to the study of molecular rotational spectra.

Among the simplest of the molecules which can be studied with microwave techniques are those of the linear *XYZ* type, when their end-to-end dissymmetry is sufficient to give them an appreciable dipole moment. Their spectra are relatively simple and intense, so that they provide a good test of theory and techniques, and a good introduction into more complex types of molecules. Only brief statements of some of the more important observations on this type of spectra have so far been published. Even though microwave study of these simple linear molecules may be regarded as just well begun, it seems

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appropriate to give a more detailed account of experiments and results.

## CARBON OXYSULFIDE

The spectrum produced by the linear molecule OCS is particularly simple because its more abundant isotopic types show no nuclear quadrupole effects. Nuclei of the most plentiful isotopic species $O^{16}C^{12}S^{32}$ have been known for some time to have zero spins, and since the nuclei can, therefore, take no preferred orientation in the molecule, no quadrupole effects are possible. Electron diffraction measurements had assigned distances 1.16±0.02A for the O−C bond and 1.56±0.03A for the C−S bond. Computation of the moment of inertia $I$ from these internuclear distances shows that of the expected series of rotational lines of frequency $2Jh/8\pi^2 I$ the one for $J=2$, or the transition from $J=1$ to $J=2$, should produce an absorption near 1.25 cm-wave-length, or in the region called "*K*" band for which oscillators and other microwave components are available.

Absorption due to this line was first reported by Walter and Hershberger,[1] using gas at atmospheric pressure, and the line located at 24,325.92 Mc by Dakin, Good, and Coles,[2] near the position predicted from electron diffraction results. Again because no nuclear quadrupole effects are present the Stark effect in this molecule is simple and lends itself to a very accurate determination of the OCS dipole moment. Dakin, Good, and Coles[3] measured the frequency separation between the two components into which this line is split by an electric field applied parallel to the microwave radiation and thus obtained a value 0.72 Debye unit for the OCS moment, in fair agreement with the value 0.65 determined by other methods.**

Intensity and shape of microwave absorption lines are given according to Van Vleck and Weisskopf[4, 5] by the expression

$$\gamma=\frac{4\pi Nf|\mu_{ij}|^2\nu^2}{3ckT\tau}\left[\frac{1}{(\nu-\nu_0)^2+(1/2\pi\tau)^2}+\frac{1}{(\nu+\nu)^2+(1/2\pi\tau)^2}\right], \quad (1)$$

where:

| | |
|---|---|
| $\gamma$ | is the absorption coefficient in $\text{cm}^{-1}$, $\gamma/2$ is the loss in nepers/cm. |
| $N$ | is the number of gas molecules per unit volume. |
| $f$ | is the fraction of molecules in the lower state of the transition $i\rightarrow j$. |
| $\nu_0$ | is the molecular resonant frequency. |
| $\tau$ | is the time between intermolecular collisions. |
| $\mu_{ij}$ | is the quantum-mechanical matrix element for the absorption transition averaged over all values of the magnetic quantum number $m$. |
| $c, k, T$ | are the velocity of light, Boltzmann constant, and absolute temperature of the gas, respectively. |

At pressures less than $\frac{1}{10}$ atmosphere the second term in brackets of expression (1) is quite negligible. The first term in brackets appears to agree well with experiment under low pressure conditions down to pressures of about $10^{-2}$ mm Hg, where various complicating effects may be of importance. For the rotational transition $J=J_0\rightarrow J_0+1$ of a linear molecule, $|\mu_{ij}|^2=\mu^2(J_0+1)/(2J_0+1)$, where $\mu$ is the molecular dipole moment, and

$$f=f_v\frac{(2J_0+1)\exp[-J_0(J_0+1)B/kT]}{\sum_J(2J+1)\exp[-J(J+1)B/kT]},$$

where $B$ is the molecular rotational constant and related to the moment of inertia $I$ by $B=h^2/8\pi^2 I$. The quantity $f_v$ is the fraction of molecules in the vibrational and electronic state under consideration—usually close to one for the lowest state. For a line occurring in the microwave region $J_0B\ll kT$ and the sum may be fairly accurately replaced by an integral so that $f=f_v(2J_0+1)B/kT$ and, neglecting the second term of (1) at low pressures,

$$\gamma=\frac{2\pi Nf_v h\mu^2\nu^2\nu_0}{3c(kT)^2\tau[(\nu-\nu_0)^2+(1/2\pi\tau)^2]}. \quad (2)$$

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[1] J. E. Walter and W. D. Hershberger, J. App. Phys. **17**, 814 (1946).

[2] T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **71**, 640 (1947).

[3] T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **70**, 560 (1946).

** The result of very recent measurement of dipole moment by dielectric effect [J. G. Jelatis, J. App. Phys. **19**, 419 (1948)] is 0.720±0.005 Debye unit. For refinement of dipole moment measurement by Stark effect, see M. W. P. Strandberg, T. Wentink, and R. Kyhl, Phys. Rev., to be published.

[4] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).

[5] C. H. Townes, Phys. Rev. **70**, 665 (1946). Note that definitions of $\gamma$ and $f$ are slightly different in this reference from those used here.

It should be noted that this formula gives a maximum absorption coefficient (when $\nu=\nu_0$) which increases approximately as the cube of the frequency $\nu_0$. This is one of the reasons why microwave absorption measurements in gases have been mostly made at as high frequencies as can conveniently be used.

Even after the molecular dipole moment is known, the peak intensity or value of $\gamma$ when $\nu=\nu_0$ cannot be predicted because it depends on the value of $\tau$, which usually must be determined empirically, although enough measurements have now been made to allow in some cases a rough guess at $\tau$. The half-width, or width in frequency of the absorption line at one-half maximum, may be used as a measure of $\tau$, since it equals $1/\pi\tau$.

The intensity and half-width of the OCS $J=1\rightarrow 2$ line have been measured at a gas pressure of a fraction of a millimeter of mercury. The half-width is $(12\pm 2)p$ megacycles/sec., where $p$ is the pressure in mm Hg, and the peak absorption coefficient is $5.1\pm 0.7\times 10^{-5}$ cm$^{-1}$ for a plane wave. Substituting the measured half-width into expression (2) and using the value $\mu=0.72\times 10^{-18}$ e.s.u., the predicted peak absorption when $T=300$°C is $5.4\pm 0.9\times 10^{-5}$ cm$^{-1}$.

Walter and Hershberger's measurement[1] of an absorption coefficient $8\pm 2\times 10^{-5}$ cm$^{-1}$ for a frequency of 24,000 Mc in OCS at atmospheric pressure is higher than this because at this pressure adjacent rotational lines $J=0\rightarrow 1$, and $J=2\rightarrow 3$ and others contribute appreciably to the absorption of 24,000 Mc. There is an additional small contribution from the second term of (1) at this pressure. Assuming the experimentally determined half-width of the $J=1\rightarrow 2$ line is correct for the other lines and assuming expression (1) holds at atmospheric pressure, the peak absorption coefficient of the $J=1\rightarrow 2$ line at low pressure may be abstracted from Walter and Hershberger's measurement as $5.6\pm 2.0\times 10^{-5}$ cm$^{-1}$.

Although most of the OCS molecules are in the ground vibrational state, an appreciable number are excited to higher vibrational states. Molecular vibrations interact slightly with the molecular rotational levels, producing small changes in the rotational constant $B$ of the order of $B^2/\omega$, where $\omega$ is the vibrational frequency. For molecules of the type discussed here, these effects are generally taken into account by writing the rotational frequencies as

$$\nu=2J[B_e-\alpha_1(v_1+\tfrac{1}{2})-\alpha_2(v_2+1)-\alpha_3(v_3+\tfrac{1}{2})], \quad (3)$$

where $B_e$ is the value of the rotational constant $B$ assuming no vibration; $\alpha_1$, $\alpha_2$, and $\alpha_3$ are coefficients representing the change in the effective value of $B$ due to vibration. The quantum numbers $v_1$, $v_2$, and $v_3$ are integers representing the degree of excitation of the three vibrational modes. Mode number two gives a contribution $\alpha_2$ rather than $\alpha_2/2$ in the ground state ($v_1=v_2=v_3=0$) because it is the degenerate bending mode. In addition, interaction between rotational and vibrational motions removes the degeneracy of this bending mode. This effect is manifested most prominently in case $v_2=1$, when the level which is doubly degenerate in the absence of rotation is split by rotation into what is known as $l$-type doublets. The rotational frequencies are then[6]

$$\nu=2J[B_e-\alpha_1(v_1+\tfrac{1}{2})-2\alpha_2\pm q/2-\alpha_3(v_3+\tfrac{1}{2})]. \quad (4)$$

The quantities $\alpha_1$, $\alpha_2$, $\alpha_3$ have been calculated by Nielsen.[7] Unfortunately they are primarily dependent on the generally unknown anharmonic force constants of vibration. A theoretical evaluation of $q$ is given by Nielsen and Shaffer.[8] This $q$ must be carefully distinguished from the $q$ sometimes used as a measure of the molecular quadrupole field. The $\alpha$'s and $q$ may be determined experimentally if rotational lines due to molecules in the ground state and various excited states can be observed. For OCS the vibrational frequencies are known so that the fraction of molecules in excited states may be calculated. The lowest vibrational frequency and hence the one most abundantly excited is the bending mode. In each of the two bending modes ($v_2=1$) there is one-thirteenth of the molecules at room temperature. Lines due to the transition $J=1\rightarrow 2$ of these excited molecules have been found and are listed in Table I. From their frequencies a value minus 10.59 Mc for $\alpha_2$ and 6.39 Mc for $q$ can be obtained. This value of $q$ does not agree exactly with Nielsen and Shaffer's theoretical evaluation,[8] nor do the values for other linear

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[6] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 377.

[7] A. H. Nielsen, J. Chem. Phys. **11**, 160 (1943).

[8] H. H. Nielsen and W. H. Shaffer, J. Chem. Phys. **11**, 140 (1943).

TABLE I. Measured OCS lines in the microwave region.

| Molecule | Designation of line | Frequency in megacycles | Line used as frequency standard | Frequency interval in megacycles between standard and measured line |
|---|---|---|---|---|
| $O^{16}C^{12}S^{32}$ | $J=1\rightarrow2$ | $24325.92\pm0.02$* | | |
| | $J=1\rightarrow2$, $v_2=1$, $l_1$ | 24355.50 | $O^{16}C^{12}S^{32}$ $J=1\rightarrow2$ | $29.58\pm0.08$ |
| | $J=1\rightarrow2$, $v_2=1$, $l_2$ | 24381.07 | $O^{16}C^{12}S^{32}$ $J=1\rightarrow2$, $v_2=1$, $l_1$ | $25.57\pm0.05$ |
| | $J=3\rightarrow4$ | 48651.7** | | |
| | $J=4\rightarrow5$ | 60814.1** | | |
| $O^{16}C^{12}S^{33}$ | $J=1\rightarrow2$ | 24020.21 | $O^{16}C^{12}S^{32}$ $J=1\rightarrow2$ | $305.71\pm0.04$ |
| $O^{16}C^{12}S^{34}$ | $J=1\rightarrow2$ | $23731.33\pm0.03$* | $O^{16}C^{12}S^{32}$ $J=1\rightarrow2$ | $594.63\pm0.04$ |
| | $J=3\rightarrow4$ | 47462.3** | | |
| $O^{16}C^{13}S^{32}$ | $J=1\rightarrow2$ | 24247.69 | $O^{16}C^{12}S^{32}$ $J=1\rightarrow2$ | $78.23\pm0.05$ |
| $O^{16}C^{13}S^{34}$ | $J=1\rightarrow2$ | 23646.92 | $O^{16}C^{12}S^{34}$ $J=1\rightarrow2$ | $84.41\pm0.10$ |
| $O^{16}C^{14}S^{32}$ | $J=1\rightarrow2$ | $24173.0\pm1.0$*** | | |
| $O^{18}C^{12}S^{32}$ | $J=1\rightarrow2$ | 22819.30 | $N^{14}H_3$ 3,2 | $14.85\pm0.05$ |

* Dakin, Good, and Coles, Phys. Rev. **71**, 640 (1947).
** Hillger, Strandberg, Wentink, and Kyhl, Phys. Rev. **72**, 157 (1947).
*** Arthur Roberts, Phys. Rev. **73**, 1405 (1948).

molecules measured here. This discrepancy will be discussed further below.

A number of other lines have been found which are due to isotopic species of OCS and to other transitions. All OCS lines which have been measured here or reported in the literature are listed in Table I. Lines are designated by the two values of $J$ involved in the transition, the vibrational quantum numbers, and in the case of $l$-type doublets, by the symbols $l_1$ and $l_2$ which indicate, respectively, the low frequency and high frequency components of the doublet. Although the lines measured by Dakin *et al.* and Hillger *et al.* were measured by comparison with a lower frequency standard, the measurements in this laboratory consisted of measurement of intervals between the unmeasured line and some line used as a standard which was accurately known. This technique will be described below. Since for most purposes frequency intervals need to be known much more accurately than absolute frequencies, Table I lists the measured intervals and their probable errors. The previously published[9] interval $O^{16}C^{12}S^{33}-O^{16}C^{12}S^{32}$ is modified by 0.04 Mc in the table as a result of new measurements.

The $O^{16}C^{12}S^{34}$ and $O^{16}C^{12}S^{33}$ lines have been observed in normal isotopic mixtures where their abundances are 4.2 percent and 0.74 percent, respectively. Since positions of lines due to rare isotopic molecules can be rather accurately calculated if the lines due to more common isotopes are known, and since lines due to various isotopic species are generally very easily resolved, sufficient improvement in sensitivity of microwave spectroscopy should make it a useful tool in detecting the presence of rare isotopes. An improvement of a factor of about 50 in sensitivity is needed to detect the $OCS^{36}$ line with the natural abundance. The $O^{16}C^{13}S^{32}$ and $O^{18}C^{12}S^{32}$ lines were observed in material enriched to 20 percent and 1.5 percent, respectively.

Failure to observe splitting in the rotational lines of these molecules due to nuclear quadrupole effects shows that the quadrupole couplings for $C^{13}$, $S^{34}$, and $O^{18}$ must be less than 0.5, 1.0, and 1.0 Mc, respectively, in these molecules assuming reasonable values of spin. The significance of this failure to find quadrupole splitting will be discussed below.

It might be expected that from the very accurate moments of inertia of various isotopic species of a molecule which can be obtained with microwave spectroscopy, very accurate internuclear distances may be determined. In addition, if lines due to three isotopic species are known, it might be supposed that the two internuclear distances could be accurately determined, and, in addition, one mass ratio. Unfortunately, this is not the case because moments of inertia are determined not only by the equilibrium internuclear distances, but in addition by the values of the three $\alpha$'s, and these $\alpha$'s differ

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[9] C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. **72**, 513 (1947).

in value from one isotopic species to another in a way which cannot be accurately known without a rather detailed knowledge of the anharmonic force constants involved. (This variation can be seen in Table IX.) As a result, the accuracy of internuclear distance determination is usually limited to about ±0.01A because of incomplete information about the $\alpha$'s, when better knowledge of these quantities would allow an accuracy better by an order of magnitude.

An illustration of these effects may be obtained by examining the simpler diatomic molecule. If the potential between the two nuclei were strictly parabolic, fluctuations in the internuclear distance taking place even in the lowest vibrational state would result in a value of $B_0$ slightly greater than $B_e$, the value for the artificial case when the nuclei are at rest at the equilibrium distance. In terms of the constant $\alpha$, this produces a negative contribution to $\alpha$. However, generally the anharmonic force constant is large enough to increase the average distance between the nuclei when vibration is present, giving a positive contribution to $\alpha$ considerably larger than the harmonic contribution. Similarly in the case of triatomic linear molecules, the harmonic contributions to $\alpha_1$ and $\alpha_3$ are negative and to $\alpha_2$ positive, but in all known cases the anharmonic terms are larger and of opposite sign so that $\alpha_1$ and $\alpha_3$ are positive and $\alpha_2$ negative. In the case of OCS, the harmonic contribution to $\alpha_2$ is approximately $+2.6$ Mc and the net value of $\alpha_2$ is $-10.6$ Mc.

Probably in only a few polyatomic molecules will it be feasible to evaluate rigorously zero-point vibration effects, so that some estimate of the errors involved in their omission is needed. Fairly direct evidence of the size of these effects is afforded by a comparison of internuclear distances determined from various pairs of isotopic lines and collected in Table II. Since there is no reason to expect the errors to be the same when lines of two sulfur isotopes and lines of two oxygen isotopes are used to calculate the distances, the inconsistencies may be taken as a measure of the total error due to all zero-point vibrations. If no zero-point vibrations were present, the various determinations should not differ by more than 0.001A, but actual differences are as large as 0.01A.

TABLE II. OCS bond distances calculated from various isotopic pairs.*

| Pair of isotopic molecules used | C–O distance | C–S distance |
|---|---|---|
| $O^{16}C^{12}S^{32}-O^{16}C^{12}S^{34}$ | 1.1647A | 1.5576A |
| $O^{16}C^{12}S^{32}-O^{16}C^{13}S^{32}$ | 1.1629 | 1.5591 |
| $O^{16}C^{12}S^{34}-O^{16}C^{13}S^{34}$ | 1.1625 | 1.5594 |
| $O^{16}C^{12}S^{32}-O^{18}C^{12}S^{32}$ | 1.1552 | 1.5653 |

* Zero-point vibrations are neglected, producing the main discrepancies between distances obtained from various isotopic pairs. Isotopic masses are taken from Mattauch (see reference 10).

Dakin, Good, and Coles[2] have given an analysis of the various sources of error in determination of internuclear distances from the $OCS^{32}$ and $OCS^{34}$ lines, and decided that uncertainty in the ratio of masses of the two sulfur isotopes produced the largest error of ±0.0047A. They omitted mention of zero-point vibration errors which appear to be larger. In addition, if one accepts the mass values for sulfur given by Mattauch,[10] the probable error due to their uncertainty is only ±0.0016A. Hillger, Strandberg, Wentink, and Kyhl[11] give internuclear distances determined from the $OCS^{32}$ and $OCS^{34}$ lines to an accuracy of 0.0001A and state that uncertainties in the value of $h$ produce the largest errors in their determination. In oral presentation of their work, however, they pointed out the difficulties due to zero-point vibrations.

Another method of demonstrating the importance of zero-point vibrations is to evaluate the difference between $B_0$, the effective rotational constant including the vibrations, and $B_e$, the hypothetical rotational constant if the atoms were all at equilibrium positions. This may be done in the case of OCS because the frequency shifts are known for isotopic change of mass of each of the three atoms. If the carbon, oxygen, and sulfur mass ratios are kept constant, but each assumed proportional to a variable $m$, it can be shown that $B_e$ is inversely proportional to $m$ and each of the $\alpha$'s is proportional to $m^{-\frac{3}{2}}$. Hence the sum of the $\alpha$'s may be evaluated from the data of Table II by calculating the change in $B_0$ due to the same fractional change in mass of all of the atoms simultaneously, and properly relating the change in $B_0$ which is not propor-

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[10] J. Mattauch, *Nuclear Physics Tables* (Interscience Publishers, Inc., New York, 1946).

[11] Hillger, Strandberg, Wentink, and Kyhl, Phys. Rev **72**, 157 (1947).

tional to this mass change to the sum of the $\alpha$'s. Thus to a good approximation

$$\frac{\alpha_1+2\alpha_2+\alpha_3}{B_0}=-\frac{8[m_om_cl_{oc}\Delta l_{oc}'+m_sm_cl_{sc}\Delta l_{sc}''+m_om_s(l_{oc}+l_{sc})(\Delta l_{oc}'+\Delta l_{sc}'+\Delta l_{oc}''+\Delta l_{sc}'')]}{m_om_cl_{oc}^2+m_sm_cl_{sc}^2+m_om_s(l_{oc}+l_{sc})^2}, \quad (5)$$

where $m_o$, $m_c$, $m_s$ are masses of oxygen, carbon, and sulfur, respectively; $l_{oc}$, $l_{sc}$, $l_{os}$ are distances between atoms represented by the subscripts; $\Delta l_{oc}'$ is the difference between the distance $l_{oc}$ determined from the isotopic carbon lines and that from the isotopic oxygen lines; $\Delta l_{sc}'$ is similar to $\Delta l_{oc}'$, but refers to the distance $l_{sc}$; $\Delta l_{oc}''$ is the difference between the distance $l_{oc}$ determined from the isotopic carbon line and that from the isotopic sulfur lines; $\Delta l_{sc}''$ is similar to $\Delta l_{oc}''$, but refers to the distance $l_{sc}$. Evaluation of expression (5) gives $\alpha_1+2\alpha_2+\alpha_3=+0.00856B_0$, or $B_e=(1+0.00428)B_0$.*** Thus the $J=1\rightarrow 2$ transition is decreased approximately 104 Mc by zero-point vibrations. In the case of diatomic molecules, it may be shown that the isotopic frequency shift calculated by neglecting zero-point vibrations will be in error by a fraction $(B_e-B_0)/2B_0$. Assuming the magnitude of this error is roughly the same in the frequency difference between the $O^{16}C^{12}S^{32}$ and $O^{16}C^{12}S^{34}$ lines, an error in the OC distance of 0.0091A would be produced. This estimate is of about the same magnitude as the deviations in Table II. Thus from evaluating $B_0-B_e$, from the variations in Table II and from similar variations for ClCN to be found below, it appears that ±0.01A is a reasonable estimate of the error in internuclear distances to be generally expected from zero-point vibrations.

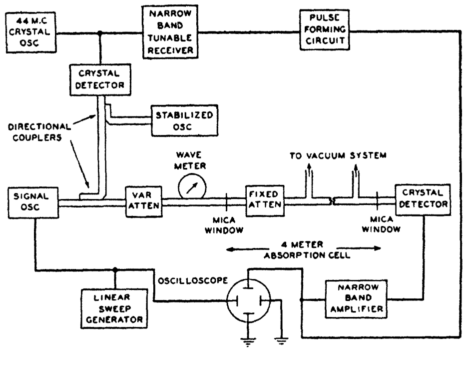

FIG. 1. System for detection and frequency measurement of absorption lines.

As was noted earlier,[9] although in most cases zero-point vibrations prevent an accurate measurement of mass ratios in this type of molecule, ratios of mass differences may be fairly accurately obtained if lines for more than two isotopes of the same element are measured. Lines for $O^{16}C^{12}S^{32}$, $O^{16}C^{12}S^{33}$, and $O^{16}C^{12}S^{34}$ provide such a case. Assume that approximate internuclear distances are known so that the isotopic shift $\Delta\nu$ between two sulfur isotopes may be calculated except for an error of the order of $[(B_e-B_0)/2B]\Delta\nu$ due to zero-point vibrations. Although the exact amount of this error is unknown, it will fortunately depend in a linear way on the mass difference $\Delta m$ of the sulfur isotopes except for quantities of the order $[(B_e-B_0)\Delta\nu/2B]\Delta m/m$ and less, where $m$ is the mass of sulfur. The entire isotopic shift is also linearly dependent on $\Delta m$ to a fractional accuracy of $\Delta m/m$. Consequently, the fractional error which might be introduced in obtaining the ratio of mass differences $(S^{33}-S^{32})/(S^{34}-S^{32})$ by completely neglecting zero-point vibrations is of the order

$$\left[\frac{(B_e-B_0)}{2B}\right]\frac{\Delta m}{m}\approx\frac{1}{15{,}000}.$$

If the ratio $(S^{33}-S^{32})/(S^{34}-S^{32})$ is calculated from the frequency intervals given in Table I, the result is 0.49975±0.0001. This agrees poorly† with the value 0.50038±0.0002 from Mattauch's tables.[10]

## EXPERIMENTAL TECHNIQUES

Discussion of OCS has afforded an introduction into the type of spectra produced by linear

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*** Recent measurements of $\alpha_1$ [A. Roberts, private communication; C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948)] as 18.12 Mc, combined with this relation, allow evaluation of $\alpha_3$ as 55.1 Mc.

† Further work [C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948)] has shown that effects due to the $S^{33}$ nuclear quadrupole moment increase the frequency of the $OCS^{33}$ line observed here by 0.54 Mc. If this is taken into account, one obtains $(S^{33}-S^{32})/(S^{34}-S^{32})=0.50066$ ±0.00015, still in poor agreement with Mattauch, but in good agreement with the value 0.50060±0.00005 from recent measurements of nuclear reactions by Davison (Paper P5, Washington meeting of Am. Phys. Soc., 1948).

$XYZ$ molecules. It appears appropriate now to describe some of the apparatus and techniques used in making the measurements quoted before progressing to other more complicated spectra.

Figure 1 shows a system used for detecting absorption lines which is similar to that previously described,[5] but includes circuits for measuring line frequencies more accurately than can be done with a simple wave meter. Radiation from the signal oscillator (type 2K50 was used throughout) traverses the absorption cell and is detected by a rectifying "crystal." The resulting signal after amplification is put on the vertical plates of an oscilloscope. The oscillator is swept over a few megacycles and the sweep put on the horizontal plates of the oscilloscope so that frequency is plotted against transmission through the absorption cell by the oscilloscope trace, and absorption lines show up as vertical pips on the trace. Frequency is measured approximately by the wave meter which may be set so that its resonance likewise produces a pip on the oscilloscope. The signal oscillator was swept about twice per second, and the band width of the circuit amplifying the detected signal was narrowed as much as possible (to about 20 cycles per second) to eliminate noise without undesirably distorting pips due to absorption lines. Such a system is simple and can detect absorption lines as weak as $10^{-6}$ cm$^{-1}$, or $5\times10^{-7}$ nepers/cm in the 4-meter absorption cell used. To obtain this sensitivity a power of about 0.1 milliwatt must be transmitted through the gas. This much power produces saturation[5,12] at low gas pressures and prevents work with very narrow lines.

Although no thorough investigation of sensitivity and sources of noise has been undertaken in these laboratories, some observations on the problem of sensitivity have been made. The systems used here for detecting absorption lines characteristically show noise and interfering effects which are approximately proportional to the microwave power used. One source of trouble is imperfect matching and consequent reflections back and forth in the cell. These reflections produce a variation in detected signal with power which can mask the variations due to absorption lines. Reflections can generally be easily reduced to the point where they produce variations of transmitted power of one percent, and with care they may be reduced by another factor of ten. Some trouble is often encountered with noise due to mechanical vibration, but this source can usually be eliminated. The random noise generally encountered can be due either to crystal noise or to noise in the signal oscillator, or both. This random noise is often many orders of magnitude above thermal noise. Noise encountered in work described here usually appeared to originate in the detecting crystal and was approximately proportional to the power absorbed by the crystal. It was found advantageous with the system described above to apply a biasing current to the crystal so that the average d.c. voltage across the crystal when it received microwave power was approximately zero. Application of this biasing current at times both increased the detected signal and decreased the random noise. Another demonstration that most of the noise originates in the crystal rather than the signal oscillator is given by the system previously described[5] which amplifies only the difference between signals from radiation which has traversed the absorption cell and a monitoring signal directly from the signal oscillator. This scheme should eliminate oscillator noise, but usually results in very little noise reduction. However, under other conditions, and with other arrangements for detecting absorption lines, oscillator noise may be of more importance. An expression for the theoretical limit of detectable absorption is given elsewhere.[13]

For some experiments a modification of the system of Fig. 1 was used which involved cutting the oscillator on and off by means of a square wave applied to the reflector electrode. This square wave was of about 2500 cycles/sec., and it was thought perhaps by detecting only a narrow band about 2500 cycles, some crystal noise might be avoided, since crystal noise is in some cases proportional to the inverse of the frequency at which noise is detected. A phase-detecting circuit, or "lock-in" amplifier, was used to amplify the detected signal and to obtain the desired narrow band about 2500 cycles. This

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[12] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. **60**, 83 (1948); T. A. Pond, and W. F. Cannon, Phys. Rev. **72**, 1121 (1947).

[13] C. H. Townes and S. Geschwind, J. App. Phys. **19**, 795 (1948).

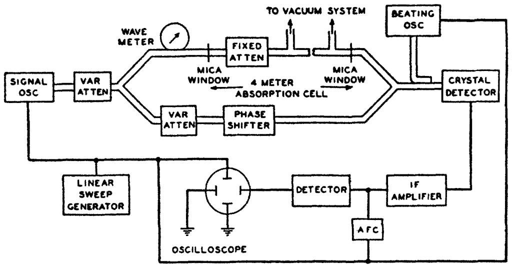

FIG. 2. Microwave spectrometer using r-f bridge and heterodyne detection.

arrangement resulted in no appreciable increase of signal to noise ratio, although it did avoid pick-up troubles due to 60 cycles and other low frequency sources.

One of the difficulties in detecting weak absorption lines is the necessity of observing small changes of a large background signal. However, there are ways of avoiding to some extent the handicap of measuring very small fractional effects. One is afforded by the Stark modulation technique described by Hughes and Wilson.[14] Another is the bridge detecting system illustrated by Fig. 2. The bridge was balanced by means of the phase adjustment and variable attenuator so that power arriving at the detecting crystal was about one-tenth of the power through either arm. An absorption line was detected as a change in this balance due to selective absorption in the absorption cell and, to a lesser extent, by phase shifts produced. This reduced the power variation at the crystal due to an absorption line by the square root of ten, but reduced the noise by about a factor of ten, so the net result was a more sensitive system. In order to detect the small amounts of power received by the crystal in this arrangement, heterodyne detection was used with a 60-Mc I.F. amplifier and an automatic frequency control (A.F.C.) circuit to maintain the beating oscillator exactly 60 Mc from the sweeping signal oscillator. Another reason for setting up this heterodyne system was to provide detection of lines with very small amounts of energy flowing through the absorption cell so as to avoid saturation and obtain very narrow lines. In some cases where high resolution was desired, power flowing through the absorption cell was reduced to about one microwatt. The sensitivity of this system was such that the $OCS^{33}$ line could just be detected in the normal isotopic mixture at room temperature with 4 meters of absorption cell. Since $S^{33}$ has an abundance of 0.74 percent this represents an absorption coefficient of $4.5\times 10^{-7}$ cm$^{-1}$ or $2.2\times 10^{-7}$ nepers/cm. Probably better balancing would afford some additional improvement. This system has the advantage of good sensitivity, and of obtaining very narrow lines. However, it is very slow and awkward to use for searching because considerable adjustment is needed at each frequency in order to obtain optimum sensitivity.

In order to study the change in relative intensity of lines with change in temperature, and in order to boost the intensity of some weak lines, a thermally insulated metal trough was built around the absorption cell of the bridge detecting system. Hot water or refrigerant could be put in the trough to vary the temperature of the absorption cell from near 100°C to liquid nitrogen temperatures. Formula (2) shows that the intensity of a rotational line in the microwave region increases rapidly with decreasing temperature. For fixed $N$, the half-width may be expected to be proportional to $(T)^{\frac{1}{2}}$, so that the absorption coefficient is generally proportional to $1/T^{5/2}$. At dry ice temperature, which proved to be a convenient working point, intensities of ground-state lines were in fact found to be about three times greater than at room temperature. For some of the weak isotopic OCS lines, the temperature was decreased to about 125°K, where the intensity is ten times greater than at room temperature, in order to look for the possibility of weak lines split from the main line by nuclear quadrupole effects.

Frequency measurements to an accuracy of two to five megacycles may be obtained with the frequency meter shown in Fig. 1. More accurate measurements of frequency differences between lines was accomplished by using the stabilized 1-cm oscillator and a 44-Mc quartz crystal oscillator shown in this same figure. If the signal oscillator, the stabilized oscillator, and the crystal oscillator are all fed into a detecting crystal, the same beat frequency is obtained for any two signal oscillator frequencies separated by an integral multiple of 44 Mc. If the receiver is tunable

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[14] R. H. Hughes and E. B. Wilson, Phys. Rev. 71, 562 (1947).

over a range of 22 Mc, it may be set so that a main beat frequency is received for any frequency of the signal oscillator, and this beat note imposed on the oscilloscope so that it coincides with the peak of an absorption line over which the signal oscillator sweeps. If the receiver is accurately calibrated, similar settings on two different absorption lines allow an accurate determination of the difference in their frequencies. This system is capable of good accuracy in measuring frequency differences, and the equipment needed is somewhat less than that required by other accurate measuring systems.[15] If the oscillator is well stabilized to eliminate difficulties with drift, the main limitations in accuracy are errors in judging the center of an absorption line. This does not provide a direct measurement of absolute frequency, but absolute frequencies can generally be obtained with more accuracy than needed by setting on one of the accurately determined ammonia lines. In the case of OCS, most of the lines were thus referred to the well measured $O^{16}C^{12}S^{32}$ line.

The oscillator was stabilized part of the time on an ammonia line by the circuit shown in Fig. 3, and part of the time by a similar circuit on a standard transmission-type wave meter.

An ammonia line is split into Stark components by the application of a constant electric field. In addition, a small a.c. field of a convenient frequency such as 10,000 cycles is applied to change the frequency of each component sinusoidally by about 0.1 Mc. A microwave signal is transmitted through the ammonia. If its frequency is approximately equal to the frequency of one of the Stark components, then its intensity at the detecting crystal will be modulated by the varying Stark field. If the oscillator frequency is higher than the average position of the Stark component, a 10,000-cycle signal of one phase will be received by the crystal; if it is lower, a similar signal of opposite phase is detected. Thus a phase-detecting circuit or "lock-in" amplifier into which the crystal signal is fed will produce a signal of one sign if the oscillator frequency is higher than the line, and of the opposite sign if the oscillator frequency is lower, providing the usual discriminator curve needed to feed back into the frequency-determining electrode of the oscillator in order to achieve stabilization. This system is particularly suited for stabilization on a gas absorption line since no part of the microwave circuit varies in synchronism with the varying Stark field except the absorption lines, and, consequently, spurious effects due to other parts of the microwave circuit are eliminated. The effectiveness of this circuit was judged by comparing the beat note produced in the frequency-measuring circuit described above with a gas absorption line over periods of several hours. No detectable variation or drift was found, which indicates that stabilization was better than about 0.05 Mc. This same type of circuit was also used with a standard frequency meter as the frequency-determining element rather than ammonia. In this case, instead of varying the frequency of peak absorption of the meter, a small signal was put on the oscillator to vary its frequency ±0.05 Mc. Of course a beat note for frequency measurement 0.1 Mc wide was then produced, but its width proved to be no handicap. In contrast to the case where ammonia was used for stabilization, some trouble was encountered while using the frequency meter with frequency drifts of the order of 0.1 Mc. These were probably caused by temperature and atmospheric changes which shifted the resonant frequency of the cavity. A temperature change of only 1°C was sufficient to produce a 0.1-Mc shift in resonant frequency of the cavity.

Intensities and half-widths of lines were measured in an apparatus of the type shown in Fig. 1. The deflection of the oscilloscope trace varies in an approximately linear way with absorption in the wave guide. In order to measure the half-

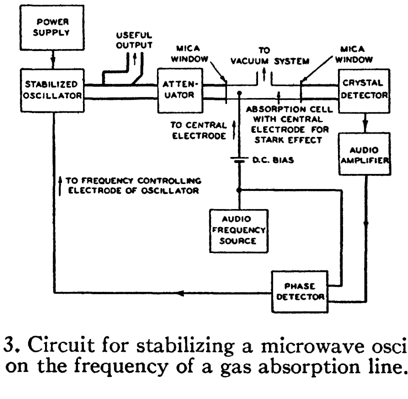

FIG. 3. Circuit for stabilizing a microwave oscillator on the frequency of a gas absorption line.

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[15] W. E. Good and D. K. Coles, Phys. Rev. 72, 157 (1947).

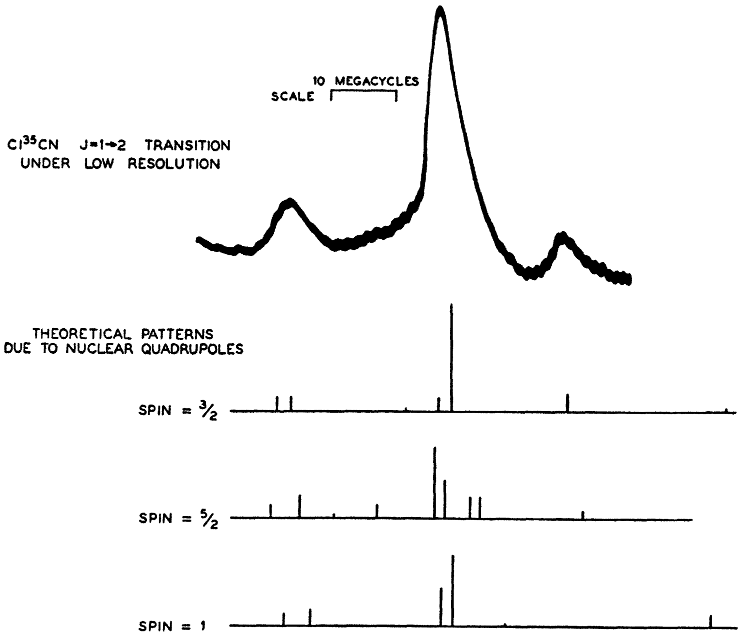

FIG. 4. Spectrum of $Cl^{35}CN$ $J=1\rightarrow 2$ transition under low dispersion and comparison with quadrupole patterns for several values of nuclear spin.

width of an absorption line, gas pressure was adjusted to obtain a convenient width such as 5 Mc, and frequency markers set at the half-height points on either side of the pip seen on the oscilloscope.

Intensities were measured by comparing the size of pip produced by the resonance of a frequency meter with that produced by the gas absorption line. The fraction of power absorbed by the frequency meter was determined by measuring the rectified crystal currents with the meter set first on and then away from the oscillator frequency. In addition, absorption due to the frequency meter was determined by comparing its effect on crystal current with that of a calibrated attenuator. This type of measurement appears to have an accuracy of about ±20 percent, and with care might be made as accurate as ±10 percent.

### CYANOGEN CHLORIDE

The $J=1\rightarrow 2$ line of ClCN shows many of the same characteristics as that due to OCS, but is considerably more complex because both the chlorine and nitrogen nuclei possess electric quadrupole moments. The major lines of the $Cl^{35}CN$ $J=1\rightarrow 2$ transition are shown under low resolution in Fig. 4. The satellite lines seen in Fig. 4 are not due to molecules in excited vibrational states. This was demonstrated by comparing their intensities relative to the main line at room temperature and at −78°C. Relative intensities for the two temperatures were found to be the same within ±20 percent, whereas the population of the lowest energy excited state should have decreased at the lower temperature by a factor of about 2.5. The $Cl^{37}CN$ $J=1\rightarrow 2$ transition shows a similar pattern, but with the satellites separated by about 25 percent less than is the case for $Cl^{35}CN$, showing that these lines depend strongly on the nature of the chlorine nucleus. Two types of nuclear effects may be expected to cause splitting of rotational molecular lines, and have been studied in other molecules by Rabi and his associates. They are nuclear magnetic dipole interactions which give energies dependent on the cosine of the angle between nuclear spin $I$ and molecular rotational momentum $J$, and nuclear electric quadrupole moments giving energies dependent on the square of this cosine. The magnetic dipole interactions are generally very small in molecules because most molecules are in $^1\Sigma$-states, and in addition the pattern to be expected is quite different from the spectrum obtained. The splitting due to a single nucleus coupled to molecular rotation of a linear molecule by electric quadrupole effects may be obtained from the basic work of Casimir.

Relative intensities and positions of the various components are readily obtained from published tables. Calculation of these quantities has been discussed in some detail in an earlier paper.[16] Plots of patterns to be expected from a $J=1\rightarrow 2$ transition assuming quadrupole interactions for a nucleus of spin 5/2, 3/2, or 1 are shown in Fig. 4 and compared with the observed $Cl^{35}CN$ spectrum. These hyperfine patterns are quite specific with respect to both the nuclear spin $I$ and the rotational transition $J\rightarrow J+1$. The spin of $N^{14}$ is well known to be 1, and the spins of $Cl^{35}$ and $Cl^{37}$ have been measured from band spectra as 5/2. The carbon, having spin zero, can contribute no quadrupole effects. It may be seen that the pattern for a spin 3/2 best fits the observed spectrum. However, more resolution is plainly needed to resolve all of the expected structure. In addition, since both N and Cl are contributing to the pattern, it is necessary to compute expected patterns when two nuclei in the same molecule show quadrupole coupling.

The case of two nuclear quadrupole couplings of arbitrary relative magnitude was solved by Bardeen, and has been described in a form convenient for calculation of spectra.[16] With this theory, it was found possible to fit very well and in detail the $Cl^{35}CN^{14}$ spectrum observed under high resolution with the heterodyne detecting system described above.[17] This fit is shown in Fig. 5. It is necessary to assume that $Cl^{35}$ has a spin of 3/2 as indicated by the low resolution

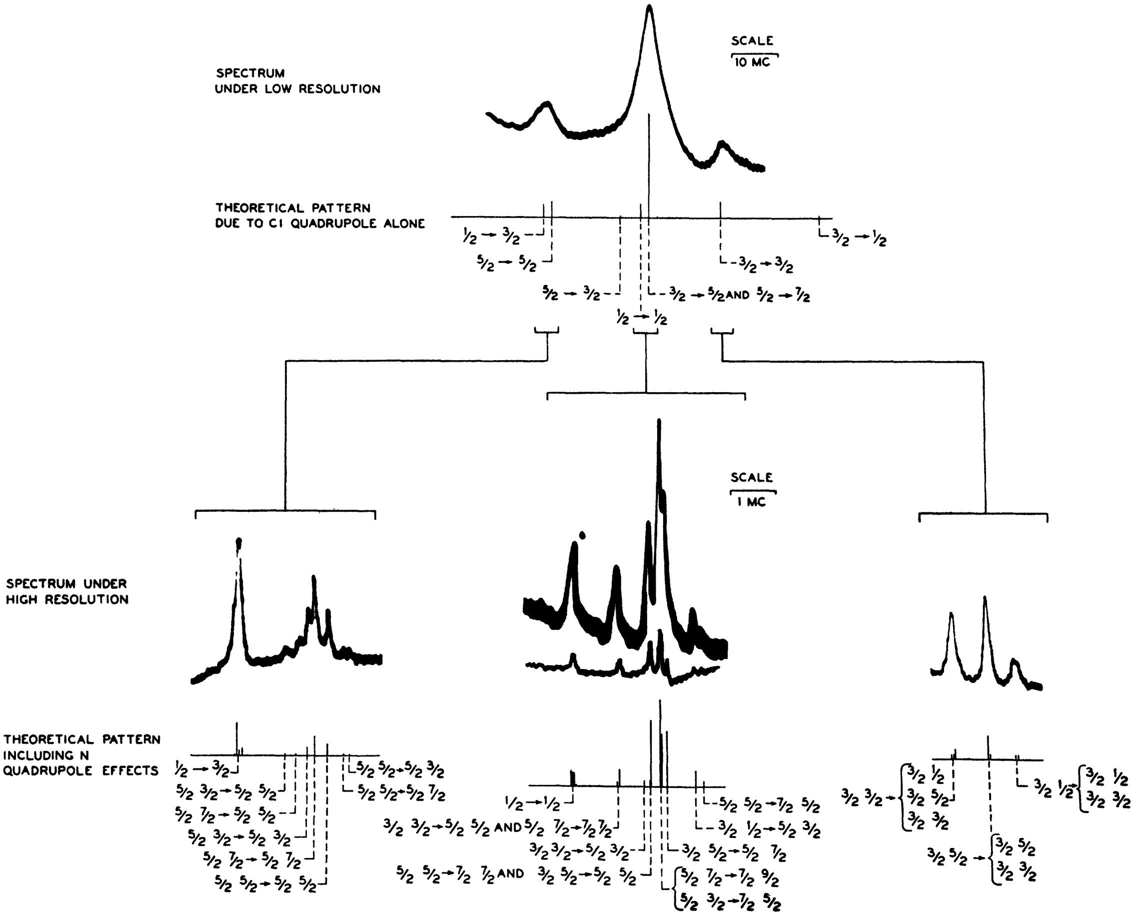

FIG. 5. Spectrum of $Cl^{35}CN$ $J=1\rightarrow 2$ transition with both low and high dispersion and comparison with theoretical pattern assuming spin of $Cl^{35}$ is 3/2.

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[16] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

[17] Townes, Holden, Bardeen, and Merritt, Phys. Rev. **71**, 644 (1947).

results. In this molecule, the quadrupole coupling, $eQ(\partial^2 V/\partial z^2)$, for chlorine 35 is found to be minus 83.2 megacycles and much larger than that of the nitrogen 14, which is minus 3.63 megacycles. This is the reason the major lines of the spectrum give the appearance of a pattern due to a nucleus of spin 3/2, these major lines being finely split by the effects of the nitrogen nuclear quadrupole. Lines are designated in Fig. 5 first by the final and initial values of $F_1$, the quantum number for the vector sum of $I_1$ and $J$, and then by final and initial values of $F$, the quantum number for the vector sum of $I_1$, $I_2$, and $J$. Here $I_1$ is the spin of the Cl nucleus, $I_2$ the spin of the nitrogen nucleus. Thus a line 5/2 7/2→7/2 9/2 indicates a transition $F_1=5/2 \rightarrow 7/2$ and $F=7/2\rightarrow 9/2$. If only one number is given in final or initial states, it is the value of $F_1$. $F_1$ has a definite value only as a first approximation, but it is a sufficiently good quantum number for identifying the lines. Every one of the lines due to chlorine splitting have been observed, including the weak 3/2→1/2 and 5/2→3/2. The weakest line, 5/2→3/2, was also observed to split into three components due to the nitrogen quadrupole in accordance with theory, but no photograph of these lines is available for inclusion in Fig. 5. Agreement between the measured spectrum and the theoretical spectrum is so extensive and detailed, assuming that $Cl^{35}$ has a spin of 3/2, that we may be sure this is the correct spin rather than the previously determined value of 5/2.

A good illustration of the resolving power of the technique used is also afforded by Fig. 5. The central group of lines is shown under high dispersion with two different gas pressures. In the lowest spectrum, the gas pressure is least (about $2\times10^{-4}$ mm Hg) and the highest resolution is obtained, although at this low pressure various effects have decreased the line strengths. Saturation has changed the relative intensities of some of the components in the lowest spectrum. The two rather strong lines 5/2 3/2→7/2 5/2 and 3/2 5/2→5/2 7/2 are separated by only 140 kilocycles, but are shown completely resolved. In the right-hand group of lines, showing how the 3/2→3/2 line is split by the N quadrupole, the small line on the right is flat on the top. This indicates that the two components 3/2 1/2 →3/2 1/2 and 3/2 1/2→3/2 3/2 are almost, but not quite, resolved. Their theoretical separation is 70 kilocycles. Doppler effect and collision with the walls of the $K$-band guide (10.7 mm×4.3 mm cross section) should produce half-widths of about 35 and 10 kilocycles, respectively, at the gas temperature (−78°C) used for the photographs, so that actual resolving power misses the theoretical limit by a factor of two. The limit on resolution is probably partly due to saturation effects which produce a broadening of the lines and a decrease in intensity. Power transmitted through the ClCN gas in $K$-band guide for highest resolution was about 1.5 microwatts, which might be expected to produce noticeable saturation effects at a gas pressure of about $5\times10^{-4}$ mm Hg, where the half-width due to intermolecular collisions should be approximately 25 kilocycles. An additional limitation on resolution, and probably an important one in the experiments here, is the fact that both signal and beat oscillators are not truly monochromatic. If care is taken to insure a very narrow frequency band produced by the oscillators, and somewhat smaller transmitted power is used, it seems reasonable to expect that resolution limited primarily by Doppler effect can be achieved, or about twice that obtained in these experiments.

As in the case for OCS, ClCN molecules excited to the first level of the bending vibrational mode are fairly abundant at room temperature, including about one-quarter of the total molecules. The lines produced by the molecules are split by $l$-type doubling as in the case of OCS, and in addition by nuclear quadrupole effects. The quadrupole pattern for these molecules excited to the bending vibrational mode is radically different from the pattern produced by molecules in the ground state. Because of the degeneracy of the excited bending mode, the molecules behave essentially like symmetric tops with unit angular momentum around the molecular axis. Quadrupole interactions are correspondingly modified. Assuming a spin of 3/2 and the same value of quadrupole coupling found for the ground state, the expected splitting has been calculated and is compared with excited state lines found in Table III. These lines are designated in a notation similar to that used for Fig. 5, but in addition vibrational states must be indi-

TABLE III. Observed lines of the $Cl^{35}C^{12}N^{14}$ $J=1\rightarrow2$ transition.

| Line designation | Measured frequency in megacycles | Theoretical frequency in megacycles | Theoretical intensity relative to strongest line |
|---|---|---|---|
| 1/2→3/2 | 23862.57 | 23862.47 | 0.32 |
| 5/2 3/2→5/2 5/2 | | 23863.46 | 0.012 |
| 5/2 7/2→5/2 5/2 | | 23863.77 | 0.013 |
| 5/2 3/2→5/2 3/2 | | 23864.00 | 0.066 |
| 5/2 7/2→5/2 7/2 | | 23864.18 | 0.14 |
| 5/2 5/2→5/2 5/2 | | 23864.52 | 0.092 |
| 5/2 5/2→5/2 7/2 | | 23864.93 | 0.013 |
| 5/2 5/2→5/2 3/2 | | 23865.07 | 0.012 |
| 5/2 3/2→3/2 1/2 | | 23878.60 | 0.0087 |
| 5/2 3/2→3/2 3/2 | | | |
| 5/2 3/2→3/2 5/2 | | | |
| 5/2 7/2→3/2 5/2 | | 23878.93 | 0.017 |
| 5/2 5/2→3/2 3/2 | | 23879.74 | 0.013 |
| 5/2 5/2→3/2 5/2 | | | |
| 1/2→1/2 | 23883.30 | 23883.28 | 0.32 |
| 5/2 7/2→7/2 7/2 | | 23884.22 | 0.28 |
| 3/2 3/2→5/2 5/2 | | | |
| 3/2 3/2→5/2 3/2 | | 23884.76 | 0.044 |
| 3/2 5/2→5/2 5/2 | | 23884.91 | 0.57 |
| 5/2 5/2→7/2 7/2 | | | |
| 5/2 7/2→7/2 9/2 | 23885.16 | 23885.16 | 1.00 |
| 5/2 3/2→7/2 5/2 | | | |
| 3/2 5/2→5/2 7/2 | | 23885.31 | 0.36 |
| 3/2 1/2→5/2 3/2 | | 23886.03 | 0.14 |
| 5/2 5/2→7/2 5/2 | | 23886.24 | 0.047 |
| 3/2 3/2→3/2 1/2 | 23899.59 | 23899.42 | 0.14 |
| 3/2 3/2→3/2 5/2 | | | |
| 3/2 3/2→3/2 3/2 | | | |
| 3/2 5/2→3/2 5/2 | 23900.20 | 23900.09 | 0.21 |
| 3/2 5/2→3/2 3/2 | | | |
| 3/2 1/2→3/2 1/2 | | 23900.67 | 0.070 |
| 3/2 1/2→3/2 3/2 | | | |
| $v_2=1$, $l_1$, 3/2→5/2 | 23917.9 | 23918.1 | 0.18 |
| 3/2→1/2 | 23920.91 | 23920.79 | 0.066 |
| $v_2=1$, $l_1$, 3/2→3/2 | 23925.5 | 23925.5 | 0.091 |
| $v_2=1$, $l_1$, 5/2→5/2 | 23928.7 | 23928.5 | 0.075 |
| $v_2=1$, $l_1$, 5/2→7/2 | 23928.6 | 23938.9 | 0.37 |
| $v_2=1$, $l_1$, 1/2→3/2 | 23944.4 | 23944.2 | 0.067 |
| $v_2=1$, $l_2$, 3/2→5/2 | 23948.2 | 23948.1 | 0.18 |
| $v_2=1$, $l_1$, 1/2→1/2 | 23954.5 | 23955.1 | 0.16 |
| $v_2=1$, $l_2$, 3/2→3/2 | | | |
| $v_2=1$, $l_2$, 5/2→5/2 | 23958.4 | 23958.5 | 0.075 |
| $v_2=1$, $l_2$, 5/2→7/2 | 23968.6 | 23968.9 | 0.37 |
| $v_2=1$, $l_2$, 1/2→3/2 | 23974.4 | 23974.2 | 0.067 |
| $v_2=1$, $l_2$, 1/2→1/2 | 23984.6 | 23984.6 | 0.067 |

cated. This is done by specifying the value of the vibrational quantum number which is not zero, e.g., $v_2=1$, and indicating each of the $l$-type doublets separately. The arbitrary label $l_1$ has been used for the low frequency component of the doublet and $l_2$ for the high frequency component. All lines which can be expected from the splitting due to Cl for these excited states are found except those corresponding to the transitions 5/2→3/2 and 3/2→1/2, which are weaker than the weakest of the other lines by a factor of three. Intensities given for the excited state lines in Table III assume room temperature (298°K) conditions. In one case two lines coincide closely and are not resolved. These lines were not examined under high resolution so that no splitting due to the nitrogen quadrupole was observed.

In fitting the excited state lines, one obtains values for the rotational constant $\alpha_2=-16.39$ Mc and the $l$-type doubling constant $q=7.50$ Mc. Thus corresponding lines of the two $l$-type doublets are separated by 30.00 Mc. The value for this splitting published earlier[9] is incorrect by 5 Mc because of an error in transcribing the data.

All observed lines of the $J=1\rightarrow2$ transition of $Cl^{35}C^{12}N^{14}$ are listed in Table III. Some of these lines were measured as described above and their frequencies obtained by reference to the nearby $N^{14}H_3$ 3,3 line. Differences between these measurements and the theoretical values, assuming the values of quadrupole coupling constants, $\alpha_2$, and $q$ given above and a value $B_0=5970.820$, are of the order of 0.1 Mc and probably represent experimental errors. That agreement between theory and both position and relative intensity of the lines is good at least among any one group can be seen by comparison of the reproduction of oscilloscope sweeps in Fig. 5 and the theoretical spectra immediately below the sweeps. Measured values are given in Table III only for those lines which were measured by superposing a frequency-measuring pip on the line, but all lines observed agree well with expectations as shown in Fig. 5.

The $Cl^{37}CN$ $J=1\rightarrow2$ transition was found to have just the same pattern as shown by $Cl^{35}CN$, giving a spin of 3/2 to $Cl^{37}$ as well as $Cl^{35}$. The three main groups of lines ($F_1=1/2\rightarrow3/2$ and $5/2\rightarrow5/2$, $F_1=1/2\rightarrow1/2$, $3/2\rightarrow5/2$, and $5/2\rightarrow7/2$, and $F_1=3/2\rightarrow3/2$) were examined under high resolution and all lines found to correspond to the $Cl^{35}CN$ lines except that a few were too weak to detect, since $Cl^{37}$ has an abundance one-third that of $Cl^{35}$. Only the measured lines are listed in Table IV, and compared with theoretical values using a value $B_0=5847.26$ and taking quadrupole coupling constants ($eQ(\partial^2V/\partial z^2)$) minus 65.7 Mc for $Cl^{37}$ and minus 3.63 Mc for $N^{14}$ as before.

The quadrupole coupling constants of $Cl^{35}$, $Cl^{37}$, and $N^{14}$ in this molecule agree well with those reported earlier from less accurate data.[17]

TABLE IV. Measured lines of the $Cl^{37}C^{12}N^{14}$ $J=1\rightarrow 2$ transition.

| Line designation | Measured frequency in megacycles | Theoretical frequency in megacycles |
|---|---|---|
| 1/2 3/2→3/2 5/2 | 23372.72 | 23372.60 |
| 1/2→1/2 | 23389.00 | 23389.04 |
| 3/2 3/2→5/2 5/2 | 23389.61 | 23389.58 |
| 5/2 7/2→7/2 9/2<br>5/2 3/2→7/2 5/2 | 23390.53 | 23390.53 |
| 3/2 5/2→3/2 5/2 | 23402.47 | 23402.38 |

The strongest group of lines ($F_1=1/2\rightarrow 1/2$, $F_1=3/2\rightarrow 5/2$, and $F_1=5/2\rightarrow 7/2$) of the isotopic molecules $Cl^{35}C^{13}N^{14}$ and $C^{37}C^{13}N^{14}$ were also observed in ClCN enriched in $C^{13}$ to 20 percent. The patterns appeared identical with those of the same molecules containing $C^{12}$, which is to be expected since the $C^{13}$ can show no quadrupole effects if its spin is 1/2 as found by Jenkins.[18] Intervals between the strongest lines (sum of 5/2 7/2→7/2 9/2 and 5/2 3/2→7/2 5/2) of the various isotopic species of ClCN were measured in order to obtain the isotopic shifts. The intervals found are listed in Table V. As previously discussed in the case of OCS, zero-point vibrations limit the accuracy with which internuclear distances can be determined, but distances computed from three pairs of isotopic molecules by neglecting zero-point vibrations are given in Table V.

Intensity and half-width of the strongest group of lines due to $Cl^{35}C^{12}N^{14}$ were measured at pressures high enough to make the half-width several times the maximum splitting. The intensity was found to be $8.0\pm 1\times 10^{-5}$ cm$^{-1}$ or $4.0\pm 0.5\times 10^{-5}$ nepers/cm for a plain wave, and the half-width (total width at half-maximum intensity) equivalent to 50±8 Mc at a gas pressure of 1 mm Hg. The dipole moment of ClCN has apparently not been measured. If expression (2) is used to evaluate the dipole moment from this intensity measurement, the value 2.66±0.25 Debye units is obtained. Since BrCN and ICN have values 2.94 and 3.71 Debye units, respectively,[19] this value for ClCN appears to be reasonable.

TABLE V. Frequency differences between various isotopic species of ClCN and computed internuclear distances neglecting zero-point vibrations.*

| Isotopic species compared | Measured interval between strongest lines (5/2 7/2→7/2 9/2) in megacycles | Computed internuclear distances assuming no zero-point vibrations Cl−C | C−N |
|---|---|---|---|
| $Cl^{35}C^{12}N^{14}$, $Cl^{37}C^{12}N^{14}$ | 494.63±0.05 | 1.6238 | 1.1700 |
| $Cl^{35}C^{13}N^{14}$, $Cl^{37}C^{13}N^{14}$ | 500.67±0.10 | 1.6246 | 1.1691 |
| $Cl^{35}C^{12}N^{14}$, $Cl^{35}C^{13}N^{14}$ | 124.18±0.05 | 1.6315 | 1.1599 |

* Isotopic masses are from Mattauch (see reference 10).

## CYANOGEN BROMIDE

The transition $J=2\rightarrow 3$ of cyanogen bromide produces a spectrum near the same frequency as that due to the $J=1\rightarrow 2$ transition of cyanogen chloride. The two spectra are similar in many respects, both involving halogens of spin 3/2 whose large quadrupole couplings produce the main lines of the spectrum. These main lines are split more finely in both cases by the smaller $N^{14}$ quadrupole coupling. All of the lines found for this transition which are produced by splitting due to quadrupole moments of the two bromine isotopes are listed in Table VI and compared with theory. In most cases these lines were not examined under high resolution. The splitting due to the $N^{14}$ quadrupole moment may of course shift the center of gravity of the line and, therefore, its neglect can cause discrepancies between measured frequencies and theoretically computed frequencies. However, in most cases this shift is less than 0.1 Mc. Resolution of one of the lines and evaluation of the size of the $N^{14}$ coupling will be discussed below. Lines in Table VI are designated in a way similar to that used in Table III. Since the splitting due to $N^{14}$ is ignored, however, only values of $F_1$ are given, that is the angular momentum in units of $h/2\pi$ resulting from the vector addition of $J$ and the angular momentum $I$ of a bromine nucleus. In addition the bromine isotope responsible for each line is indicated as part of the line designation, since there is appreciable overlap of the spectra of the two isotopes.

Assuming quadrupole couplings†† plus 573.5 Mc for $Br^{81}$ and plus 686.5 Mc for $Br^{79}$, lines of the ground vibrational state may be fairly accurately fitted by using Casimir's expression[16] for

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[18] F. A. Jenkins, Phys. Rev. **72**, 169 (1947).

[19] L. G. Wesson, *Tables of Electric Dipole Moments* (Laboratory of Insulation Research, M.I.T. 1947), pp. 15 and 17.

†† Values of quadrupole coupling constants given by the authors in reference 17 are somewhat in error due to an oversight, and are not the values which give the theoretical fit for the BrCN spectrum shown there.

quadrupole interaction energy

$$-eQ\frac{\partial^2 V}{\partial z^2}\frac{\frac{3}{4}C(C+1)-I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)}.$$

However, there are deviations from this fit for both isotopes. These deviations are due primarily to the fact that the bromines have such a large quadrupole coupling that first-order perturbation

TABLE VI. Lines due to $J=2\rightarrow3$ transition of BrCN.

| Designation of line | Measured frequency in megacycles | Theoretical frequency including only first-order effects of bromine quadrupole | Difference in megacycles | Correction due to second-order effects of bromine quadrupole | Measured intensity relative to strongest line | Theoretical relative intensity |
|---|---|---|---|---|---|---|
| 81 3/2→3/2 | 24465.33 | 24465.87 | +0.54 | +0.66 | 0.05 | 0.065 |
| 81 $v_1=1$<br>5/2→7/2<br>7/2→9/2 | 24506.75 | 24506.37 | −0.38 | −0.05 | 0.15 | 0.15 |
| 81 5/2→5/2 | 24507.38 | 24506.84 | −0.54 | −0.65 | | |
| 81 $v_1=1$<br>1/2→3/2<br>3/2→5/2 | 24541.18 | 24541.87 | +0.69 | +0.16 | | 0.025 |
| 81 5/2→7/2<br>7/2→9/2 | 24573.86 | 24573.75 | −0.05 | −0.05 | 1.0 | 0.98 |
| 79 3/2→3/2 | 24583.00 | 24583.87 | +0.87 | +0.97 | 0.1 | 0.066 |
| 81 1/2→3/2<br>3/2→5/2 | 24608.92 | 24609.25 | +0.33 | +0.16 | 0.4 | 0.42 |
| 81 $v_2=1$, $l_1$<br>1/2→3/2<br>7/2→9/2 | 24622.93 | 24622.90 | −0.03 | | 0.1 | 0.12 |
| 79 5/2→5/2 | 24633.71 | 24632.88 | −0.83 | −0.94 | 0.1 | 0.086 |
| 81 $v_2=1$, $l_2$<br>1/2→3/2<br>7/2→9/2 | 24645.82 | 24645.97 | +0.15 | | 0.1 | 0.18 |
| 79 $v_1=1$<br>5/2→7/2<br>7/2→9/2 | | 24644.94 | | | | |
| 81 $v_2=1$, $l_1$<br>3/2→3/2<br>5/2→7/2 | 24658.89 | 24658.94 | +0.05 | | 0.1 | 0.11 |
| 81 $v_2=1$, $l_2$<br>3/2→5/2<br>5/2→7/2 | 24682.13 | 24682.01 | −0.10 | | 0.1 | 0.11 |
| 79 $v_1=1$<br>1/2→3/2<br>3/2→5/2 | 24687.11 | 24687.36 | +0.25 | +0.25 | | 0.025 |
| 79 5/2→7/2<br>7/2→9/2 | 24713.05 | 24712.97 | −0.08 | −0.08 | 1.0 | 1.00 |
| 81 7/2→7/2 | 24717.19 | 24717.13 | −0.06 | −0.17 | | 0.066 |
| 79 1/2→3/2<br>3/2→5/2 | 24755.22 | 24755.47 | +0.25 | +0.21 | 0.4 | 0.43 |
| 79 $v_2=1$, $l_1$<br>1/2→3/2<br>7/2→9/2 | 24760.76 | 24760.31 | −0.45 | | 0.1 | 0.13 |
| 79 $v_2=1$, $l_2$<br>1/2→3/2<br>7/2→9/2 | 24784.02 | 24783.78 | −0.24 | | 0.1 | 0.13 |
| 79 $v_2=1$, $l_1$<br>3/2→5/2<br>5/2→7/2 | 24803.00 | 24803.46 | +0.46 | | 0.1 | 0.11 |
| 79 $v_2=1$, $l_2$<br>3/2→5/2<br>5/2→7/2 | 24826.70 | 24826.93 | +0.23 | | 0.1 | 0.11 |
| 79 7/2→7/2 | 24884.57 | 24884.59 | +0.02 | −0.25 | 0.05 | 0.066 |

theory is not sufficiently accurate, and the value of $J$ in either upper or lower state of the transition is not truly constant. Bardeen has calculated the matrix elements necessary to evaluate the second-order corrections. These have been published and the theoretical corrections derived from them shown to fit well the somewhat larger second-order effects in ICN.[20] The second-order terms are proportional to $(eqQ)^2/B_0$, so they differ by about 40 percent for the two bromine isotopes. A comparison of the second-order corrections and deviations from the first-order theory displayed in Table VI shows that the deviations are primarily due to this cause. The remaining discrepancies are of the order of 0.1 Mc and probably due to shifts produced by the $N^{14}$ quadrupole moment and to experimental error. Experimental relative intensities listed in the table are those originally published[21] before these lines were understood and analyzed. The relative intensity measurements have not been refined or measurements made on the new lines because in all cases so far tested, experimental relative intensities agree within the accuracy of measurement with theoretical values, and theoretical values are probably much more accurate and reliable.

Lines due to BrCN molecules excited to the bending vibrational mode have been found and exhibit $l$-type doubling as described above with the $l$-type doubling constant $q=3.912$ Mc and 3.845 Mc for $Br^{79}CN$ and $Br^{81}CN$, respectively. The value of $\alpha_2$ is minus 11.49 Mc for both $Br^{79}CN$ and $Br^{81}CN$. The lines are split by quadrupole effects into the pattern characteristic of a symmetric top with $K=1$. The four strong components produced by the Br quadrupole for each isotope approximately coincide in pairs, giving two lines which predominate in the quadrupole pattern of each $l$-type doublet. Lines produced by molecules in this excited state are listed in Table VI and compared with theory. As a verification that the lines so identified were produced by molecules in an excited vibrational state, intensities of the lines at 24622.93 Mc and 24645.82 Mc were compared with intensity of the ground-state line at 24633.71 Mc for temperatures $-40°C$ and $+85°C$. This temperature variation gives a computed change in the relative intensity of ground-state lines to those in the first excited bending mode of 2.2, which was confirmed by observation.

One of the stretching vibrational frequencies, $\nu_1$, is also low enough to allow observation of some of its stronger lines at room temperature. The quadrupole pattern for this excited state is identical with that of the ground state assuming the quantity $\partial^2 V/\partial z^2$ is not appreciably changed, and intensity of corresponding lines are in the ratio 1:16.5 because of the Boltzmann factor. For $Br^{81}CN$ the two strongest lines due to this excited state were found and are listed in Table VI. The stronger almost coincides with the $5/2 \rightarrow 5/2$ line of the ground state. Only one of the lines due to the same excited state of $Br^{79}CN$ is given in Table VI, the other strong line being masked by the line at 24645.82 Mc which approximately coincides with it. The separation of the two strong lines of $Br^{81}CN$ excited to this stretching mode is somewhat smaller than that for the corresponding ground state lines, indicating perhaps a small difference in the value of $\partial^2 V/\partial z^2$ for the two cases. The difference is not, however, larger than might be accounted for by error in measurement of these weak lines. The molecular constant $\alpha_1$ obtained from measurement of these excited state lines is 11.36 Mc and 11.23 Mc, respectively, for $Br^{79}CN$ and $Br^{81}CN$.

The $J=3\rightarrow 4$ transition of BrCN has been studied by Gordy, Smith, Smith, and Ring.[22] They found and identified lines due to molecules excited to the low frequency stretching mode, $\nu_1$, and as well as can be judged from their published plot of lines, the value of $\alpha_1$ obtained from their measurements would agree with ours. In addition, a number of lines due to molecules excited to the first bending mode are shown in their plot, but these were not identified.

So far in this discussion, splitting of the BrCN lines by the $N^{14}$ quadrupole has been neglected. The measurements given in Table VI were made under conditions of moderately low resolution,

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[20] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 627 (1948).

[21] C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. **71**, 64 (1947).

[22] Gordy, Smith, Smith, and Ring, Phys. Rev. **72**, 259 (1947). Cf. also further measurements by Gordy *et al.* [Smith, Ring, Smith, and Gordy, Phys. Rev. **74**, 370 (1948)] which have appeared after this writing.

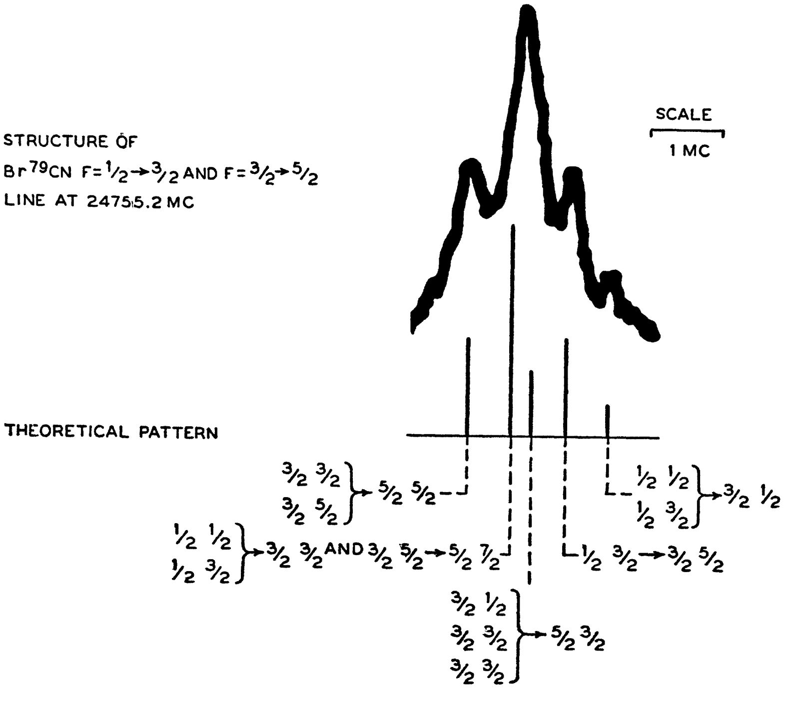

FIG. 6. Structure of $Br^{79}CN$ $J=2\rightarrow 3$, $F=1/2\rightarrow 3/2$, and $F=3/2\rightarrow 5/2$ transitions.

and hence probably measure the center of gravity of the group of lines produced in each case by the nitrogen quadrupole. Figure 6 shows one of these groups under somewhat higher resolution. This is a composite of patterns of the lines $1/2\rightarrow 3/2$ and $3/2\rightarrow 5/2$ of $Br^{79}CN$ which should coincide exactly, assuming no nitrogen quadrupole moment and only first-order bromine quadrupole effects. Second-order bromine quadrupole effects separate the two lines by 0.76 Mc, and the nitrogen quadrupole moment splits each into several components, resulting in the theoretical pattern shown in Fig. 6. Because the second-order effects in $Br^{81}CN$ are about 40 percent less than those for $Br^{79}CN$, the appearance of the group of lines due to the transitions $1/2\rightarrow 3/2$ and $3/2\rightarrow 5/2$ of $Br^{81}CN$ is somewhat different. From the measurements of separations of various components of the group of lines shown in Fig. 6 and a comparison with the theoretical pattern computed in a way similar to that used for ClCN, the value of the $N^{14}$ quadrupole coupling in this molecule may be determined as minus 3.83 Mc. The difference between this value and the value minus 3.63 Mc found for ClCN is not much larger than the sum of expected experimental errors in each, but it is thought to be significant.

Values of $B_0$ used to compute theoretical frequencies in Table VI are 4120.19 Mc and 4096.76 Mc, respectively, for $Br^{79}CN$ and $Br^{81}CN$. From these, internuclear distances may be computed as 1.158A for the C−N distance, and 1.790A for the Br−C distance. This computation again neglects the effect of zero-point vibrations, and as a consequence, the difference between the C−N distance obtained for BrCN, and that obtained for ClCN (see Table V) may not be significant.

Intensity and half-width of the $Br^{81}CN$ $5/2\rightarrow 7/2$ and $7/2\rightarrow 9/2$ line were measured at room temperature. The peak intensity was found to be $6.0\pm 1\times 10^{-5}$ cm$^{-1}$ for a plane wave and the half-width equivalent to $42\pm 6$ Mc for one-mm Hg gas pressure. Taking the value 2.94 Debye units[19] for the dipole moment of BrCN and using the measured half-width, expression (2) gives a theoretical intensity of $7.2\pm 1\times 10^{-5}$ cm$^{-1}$.

## CYANOGEN IODIDE

A pure rotation transition of ICN was first reported by Gordy, Smith, Smith, and Ring,[22] who measured the $J=4\rightarrow 5$ transition and gave a value $260\times 10^{-40}$ g cm$^2$ for the moment of inertia and $2070\pm 20$ Mc for the quadrupole coupling. In

TABLE VII. Lines due to $J=3\rightarrow 4$ transition of ICN.

| Designation of line | Measured frequency in megacycles | Theoretical frequency including first- and second-order effects of iodine quadrupole | Theoretical intensity relative to $11/2\rightarrow 13/2$ line |
|---|---|---|---|
| $v_2=2$, $l=2$ | | | |
| $11/2\rightarrow 13/2$ | 26046.32 | 26046.21 | 0.088 |
| $5/2\rightarrow 5/2$ | 25991.92 | 25991.58 | 0.14 |
| $3/2\rightarrow 3/2$ | 25969.58 | 25969.55 | 0.092 |
| $7/2\rightarrow 7/2$ | 25954.36 | 25954.24 | 0.16 |
| $v_2=1$, $l_2$ | | | |
| $11/2\rightarrow 13/2$ | 25927.66 | 25927.79 | 0.21 |
| $v_2=1$, $l_1$ | | | |
| $11/2\rightarrow 13/2$ | 25906.28 | 25906.29 | 0.21 |
| $v_2=1$, $l_2$ | | | |
| $9/2\rightarrow 11/2$ | 25893.73 | 25893.56 | 0.16 |
| $v_2=1$, $l_1$ | | | |
| $9/2\rightarrow 11/2$ | 25872.24 | 25872.06 | 0.16 |
| $v_2=1$, $l_2$ | | | |
| $7/2\rightarrow 9/2$ | 25850.78 | 25850.48 | 0.12 |
| $9/2\rightarrow 11/2$ | 25837.64 | 25837.71 | 0.76 |
| $v_2=1$, $l_1$ | | | |
| $7/2\rightarrow 9/2$ | 25829.31 | 25828.98 | 0.12 |
| $11/2\rightarrow 13/2$ | 25823.08 | 25823.08 | 1.00 |
| $v_2=1$, $l_1$ | | | |
| $3/2\rightarrow 5/2$ | 25815.34 | 25815.55 | 0.058 |
| $v_2=1$, $l_1$ | | | |
| $5/2\rightarrow 7/2$ | 25802.92 | 25803.34 | 0.085 |
| $9/2\rightarrow 9/2$ | 25789.85 | 25789.88 | 0.15 |
| $7/2\rightarrow 9/2$ | 25783.50 | 25783.56 | 0.56 |
| $v_1=1$ | | | |
| $9/2\rightarrow 11/2$ | 25763.23 | 25763.06 | 0.076 |
| $1/2\rightarrow 3/2$ | 25752.65 | 25752.73 | 0.18 |
| $v_1=1$ | | | |
| $11/2\rightarrow 13/2$ | 25748.18 | 25748.43 | 0.10 |
| $5/2\rightarrow 7/2$ | 25728.77 | 25728.73 | 0.40 |
| $3/2\rightarrow 5/2$ | 25711.50 | 25711.53 | 0.28 |
| $11/2\rightarrow 11/2$ | 25393.87 | 25393.69 | 0.097 |

terms of the quadrupole coupling constant as defined here, their value is 2588±25 Mc. The value of $B$ obtained from a moment of inertia $260\times 10^{-40}$ g cm$^2$ is 3230 Mc. The $J=3\rightarrow 4$ transmission has been measured here with more accuracy than that obtained by earlier measurements, and the various components have been somewhat more thoroughly analyzed. Values of the molecular constants found here are consistent with those given by Gordy, Smith, Smith, and Ring, except that the value of quadrupole coupling constant obtained is considerably outside of their quoted experimental error.††† This may be due to the presence of second-order effects which were not recognized in these early measurements.‡ Table VII lists the measured line frequencies and the theoretical frequencies and relative intensities. Rather rough relative intensity measurements which were made agreed with the theoretical values listed in the table.

As in the case of BrCN, the further line splitting due to the $N^{14}$ quadrupole is ignored in ICN, the lines having been measured under relatively low resolution conditions. Their positions may be shifted in some cases as much as 0.1 Mc by effects of the nitrogen nucleus, but since this is about the accuracy of measurement, these shifts have not been taken into account. In some cases rather large shifts are contributed by second-order effects because of the large size of the iodine quadrupole coupling. A more detailed statement of these second-order effects has been given elsewhere.[20] The two lines of the ground state $7/2\rightarrow 9/2$ and $9/2\rightarrow 9/2$ should coincide so far as first-order effects of the iodine quadrupole are concerned. Actually they are separated by 6.35 megacycles due to second-order effects. The separation between the two intense lines $11/2\rightarrow 11/2$ and $11/2\rightarrow 13/2$ is very large (429.21 Mc) and allows a rather accurate determination of the iodine quadrupole coupling constant, minus 2420 Mc.

A considerable number of lines due to molecules in the excited bending mode ($v_2=1$) are listed in Table VII. The value of $\alpha_2$ obtained is minus 9.501 Mc and the $l$-type doubling constant $q$ equals 2.688 Mc. Second-order quadrupole effects are again in evidence and are somewhat larger than for the ground state because non-zero matrix elements exist between rotational states with $J$ values differing by only one as well as those for $J$ values differing by two which occur in the ground state case.

One line is listed which is due to molecules doubly excited in the bending mode ($v_2=2$). In this case, the theory of Nielsen and Shaffer[8] shows that the three degenerate levels with $v_2=2$ form two states for which the angular momentum $l$ about the molecular axis is $2\hbar$, and one state with this angular momentum equal to zero. The $l$-type doubling for the two states with $l=2$ is less by a factor $B/\omega_2$ than the doubling when $l=1$, and hence is not observed. The strongest line due to this excited vibrational state, $v_2=2$, is therefore the transition $11/2\rightarrow 13/2$ when $l=2$, and its measured position agrees well with that predicted

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††† Very recent measurements by Gordy *et al.* [A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. **74**, 370 (1948)] show very good agreement with results presented here.

‡ Cf. O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. **73**, 635 (1948).

by using the molecular constants determined from other states. Second-order quadrupole effects must again be taken into account. Several weak lines between 25,800 Mc and 26,000 Mc were found which coincide approximately with other transitions of molecules in the states $v_2=2$, $l=2$, and $v_2=2$, $l=0$, but these were not accurately measured and hence are not included in Table VII.

Peak intensity of the strongest line ($11/2 \rightarrow 13/2$) was measured at room temperature and found to be $8.7\pm1\times10^{-5}$ cm$^{-1}$. Half-width of this same line was $4.0\pm0.6$ Mc when the gas was in equilibrium with a trap at zero degrees centigrade. From the measurements of Ketelaar and Kruger[23] this would represent a vapor pressure of 0.10 mm Hg, so that the half-width at one mm Hg pressure would be $40\pm6$ Mc. Unfortunately, ICN attacked the mercury in a McCleod gauge so rapidly that no direct measurement of vapor pressure could be made. Using a value of 3.72 Debye units for the dipole moment, expression (2) gives a theoretical peak intensity $10\pm1.4\times10^{-5}$ cm$^{-1}$.

Since only one isotopic variety of ICN was measured, the two internuclear distances cannot be determined from the microwave measurements on this molecule alone. If the value 1.158A found above for BrCN is taken as the $C-N$ distance, then the $I-C$ distance may be determined as 1.995A.

## PREPARATION OF SUBSTANCES MEASURED

The OCS used in this work was prepared by the acid hydrolysis of aqueous alkali thiocyanate.[24] In the case of $OC^{13}S$, 5 g KCN of 21.4 atom percent $C^{13}$, obtained from the Eastman Kodak Company, was converted to thiocyanate by dissolving it in a freshly boiled mixture of 3 g sulfur and 10 cc distilled water and maintaining the solution at 60°C under an atmosphere of nitrogen for two days with occasional agitation. The resulting solution was cooled to 0°C and poured rapidly into a mixture at 0°C of 100 g $H_2SO_4$ and 50 cc $H_2O$. The mixture was allowed to warm slowly to 40°C over three hours with occasional agitation, the OCS slowly evolved being bubbled through 15 cc of a 30 percent NaOH solution cooled to 0°C, and condensed in a trap cooled with dry ice—acetonic mixture. In the case of $O^{18}CS$, the thiocyanate solution consisted of 7 g $NH_4SCN$ dissolved in 5 cc of $H_2O$ of 1.5 atom percent $O^{18}$ obtained from the Atomic Energy Commission, and the acid solution was prepared by saturating 15 cc of the same water, cooled to $-15$°C with an ice-salt mixture, with HCl obtained by slowly dropping 100 g concentrated $H_2SO_4$ on 60 g NaCl moistened with ordinary water. The remainder of the procedure was the same, ordinary water being used for the NaOH solution.

The ClCN was prepared[25] by the action of $Cl_2$ on KCN in the presence of $Zn^{++}$. In the case of $ClC^{13}N$, 5 g of the same KCN as was used for the preparation of $OC^{13}S$, and 5 g of $ZnSO_4\cdot 7\,H_2O$, were dissolved in 25 cc $H_2O$, and through the solution cooled to 0°C was passed a slow stream of $Cl_2$ from a commercial cylinder. When the solution was saturated with $Cl_2$, it was slowly warmed to 40°, a very slow stream of $Cl_2$ being maintained, and the evolved ClCN was passed over anhydrous $CaCl_2$ and collected in a U-tube cooled to $-10$°C with an ice-salt mixture.

The ICN was prepared by the method of Comastri[26] as described in Chemical Abstracts.

The BrCN was purchased from the Eastman Kodak Company.

## SUMMARY

The microwave measurements described above allow determination of a number of molecular and nuclear quantities. Many of these are summarized in Tables VIII to XI.

Although line widths may eventually give considerable information about intermolecular forces, half-widths have been investigated here primarily with a view to checking theoretical intensities and to provide some basis for estimation of line intensities in the microwave region. Line half-widths (total widths at half-maximum absorption) are listed in Table VIII for a number of molecules. For the linear molecules there appears to be a rough correlation between line

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[23] J. A. A. Ketelaar and S. Kruger, Rec. Trav. Chim. **62**, 550 (1943).

[24] See, e.g., A. Stock, W. Siecke, and E. Pohland, Ber. d. D. chem. Ges. **57**, 719 (1924).

[25] See, e.g., A. Klemenc and G. Wagner, Zeits. f. anorg. allgem. Chemie **235**, 427 (1938).

[26] H. T. Comastri, Anales Asoc. Quim. Argentina **27**, 45 (1939); Chem. Abs. **33**, 6743 (1939).

TABLE VIII. Measured half-width (total width at half-maximum intensity) of lines near 1 cm wave-length.

| Molecule | Dipole moment in debye units | Frequency of line in megacycles | Half-width at pressure of 1 mm Hg |
|---|---|---|---|
| $ICl^{35}$* | approx. 0.65 | 27337 | $11\pm2$ |
| $O^{16}C^{12}S^{32}$ | 0.72 | 24526 | $12\pm2$ |
| $Cl^{35}C^{12}N^{14}$ | approx. 2.5 | 23885 | $50\pm8$ |
| $Br^{81}C^{12}N^{14}$ | 2.94 | 24574 | $42\pm6$ |
| $I\ C^{12}N^{14}$ | 3.71 | 25823 | $40\pm6$ |
| $N^{14}H_3$** | 1.45 | 23870 | $59\pm2$ |
| $H_2O$*** | 1.84 | 22235 | $14\pm3$ |

* C. H. Townes, B. D. Wright, and F. R. Merritt, Phys. Rev. **73**, 1334 (1946).
** C. H. Townes, Phys. Rev. **70**, 665 (1946); B. Bleaney and R. P. Penrose, Proc. Roy. Soc. **189**, 358 (1947).
*** C. H. Townes and F. R. Merritt, Phys. Rev. **70**, 558 (1946).

width and dipole moment of the molecule. The line widths for ammonia and water are included, however, to show that other types of molecules show wide deviations from this behavior. The 3,3-line of ammonia, which has a dipole of moderate size, displays the largest half-width, whereas water, with a somewhat larger dipole moment, produces a line in the microwave region with an exceptionally small half-width. Using the half-widths determined here, intensities of lines measured correspond within experimental error (about 20 percent) to the theoretical expectations.

Molecular rotational constants for the molecules OCS, ClCN, BrCN, and ICN are given in Table IX. The last column in this table gives a value of the $l$-type doubling constant $q$ obtained from the theory of Nielsen and Shaffer.[8] The result given in their paper as noted earlier[9] involved a numerical error of a factor of two, so that their theoretical value of $q$ is actually $2B/\omega_2$.‡‡ A distinct and consistent disagreement between the theoretical and experimental values of $q$ are shown by the table. There appears to be remarkable uniformity in the values of $\alpha_1$ and $\alpha_2$ found for these molecules, which is somewhat surprising considering the dependence of the $\alpha$'s on anharmonic force constants.

Internuclear distances determined are listed in Table X. In several cases these distances are averages of the values obtained from various pairs of isotopes. Uncertainties in these distances as discussed above are primarily due to the effects of zero-point vibration, which are rather difficult to determine completely. An accuracy near 0.001A rather than 0.01A in these distances could generally be obtained if the zero-point vibration effects could be determined.

Various nuclear quadrupole coupling constants $[eQ(\partial^2 V/\partial z^2)$ or $eqQ]$ obtained from the present measurements are given in Table XI, as well as estimates of $\partial^2 V/\partial z^2$ and $Q$ derived from these values. The basis on which $\partial^2 V/\partial z^2$ is obtained has been previously discussed.[27] The quadrupole moment evaluated by this method for $Cl^{35}$ agrees reasonably well with the value $-7.9\pm0.2\times10^{-26}$ cm$^2$ recently obtained from molecular beam measurements on atomic chlorine.[28] The quadru-

TABLE IX. Molecular rotational constants. (All quantities are expressed in megacycles.)

| Molecule | $B_0$ | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $q$ ($l$-type doubling constant) | Theoretical value of $q$ |
|---|---|---|---|---|---|---|
| $O^{16}C^{12}S^{32}$ | $6081.480\pm0.005$* | $18.12\pm0.06^{a,c}$ | $-10.59\pm0.02$ | 55.1 | $6.393\pm0.013$ | 4.70 |
| $O^{16}C^{12}S^{33}$ | $6004.918\pm0.02$ | | | | | |
| $O^{16}C^{12}S^{34}$ | $5932.843\pm0.01$ | | $-10.37\pm0.06^{a}$ | | $6.07\pm0.06^{a}$ | |
| $O^{16}C^{13}S^{32}$ | $6061.923\pm0.015$ | | | | | |
| $O^{16}C^{13}S^{34}$ | $5911.730\pm0.03$ | | | | | |
| $O^{16}C^{14}S^{32}$ | $6043.25\ \pm0.25^{b}$ | | $-9.4\ \ 0.3^{b}$ | | $6.7\pm0.1^{b}$ | |
| $O^{18}C^{12}S^{32}$ | $5704.825\pm0.015$ | | | | | |
| $Cl^{35}C^{12}N^{14}$ | $5970.820\pm0.02$ | | $-16.39\pm0.02$ | | $7.500\pm0.015$ | 5.98 |
| $Cl^{37}C^{12}N^{14}$ | $5847.260\pm0.02$ | | | | | |
| $Cl^{35}C^{13}N^{14}$ | $5939.775\pm0.03$ | | | | | |
| $Cl^{37}C^{13}N^{14}$ | $5814.705\pm0.03$ | | | | | |
| $Br^{79}C^{12}N^{14}$ | $4120.190\pm0.02$ | $11.36\pm0.05$ | $-11.49\pm0.02$ | | $3.912\pm0.02$ | 3.07 |
| $Br^{81}C^{12}N^{14}$ | $4096.760\pm0.02$ | $11.23\pm0.05$ | $-11.49\pm0.02$ | | $3.845\pm0.02$ | |
| $I^{127}C^{12}N^{14}$ | $3225.527\pm0.02$ | $9.33\pm0.02$ | $-9.501\pm0.01$ | | $2.688\pm0.01$ | 2.16 |

* $B_e=6107.5$.
[a] C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948).
[b] Arthur Roberts, Phys. Rev. **73**, 1405 (1948).
[c] Arthur Roberts, private communication.

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‡‡ Professor Nielsen has kindly confirmed by private communication that this is the correct result of his theoretical treatment.

[27] C. H. Townes, Phys. Rev. **71**, 909 (1947).

[28] L. Davis, B. T. Feld, C. W. Zabel, and J. R. Zacharias, Phys. Rev. **73**, 525 (1948).

TABLE X. Internuclear distances. These are effective distances in ground vibrational state, and error in each is probably less than 0.01A. The I−C distance in ICN is obtained by assuming 1.158 for the C−N distance; for other molecules both distances are determined by use of isotopic pairs of moments of inertia.

| Molecule | Nuclei | Distance in angstroms |
|---|---|---|
| OCS | O−C | 1.161 |
| OCS | C−S | 1.561 |
| ClCN | Cl−C | 1.629 |
| ClCN | C−N | 1.163 |
| BrCN | Br−C | 1.790 |
| BrCN | C−N | 1.158 |
| ICN | I−C | 1.995 |

pole moment given here for iodine is somewhat larger than the value −0.45±0.15 obtained from atomic spectra. A comparison of the various quadrupole coupling constants obtained by microwave spectroscopy for $N^{14}$ in various molecules appears to give good evidence that the nitrogen bonds show considerable $s-p$ hybridization, and it is on this basis that the value of $\partial^2 V/\partial z^2$ is obtained from Table XI. Although nitrogen is not an atom heavy enough to provide a favorable case for the application of the atomic orbital approximation, it is believed that at least the sign and approximate magnitude of the nitrogen quadrupole moment have been correctly obtained. Similarly, in the case of $S^{33}$, the character of the C−S band is quite uncertain, but the sign and approximate magnitude of the $S^{33}$ quadrupole moment given here should be correct. It is expected that evaluation of $\partial^2 V/\partial z^2$ will be discussed more fully in a later paper.

TABLE XI. Quadrupole coupling constants and values of $Q$.

| Molecule | Nucleus | Quadrupole coupling constant $[eqQ \equiv e(\partial^2 V/\partial z^2)Q]$ in megacycles | Atomic orbital approximation to $\partial^2 V/\partial z^2$ in e.s.u. | Nuclear quadrupole moments $Q$ in units $10^{-24}$ cm$^2$ |
|---|---|---|---|---|
| OCS | $S^{33}$ | −28.5 ±0.7* | $\sim 7\times 10^{15}$ | ∼−0.05 |
| OCS | $S^{34}$ | <1 | $\sim 7\times 10^{15}$ | <0.002 |
| OCS | $O^{18}$ | <1 | $\sim 3\times 10^{15}$ | <0.004 |
| ClCN | $Cl^{35}$ | −83.2 ±0.5 | $17\times 10^{15}$ | −0.066 |
| ClCN | $Cl^{37}$ | −65.7 ±0.5 | $17\times 10^{15}$ | −0.052 |
| BrCN | $Br^{79}$ | 686.5 ±0.5 | $34\times 10^{15}$ | 0.28 |
| BrCN | $Br^{81}$ | 573.5 ±0.5 | $34\times 10^{15}$ | 0.23 |
| ClCN | $N^{14}$ | −3.63±0.1 | $\sim -3\times 10^{15}$ | ∼0.02 |
| BrCN | $N^{14}$ | −3.83±0.08 | | |
| ICN | $N^{14}$ | −3.80** | | |
| ICN | $I^{127}$ | −2420±1 | $45\times 10^{15}$ | −0.75 |

* C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948).
** Smith, Ring, Smith, and Gordy, Phys. Rev. **73**, 633 (1948).

No quadrupole splitting was observed for the molecules $O^{18}C^{12}S^{32}$ or $O^{16}C^{12}S^{34}$, and in these cases the upper limit to the value of the quadrupole coupling constant which would have produced a noticeable splitting is given in Table XI. Since both oxygen and sulfur in this molecule have an incomplete shell of penetrating electrons, the value of $\partial^2 V/\partial z^2$ may be expected to be rather large, so that the failure to observe quadrupole splitting indicates that the nuclear quadrupole moments of $O^{18}$, $S^{34}$ are very small. This is evidence that the spins of $O^{18}$ and $S^{34}$ are zero, since spins of either 0 or 1/2 necessitate zero quadrupole moments. If, for example, $S^{34}$ had a spin of one or two, a quadrupole coupling constant of approximately the same size as for the chlorine nuclei or for $S^{33}$ might be expected, instead of a coupling constant less than one-thirtieth as large. However, more measurements of quadrupole moments and coupling constants must be made before one can be sure that small values are unlikely even with spins greater than one-half.

No interactions of the type $c\mathbf{I}\cdot\mathbf{J}$ due to coupling between the nuclear magnetic moment and a molecular field were observed, but interactions of this type as small as those reported by Nierenberg and Ramsey[29] in the alkali halides may be present and undetected.

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[29] W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947).