

The matrix elements of  $(3I_{Nz}^2 - I_N^2)$ ,  $(\bar{I}_{Nx}^2 - \bar{I}_{Ny}^2)$ , and  $(\bar{I}_{Nx}\bar{I}_{Ny} + \bar{I}_{Ny}\bar{I}_{Nx})$  transform under rotation as certain linear combinations of second-degree spherical harmonics and may therefore be written as:<sup>27</sup>

$$\begin{aligned} \text{(a)} \quad & \langle \bar{I}_N F_1 J K | \bar{I}_{Nx}^2 - \bar{I}_{Ny}^2 | \bar{I}_N F_1 J K' \rangle \\ & = (\Omega_2(J, I_N) / J(J+1)) \langle JK | J_x^2 - J_y^2 | JK' \rangle, \\ \text{(b)} \quad & \langle \bar{I}_N F_1 J K | (\bar{I}_{Nx}\bar{I}_{Ny} + \bar{I}_{Ny}\bar{I}_{Nx}) | \bar{I}_N F_1 J K' \rangle \\ & = (\Omega_2(J, I_N) / J(J+1)) \langle JK | J_x J_y + J_y J_x | JK' \rangle, \\ \text{(c)} \quad & \langle \bar{I}_N F_1 J K | 3\bar{I}_{Nx}^2 - \bar{I}_N^2 | \bar{I}_N F_1 J K' \rangle \\ & = (\Omega_2(J, I_N) / J(J+1)) \langle JK | 3J_z^2 - J^2 | JK' \rangle, \quad (\text{A23}) \end{aligned}$$

where the factor of proportionality  $(\Omega_2(J, I_N) / J(J+1))$  is the same for all matrix elements of this type.  $\Omega_2(J, I_N)$  can most readily be evaluated from (A23c) with the help of matrix elements tabulated in Condon and Shortley.<sup>18</sup> One finds after considerable algebra the result given in Eq. (13). Substituting relations (A22) and (A23) into (10.4) one obtains Eq. (13.4) of the text. (Note that the signs of  $I$ ,  $I_N$  have been restored to their normal values and compensating changes in sign made in their coefficients.)

Finally the proportionality factors of the type (A18)

can be evaluated from Condon and Shortley.<sup>18</sup> Thus

$$\begin{aligned} \left( 1 + \frac{3(I_1^2 - I_{23}^2)}{I(I+1)} \right) &= \begin{pmatrix} -4 & 0 \\ 0 & 4 \end{pmatrix}, \\ \left( 1 - \frac{3I_{23} \cdot I}{I(I+1)} \right) &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \\ \frac{(I_2 - I_3) \cdot I}{I(I+1)} &= \begin{pmatrix} 0 & 2/\sqrt{3} \\ 2/\sqrt{3} & 0 \end{pmatrix}, \end{aligned}$$

where the rows and columns are to be labeled by values of  $I_{23} = 1, 0$  in that order.

Elements of the type  $\langle \bar{I}_N F_1 J K | J_x^2 | \bar{I}_N F_1 J K' \rangle$  are evaluated in a similar fashion substituting  $K$  for  $M$  in the Condon and Shortley matrix elements and changing the sign of  $i$ , thus:<sup>27</sup>

$$\begin{aligned} \langle JK | J_x^2 - J_y^2 | JK \rangle &= 0, \quad \langle JK | J_x J_y + J_y J_x | JK \rangle = 0, \\ \langle J-1 | J_x^2 - J_y^2 | J+1 \rangle &= \frac{1}{2} J(J+1), \\ \langle J+1 | J_x J_y + J_y J_x | J-1 \rangle &= \frac{1}{2} i J(J+1), \\ \langle J+1 | J_x^2 - J_y^2 | J-1 \rangle &= \frac{1}{2} J(J+1), \\ \langle J-1 | J_x J_y + J_y J_x | J+1 \rangle &= -\frac{1}{2} i J(J+1). \end{aligned}$$

<sup>27</sup> See reference 13, Chap. XXI, Sec. 5.

## Sulfur Bonds and the Quadrupole Moments of O, S, and Se Isotopes\*

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Quadrupole couplings of S<sup>33</sup> in HDS, SO<sub>2</sub> and CH<sub>3</sub>SH have been measured. These and previously measured quadrupole couplings of S<sup>33</sup> in OCS, HNCS, CS, and S<sub>8</sub> are examined to determine the nature of sulfur bonds and the best value for the S<sup>33</sup> quadrupole moment.  $s-p$  hybridization is found to be common, but not universal, in sulfur bonds. The S<sup>33</sup> quadrupole moment is  $-0.064 \pm 0.01 \times 10^{-24}$  cm<sup>2</sup>. If O and Se bonds are assumed to be similar to those of S, the quadrupole moments of O<sup>17</sup> and Se<sup>79</sup> are  $-0.004 \times 10^{-24}$  cm<sup>2</sup> and  $0.9 \times 10^{-24}$  cm<sup>2</sup>, respectively.

### INTRODUCTION

COUPLING of the nuclear quadrupole moments of the halogens in molecules has been extensively studied and interpreted in terms of bond structure, but attention given to quadrupole hyperfine structure of O, S, or Se has been rather small by comparison. We have attempted to study the quadrupole coupling of S<sup>33</sup> in a variety of bond structures in order to obtain information about the nature of sulfur bonds, and in

addition to obtain improved values for the nuclear quadrupole moments of S<sup>33</sup>, S<sup>35</sup>, and isotopes of the chemically similar elements, O and Se.

The most abundant sulfur nuclei, S<sup>32</sup> and S<sup>34</sup>, have zero spin and hence no quadrupole moment, but the less common S<sup>33</sup> (0.75 percent abundance) has a spin of 3/2 and a quadrupole moment.  $\epsilon$  quadrupole hyperfine structure due to this isotope was first observed by Townes and Geschwind<sup>1</sup> in OCS, and its quadrupole coupling constant in this molecule has been determined with increasing accuracy by several workers, White's value<sup>2</sup>  $eqQ = -29.130 \pm 0.008$  Mc/sec being the most

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<sup>1</sup> C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948).

<sup>2</sup> R. L. White, Columbia Radiation Laboratory Quarterly Report, March 31, 1953, p. 21 (unpublished).

accurate. Townes and Dailey<sup>3</sup> have discussed the bond structure of OCS in terms of two reasonable configurations and set upper and lower limits of 100 Mc/sec and 50 Mc/sec on the coupling constant per unbalanced  $p$  electron for S<sup>33</sup>. A corresponding uncertainty applies to the determination of the quadrupole moment from this coupling constant.

Measurements of hyperfine structure due to S<sup>33</sup> in the molecules HDS, SO<sub>2</sub>, and CH<sub>3</sub>SH are reported and discussed below. Dousmanis, Sanders, Townes, and Zeiger<sup>4</sup> have recently determined the quadrupole coupling constant of S<sup>33</sup> in HNCS. Mockler and Bird are reporting the coupling in CS in a separate work to be published soon. Dehmelt<sup>5</sup> has recently determined the coupling constant in solid rhombic sulfur by measuring the pure quadrupole resonance.

Quadrupole effects in these six molecules and in OCS allow fairly extensive intercomparison between different types of bonds.

#### HDS (Partially Deuterated Hydrogen Sulfide)

The microwave spectrum of HDS has been analyzed by Hillger and Strandberg.<sup>6</sup> From their measurements the frequencies of the transitions  $2_{2,0} \leftarrow 2_{2,1}$  and  $4_{3,1} \leftarrow 4_{3,2}$  of HDS<sup>33</sup> were known to be about 11 258 and 10 831 Mc/sec, and the difficulty of locating and identifying asymmetric rotor transitions was eliminated. The sample of HDS was prepared by Dr. G. Silvey from natural sulfur and hydrogen containing 50 percent deuterium. Nine weak lines were observed over a range of 15 Mc/sec centered about the predicted frequency of the  $2_{2,0} \leftarrow 2_{2,1}$  line and one of these was partially resolved to give the required total of ten lines. Four lines corresponding to  $\Delta F=0$  transitions were observed within one Mc/sec of the predicted frequency of the  $4_{3,1} \leftarrow 4_{3,2}$  line. In this case the  $\Delta F=\pm 1$  components should be very much weaker than the observed  $\Delta F=0$  components and hence were not observed. The frequencies of the two rotational transitions without hyperfine structure were computed from the measurements to be 11 259.10 Mc/sec and 10 831.12 Mc/sec, but these absolute frequencies are probably less precise than the coupling constants since only frequency differences were desired and no precautions were taken against inaccuracies in absolute frequencies due to time-delays in the measurements. The eight fully-resolved lines of the  $2_{2,0} \leftarrow 2_{2,1}$  transition were all measured at least twice and fitted by least squares to a first order quadrupole calculation with a rms deviation of 0.07 Mc/sec. Most of this deviation probably arises from distortion of the various lines by Stark components of adjacent lines, an effect which could not be completely eliminated.

<sup>3</sup> C. H. Townes and B. P. Dailey, *J. Chem. Phys.* **17**, 782 (1949).

<sup>4</sup> Dousmanis, Sanders, Townes, and Zeiger, Columbia Radiation Laboratory Quarterly Report, March 31, 1953 (unpublished).

<sup>5</sup> H. Dehmelt, *Phys. Rev.* **91**, 313 (1953).

<sup>6</sup> R. E. Hillger and M. W. P. Strandberg, *Phys. Rev.* **83**, 575 (1951).

Since closed expressions for  $E(\kappa)$ , the asymmetric rotor reduced energy, are available for all of the levels involved in these transitions, the expression given by Bragg and Golden<sup>7</sup> was more convenient than the alternative expression involving asymmetric rotor line strengths. That is,  $W_Q = eQ \langle V_{zz} \rangle_{Av} f(I, J, F)$ , where  $f(I, J, F)$  is Casimir's function, and

$$\langle V_{zz} \rangle_{Av} = \frac{1}{J(J+1)} \left\{ \frac{\partial^2 V}{\partial a^2} [J(J+1) + E(\kappa) - \kappa + 1] + \frac{2\partial^2 V}{\partial b^2} \frac{\partial E}{\partial \kappa} + \frac{\partial^2 V}{\partial c^2} [J(J+1) - E(\kappa) + \kappa - 1] \right\}.$$

Values of  $x$  were obtained for HDS<sup>32</sup> and HDS<sup>34</sup> by rigid rotor calculations on the frequencies for the transitions  $1_{1,0} \leftarrow 1_{1,1}$  and  $2_{2,0} \leftarrow 2_{2,1}$  given by Hillger and Strandberg,<sup>6</sup> and these were simply averaged to give a value accurate enough for the calculations on HDS<sup>33</sup>. The least square fit gave values for  $eQ \langle V_{zz} \rangle_{Av}$  of  $-23.4_3$  and  $-31.1_6$  Mc/sec for the initial and final states respectively. Because of the mathematical symmetry of a  $\Delta J=0$  transition, an equally good fit could be obtained by reversing the order and signs of these numbers, but this led to unreasonable values of the molecular coupling constants and was rejected. The coupling constants obtained are  $eQ(\partial^2 V / \partial a^2) = -23.4_3$  Mc/sec and  $eQ(\partial^2 V / \partial b^2) = -17.5_4$  Mc/sec. As a check on the accuracy of measurement, assignment, and calculation, these constants were used to calculate the fine structure of the  $4_{3,1} \leftarrow 4_{3,2}$  transition. The calculated value of  $-3.22$  Mc/sec compared favorably with the measured value of  $-3.18$  Mc/sec for the single constant required to determine the splitting of the  $\Delta F=0$  lines, with the difference representing an error of 0.01 Mc/sec in the splitting of the two strongest lines.

Before a final evaluation of this data could be made, it was necessary to carry out a rotation from the inertial axes of HDS to the electrical symmetry axes, which presumably coincide with the H-D direction and the bisector of the HSD angle. The angle of rotation must be calculated from molecular parameters, and these parameters may not simply be taken as identical with the infrared parameters of H<sub>2</sub>S, since zero-point vibrations in such a light molecule will certainly produce some change in the effective structure of the molecule with isotopic substitution. For many other purposes these changes are negligible, but in this case the angle of rotation and the final coupling constants depend rather critically on the bond angle.

Angles of rotation have been calculated for several structures by Mr. George Dousmanis. One of these was obtained by taking Hillger and Strandberg's<sup>6</sup> frequencies for the HDS<sup>32</sup> transitions  $1_{1,0} \leftarrow 1_{1,1}$  and  $2_{2,0} \leftarrow 2_{2,1}$  and their calculated value of the inertial defect and determining the structure from  $A$  and  $B$

<sup>7</sup> J. K. Bragg and S. Golden, *Phys. Rev.* **75**, 735 (1949).

on a rigid rotor basis. This led to a bond angle of  $93^{\circ}18'$  and bond distances (assumed equal) of 1.3455Å. The angles of rotation calculated from these parameters were  $36^{\circ}29'$  for HDS<sup>32</sup> and  $36^{\circ}51'$  for HDS<sup>33</sup>. In another structure the S—D distance from the first structure was shortened by 0.01Å to test the dependence of rotation angle on such an inequality in effective bond distances as might be caused by zero-point vibrations. This changed the angle of rotation from  $36^{\circ}51'$  to  $36^{\circ}24'$  for HDS<sup>33</sup>.

The coupling constants calculated from the first structure are

$$eQ(\partial^2V/\partial a'^2) = -31.0 \text{ Mc/sec,}$$

$$eQ(\partial^2V/\partial b'^2) = -10.0 \text{ Mc/sec.}$$

Here  $a'$  refers to the H—D direction and  $b'$  to the bisector of the HSD angle. Those calculated from the second differ by about one Mc/sec from these values. The sum of the two constants is independent of the angle of rotation.

Essentially the above results were obtained some time ago and sent privately to Dehmelt, who has already commented<sup>5</sup> on the significance of the large difference between  $eQ(\partial^2V/\partial a'^2)$  and  $eQ(\partial^2V/\partial b'^2)$ . Burrus and Gordy<sup>8</sup> have confirmed the experimental result by obtaining the similar quantities for H<sub>2</sub>S<sup>33</sup> and also have discussed its significance. Their values for H<sub>2</sub>S are  $eQ(\partial^2V/\partial a'^2) = -32.0 \text{ Mc/sec}$  and  $eQ(\partial^2V/\partial b'^2) = -8.0 \text{ Mc/sec}$ , with an H—S—H angle of  $92^{\circ}6'$ . It is not clear whether the small differences between results for H<sub>2</sub>S and HDS are due to experimental uncertainties or to changes in the effects of zero-point vibrations. A change in bond angle as large as  $1^{\circ}$  is not unreasonable for substitution of D in place of H.

The importance of the observed difference between  $eQ(\partial^2V/\partial a'^2)$  and  $eQ(\partial^2V/\partial b'^2)$  lies in the fact that if H<sub>2</sub>S involved nearly pure  $p$  bonds, as has often been assumed because the bond angle is so near to  $90^{\circ}$ , these two constants must necessarily be equal. The three  $p$  orbitals would not be equally filled since the orbital perpendicular to the molecular plane would be occupied by two nonbonding electrons, which would give a field gradient symmetric about this direction and equivalent to that produced by one atomic  $p$  electron. This is not as poor an approximation as it might seem since the observed difference between  $eQ(\partial^2V/\partial a'^2)$  and  $eQ(\partial^2V/\partial b'^2)$  may be accounted for by a small amount of  $s$  hybridization for each bond. Assuming 4 percent ionic character for the S—H bond, and that the bond is an  $s-p$  hybrid, one obtains from the above coupling constants a value 14.6 percent for the  $s$ -hybridization and a quadrupole coupling constant per pure  $p$  bond of 50.0 Mc/sec. The rather small amount of ionic character assumed here has little effect on the quadrupole coupling and has been omitted from Table II for the sake of simplicity.

<sup>8</sup> C. A. Burrus, Jr., and W. Gordy, Phys. Rev. **92**, 274 (1953).

The difference between the observed HSD angle of  $93^{\circ}18'$  and the angle of  $100^{\circ}$  required by the indicated  $s-p$  hybridization is somewhat puzzling. Dehmelt<sup>5</sup> has suggested the possibility of  $d$  hybridization, which might modify the angle. If this explanation is correct, the coupling constant per  $p$  electron given above is too small by 10 to 20 percent. An alternative explanation might be that the localization of a bond along the internuclear line is a poor approximation for very light molecules. This idea is given some support by the difficulties in fitting the NH<sub>3</sub> coupling constant with a hybridization scheme determined by the bond angles, and by the fact that arsine and stibine also have HXH angles very nearly  $90^{\circ}$  but quadrupole coupling constants which require a sizeable degree of  $s-p$  hybridization.<sup>9,10</sup> In contrast to arsine and stibine, the heavier molecules AsF<sub>3</sub> and SbCl<sub>3</sub> have bond angles which agree with the amount of hybridization indicated by their quadrupole coupling constants.<sup>10</sup>

### Sulfur Dioxide

Sulfur dioxide has been the subject of several investigations.<sup>11</sup> No transitions of the less abundant isotopic species of sulfur were identified in any of these researches, and this proved to be a major hindrance to the present work, since weak lines had to be found and identified.

The frequencies of the isotopic lines were calculated from Crable and Smith's frequencies for the S<sup>32</sup>O<sub>2</sub> transitions  $1_{1,1} \leftarrow 0_{0,0}$ ,  $2_{1,1} \leftarrow 2_{0,2}$ , and  $4_{0,4} \leftarrow 3_{1,3}$  and the rigid rotor approximation. This calculation was performed with fifth power series in  $\delta$ , the prolate asymmetry parameter, and the following approximations were used:

$$I_B^{32} = I_B^{33}, \quad \Delta^{32} = \Delta^{33},$$

$$I_A^{32} \left( \frac{M_{S^{33}}}{M_{S^{32}}} \right) \left( \frac{M_{S^{32}} + 2M_{O^{16}}}{M_{S^{33}} + 2M_{O^{16}}} \right) = I_A^{33}.$$

The surprising feature of this calculation was the close agreement with the frequencies later measured, most of the difference being accounted for by the rigid rotor approximation used to calculate the moments of the principal isotopic species. The calculated and observed frequencies are given in Table I. Since the desired lines are weak, and the  $J$  values fairly high, only the four hyperfine structure lines having  $\Delta F = \Delta J$  had observable intensities when SO<sub>2</sub> with natural abundances was examined. Casimir's function has the peculiarity that for any value of  $J$  and a spin of  $3/2$ ,  $f(3/2, J, J+3/2) - f(3/2, J, J+1/2) = f(3/2, J, J-3/2) - f(3/2, J, J-1/2) = 1/4$ . When only  $\Delta F = \Delta J$  transitions are observed, this relation can prove whether or not a given

<sup>9</sup> C. C. Loomis and M. W. P. Strandberg, Phys. Rev. **81**, 798 (1951).

<sup>10</sup> P. Kisliuk, J. Chem. Phys. **22**, 86 (1954).

<sup>11</sup> Dailey, Golden, and Wilson, Phys. Rev. **72**, 871 (1947); M. H. Sirvetz, J. Chem. Phys. **19**, 938 (1951); G. F. Crable and W. V. Smith, J. Chem. Phys. **19**, 676 (1951).

TABLE I. Frequencies of SO<sub>2</sub> transitions.<sup>a</sup>

Line	Observed frequency Mc/sec	Calculated frequency Mc/sec
S <sup>32</sup> O <sub>2</sub> 4 <sub>0,4</sub> ←3 <sub>1,3</sub>	(29 321.22)	(29 321.2)
S <sup>33</sup> O <sub>2</sub> 4 <sub>0,4</sub> ←3 <sub>1,3</sub>	30 194.09	30 191.3
S <sup>34</sup> O <sub>2</sub> 4 <sub>0,4</sub> ←3 <sub>1,3</sub>	31 011.19	31 006.4
S <sup>32</sup> O <sub>2</sub> 5 <sub>2,4</sub> ←6 <sub>1,5</sub>	(23 414.33)	23 435.2
S <sup>33</sup> O <sub>2</sub> 5 <sub>2,4</sub> ←6 <sub>1,5</sub>	20 605.97	20 632.1
S <sup>34</sup> O <sub>2</sub> 5 <sub>2,4</sub> ←6 <sub>1,5</sub>	17 970.42	18 001.0

<sup>a</sup> ( ) indicates an observation by Crable and Smith (reference 11).

group of lines is a quadrupole pattern arising from a nucleus of spin 3/2, but prevents the identification of the  $J$  values of the pattern from spacings observed. It also requires careful observation of the relative intensities of such a pattern to determine the assignment of  $F$  values to the lines.

The four lines of the 4<sub>0,4</sub>←3<sub>1,3</sub> transition centered at 30 194.09 Mc/sec were observed at room temperature and at -70°C. With these and all other frequency measurements on SO<sub>2</sub>, slow triangular sweeps or stabilization were used to eliminate time delays in the frequency and line presentation circuits, since it was felt that other investigators might make use of the absolute frequencies so measured. The combination rule just mentioned was applied as a test of accuracy, and discrepancies not larger than about 0.05 Mc/sec were observed among the four frequencies thus compared. Here, too, the principal source of inaccuracy was probably distortion of the lines by Stark components from neighbors. The four lines of the 5<sub>2,4</sub>←6<sub>1,5</sub> transition were observed at room temperature and at -70°C, and assignments based on calculations from the above transition verified by intensities and spacings. One of the four lines nearly coincided with a multiple of 30 Mc/sec and could not be measured accurately with the frequency standard available; for this reason the combination rule could not be applied.

Calculation of the coupling constants was performed with the expression given above. The earlier use of the  $\delta$  series proved to be particularly helpful, since the necessary reduced energy terms  $E(\kappa)$  and  $\partial E/d\kappa$  could be obtained by differentiating the series and using the relationships  $E(\kappa)=E(\delta)$  and  $dE/d\kappa=\frac{1}{2}dE/d\delta$ . The value of  $\delta$  was obtained from the calculation of moments of inertia by the approximations already given. Since it predicted the location of the observed transitions satisfactorily, it was considered good enough for the less precise quadrupole data. This procedure is good only for small values of  $\delta$  since the  $dE/d\delta$  series will converge less rapidly than the original  $E(\delta)$  series.

The calculated values of the coupling constants obtained from the 4<sub>0,4</sub>←3<sub>1,3</sub> transition are as follows:

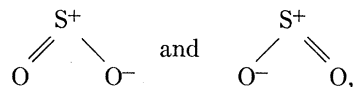
$$eQ(\partial^2V/\partial a^2) = -1.7 \pm 0.2 \text{ Mc/sec,}$$

$$eQ(\partial^2V/\partial b^2) = +25.71 \pm 0.03 \text{ Mc/sec.}$$

The uncertainties given represent the average deviation

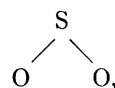
of calculations based on different frequency measurements.

The electronic structure of SO<sub>2</sub> has been considered as mainly consisting of the two identical resonant forms,

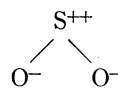


with  $sp^2$  hybridization accounting for the observed bond angle of nearly 120°. The quadrupole coupling constants for such a structure would be  $eQ(\partial^2V/\partial a^2) = -\frac{1}{6}eq_p^+Q$  and  $eQ(\partial^2V/\partial b^2) = \frac{1}{3}eq_p^+Q$ , where  $eq_p^+Q$  is the coupling constant for one  $p$  electron in S<sup>+</sup>, or about 70 Mc/sec. This structure gives the correct signs for the coupling constants, but not precisely correct values.

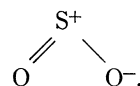
In order to obtain the measured coupling constants, it is necessary to modify the above structure by decreasing the probability for an electron to be in the  $p$  orbital about the S atom which is perpendicular to the plane of the molecule. The structure,



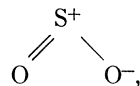
is not favorable, since it puts two electrons in this  $p$  orbit. Some importance for the structure



would give the correct effect as would also  $d$ -hybridization of the  $\pi$  component of the double bond in the structure



Assuming that the structure of primary importance is



and that the probability for the electron being removed from the  $\pi$  orbital by some mechanism such as those mentioned is  $\epsilon$ , one can obtain  $\epsilon$  and  $eq_pQ$  from the measured coupling constants. They are  $\epsilon=0.27$  and  $eq_pQ=55$  Mc/sec in reasonable agreement with the result from HDS.

### Methyl Mercaptan

Methyl mercaptan has been subjected to a number of microwave investigations, the most recent and exhaustive being that of Solimene and Dailey.<sup>12</sup> These authors kindly provided detailed information on their work and a sample of CH<sub>3</sub>SH with sulfur in natural abundance. They had identified a pair of lines at

<sup>12</sup> N. Solimene and B. P. Dailey, Phys. Rev. **91**, 464 (1953).

25 291.87 Mc/sec and 25 290.92 Mc/sec as the transition  $1_{0,1} \leftarrow 0_{0,0}$  (the line is double as a result of internal torsion) of the principal isotopic species, and a line at 25 879.08 Mc/sec as the unresolved doublet corresponding to the same transition for the species  $\text{CH}_3\text{S}^{34}\text{H}$ . With the high-sensitivity spectrograph described by Fletcher and Hardy<sup>13</sup> this line was easily resolved into a corresponding doublet (24 879.83 Mc/sec and 24 878.91 Mc/sec) confirming their assignment. Midway between these pairs of lines a group of three very weak doublets was found with appropriate doublet and quadrupole spacings. The central frequencies of the two groups of three lines were 25 079.64 Mc/sec and 25 078.70 Mc/sec. Only one of the two asymmetric rotor coupling constants may be obtained from this particular transition; it is  $eQ(\partial^2V/\partial a^2) = -27.57 \pm 0.05$  Mc/sec. No other transitions of normal methyl mercaptan have been identified except for a  $J=2 \leftarrow 1$  transition at about twice the frequency of the  $J=1 \leftarrow 0$  transition. A search for the corresponding isotopic transitions was not attempted because of the difficulty of looking for a group of weak lines in a very dense spectrum.

The  $a$  axis in methyl mercaptan coincides quite closely with the C—S direction, being tipped only  $2.5^\circ$  out of this direction by the hydrogen bonded to the sulfur.<sup>12</sup> The C—S—H bond angle is  $99^\circ 26'$  suggesting an  $s$  hybridization of about 14 percent for the  $p$  bonds as was found in HDS. If the electric fields surrounding the S in methyl mercaptan were similar to those in HDS, one would expect a value  $eQ(\partial^2V/\partial a^2) = -23.2$  Mc/sec, which is not far different from the observed value of  $-27.6$  Mc/sec. A measurement of the coupling constant  $eQ(\partial^2V/\partial b^2)$  would permit a more complete interpretation of the sulfur bonds in this molecule.

### $\text{S}_8$ , CS, and HNCS

Dehmelt<sup>5</sup> has observed the pure quadrupole resonance of  $\text{S}^{33}$  in solid rhombic sulfur ( $\text{S}_8$ ) from which a quadrupole coupling constant of  $\pm 45.8$  Mc/sec is obtained. The coupling constant for a pure  $p$  electron can be deduced from this if the amount of hybridization can be satisfactorily determined. Dehmelt argues against as much as 21 percent hybridization, which is indicated by the angle, and assumes 10 percent  $s-p$  hybridization so that a coupling constant per  $p$  electron of 50.4 Mc/sec is obtained. Dehmelt's argument against larger hybridization is based, however, on multiplying the total bond energy by a rough estimate of the percentage increase in overlap due to hybridization and comparing this product with the energy needed to promote 21 percent of one electron from an atomic  $3s$  to a  $3p$  orbit. The total bond energy of course involves repulsive interactions as well as overlap energies, and

only a considerably more refined calculation would give good information about the hybridization. If 21 percent  $s$  hybridization is assumed, the coupling constant per  $p$  electron would be 58.0 Mc/sec rather than the 50.4 Mc/sec obtained by Dehmelt.

That  $s$  hybridization in sulfur bonds can be large is strikingly demonstrated by the quadrupole coupling of  $\text{S}^{33}$  in CS reported by Mockler and Bird.<sup>14</sup> In this case the most reasonable way of obtaining the correct sign for the coupling constant is to assume that the structure  $\text{C}^-\equiv\text{S}^+$  is important and that the  $\sigma$  component of this bond involves considerable  $3s$  character. It is possible to obtain the positive coupling constant of CS by assuming the structure  $\text{C}^-\equiv\text{S}^+$  to have  $d$  hybridization in the  $\pi$  orbitals rather than  $s$  hybridization in the  $\sigma$  orbital. However, there appears no reason why  $d$  hybridization of the  $\pi$  orbitals should not occur also in OCS, where it would be inconsistent with the measured coupling constant for  $\text{S}^{33}$ .

The various possible electronic structures for OCS were discussed some time ago by Townes and Dailey.<sup>3</sup> At that time, it was not clear whether or not the  $\sigma$  orbital was hybridized, and hence structures with or without  $s$  hybridization were suggested as alternatives. It now appears that if the coupling constant of  $\text{S}^{33}$  in OCS is to be made consistent with those of the above molecules, very little  $s$  hybridization can be allowed. This is in contrast to the case of CS, where  $s$  hybridization of the  $\sigma$  orbital seems essential. The difference between the OCS and CS cases is presumably connected with the difference between the carbon orbitals which are available. It illustrates the hazards involved in the simplifying assumption of an invariable amount of hybridization.

The coupling constant for HNCS is  $-27.5$  Mc/sec which is very nearly equal to that for OCS, indicating the similarity of the sulfur bonds in the two cases. It is interesting that the small difference between the coupling constants in HNCS and OCS is fairly well predicted, however, from the variations in multiple bonding obtained by using the measured internuclear distances. This is shown in Table II.

### Summary of S Bonds

The most reasonable structures which fit all the measured quadrupole couplings of  $\text{S}^{33}$  are listed in Table II. The quadrupole coupling per  $p$  electron for atomic  $\text{S}^{33}$  is assumed to be  $-55$  Mc/sec for these cases. The sign of this coupling constant corresponds to a negative nuclear quadrupole moment for  $\text{S}^{33}$ . Most weight in determining the coupling constant has been given to hydrogen sulfide,  $\text{S}_8$ , and  $\text{SO}_2$ , in decreasing order of importance, since their structures seem to be most simply and uniquely interpretable. It is thought

<sup>13</sup> P. Fletcher and W. A. Hardy, Columbia Radiation Laboratory Quarterly Report, March 31, 1953, p. 20 (unpublished).

<sup>14</sup> R. Mockler and G. Bird (to be published).

TABLE II. Probable bond structures of molecules containing S and comparison between experimentally measured quadrupole coupling constants of  $S^{33}$  and those predicted from the structures. The coupling constant per  $p$  electron is assumed throughout to be  $-55$  Mc/sec. Percentage importances of multiply bonded structures are determined from internuclear distances.

Molecule	Structure	Importance (percent)	Hybridization of sulfur bonds (percent)	Predicted coupling constants (Mc)	Measured coupling constants (Mc)
$H_2S$		100	15 $s$	$eQ(\partial^2V/\partial a'^2) = -34.2$	$-31.0$
(HDS) $CH_3SH$		100	15 $s$	$eQ(\partial^2V/\partial b'^2) = -10.5$	$-10.0$
$S_8$		100	21 $s$	$eQ(\partial^2V/\partial a^2) = -24.4$ $eQ(\partial^2V/\partial z^2) = -43.5$	$\pm 45.8$
$SO_2$		100	33 $s$ for $\sigma$ bonds See text for discussion of $\pi$ bond	$eQ(\partial^2V/\partial a^2) = -1.9$	$\pm 1.7$
$CS$	$C=S$	60	50 $s$ for $\sigma$ bond	$eQ(\partial^2V/\partial b^2) = 28.2$	$+25.7$
	$C\equiv S^+$	40		$eQ(\partial^2V/\partial z^2) = 13.8$	$+12.84$
	$O=C=S$	58			
$OCS$	$O^+\equiv C-S^-$	28	none	$eQ(\partial^2V/\partial z^2) = -28.3$	$-29.13$
	$O^- - C\equiv S^+$	14			
	$H-N=C=S$	63			
$HNCS$	$H-N^--C\equiv S^+$	19	none	$eQ(\partial^2V/\partial z^2) = -25.2$	$-27.5$
	$H-N^+\equiv C-S^-$	18			

that the coupling constant per  $p$  electron is accurate to about 15 percent.

#### Quadrupole Moments of $O^{17}$ , $S^{33}$ , $S^{35}$ , and $Se^{79}$

The quadrupole coupling  $eQ(\partial^2V/\partial z^2)$  per  $p$  electron determined above may be used to evaluate the quadrupole moment of  $S^{33}$  if the quantity  $\partial^2V/\partial z^2 = \frac{4}{5}e/\langle r^3 \rangle_{Av}$  is known. By using the value of  $\langle 1/r^3 \rangle_{Av}$  given by Barnes and Smith,<sup>15</sup> we obtain a value  $Q_{S^{33}} = -0.058 \times 10^{-24}$  cm<sup>2</sup>. This should be further corrected by a factor of about 1.10 to allow for screening effects,<sup>16</sup> so that the corrected value is  $Q_{S^{33}} = -0.064 \times 10^{-24}$  cm<sup>2</sup>. This may be compared with the original value  $-0.05 \times 10^{-24}$  given by Townes and Geschwind<sup>1</sup> and the very recent values  $0.05 \times 10^{-24}$  and  $0.06 \times 10^{-24}$  given by Dehmelt<sup>5</sup> and by Burrus and Gordy,<sup>8</sup> respectively. Since the ratio of the  $S^{35}$  moment to that of  $S^{33}$  is  $-0.695$ ,<sup>17</sup> the  $S^{35}$  moment is then  $Q_{S^{35}} = 0.045 \times 10^{-24}$  cm<sup>2</sup>.

The quadrupole coupling constants of  $O^{17}$  and  $Se^{79}$

have been measured in OCS and OCSe.<sup>18,19</sup> Although the oxygen and selenium bonds are certainly not precisely like those of S, they may be assumed to be reasonably similar in the molecules OCS and OCSe. Previous evaluation of  $Q$  for  $O^{17}$  and  $Se^{79}$  can hence be improved as a result of our more precise knowledge of the S bonds in OCS. Assuming that the structure of OCS is as given in Table II, that the oxygen bonds, like those of S, are not hybridized in this molecule, and using the measured<sup>18</sup> coupling constant of  $O^{17}$  in OCS, the quadrupole coupling constant per  $p$  electron for  $O^{17}$  is  $-3.30$  Mc/sec. Assuming that the bond structure of OCSe is similar to that of OCS, and using the measured coupling constant for  $Se^{79}$ , the quadrupole coupling per  $p$  electron for  $Se^{79}$  is 1430 Mc/sec. Using values of  $\langle 1/r^3 \rangle_{Av}$  from Barnes and Smith,<sup>15</sup> and applying corrections of 10 percent for screening,<sup>16</sup> one obtains the nuclear quadrupole moments  $Q_{O^{17}} = -0.004 \times 10^{-24}$  cm<sup>2</sup> and  $Q_{Se^{79}} = 0.9 \times 10^{-24}$  cm<sup>2</sup>.

<sup>15</sup> R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

<sup>16</sup> R. Sternheimer, Phys. Rev. **84**, 244 (1951).

<sup>17</sup> Cohen, Koski, and Wentink, Phys. Rev. **81**, 948 (1951).

<sup>18</sup> Geschwind, Gunther-Mohr, and Silvey, Phys. Rev. **85**, 474 (1952).

<sup>19</sup> Hardy, Silvey, and Townes, Phys. Rev. **85**, 494 (1952).