Nuclear Quadrupole Resonance in Rhombic Sulfur and the Quadrupole Moments of S^{33} and S^{35}[†]

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(Received April 6, 1953)

Four closely spaced absorption lines due to nuclear quadrupole resonance of the S^{33} isotope have been observed near 22.9 Mc/sec in a sample of rhombic sulfur, containing this isotope in its natural abundance of 0.74 percent. As the nuclear spin of S^{33} is $\frac{3}{2}$, these lines correspond to the transition $m = \pm\frac{1}{2} \leftrightarrow m = \pm\frac{3}{2}$ and an average quadrupole coupling constant $eQ^{33}q_{zz}/h = 45.8$ Mc/sec. The bond structure of the S_8 molecule is discussed with respect to the evaluation of q_{zz}, the gradient of the electric field at the site of the nucleus. From the measured coupling constant $eQ^{33}q_{zz}$ and the calculated q_{zz}, the value $Q^{33} = -0.050 \times 10^{-24}$ cm^2 is obtained for the nuclear quadrupole moment of S^{33}. With the ratio Q^{35}/Q^{33} known from microwave data, this leads to $Q^{35} = +0.035 \times 10^{-24}$ cm^2 for S^{35}.

ABSORPTION lines due to nuclear quadrupole resonance[1] of the S^{33} isotope have been observed in a 3000-cm^3 sample of rhombic sulfur containing this isotope in its natural abundance of 0.74 percent. The spectrum consisted of four closely spaced lines (see Fig. 1) whose frequencies are given in Table I. The lines were observed at room temperature using a recording super-regenerative spectrometer employing square wave Zeeman modulation. As it was possible to keep the sensitivity within reasonable limits over a frequency range of 1 to 1.5 simply by ganging the rf oscillator and quench voltage generator frequency controls and so keeping the ratio of these frequencies approximately constant, no stabilization circuits were found necessary.

The four observed lines all belong to the same transition $m = \pm\frac{1}{2} \leftrightarrow m = \pm\frac{3}{2}$, the only one allowed for $I = \frac{3}{2}$. This spin value had already been established for S^{33} by an investigation[2] of the hfs of the rotational spectrum of OCS^{33} in the microwave region, which also allowed the determination of the sign and the approximate value for the quadrupole moment[3] given in Table II.

Sulfur forms a typical molecular crystal, whose units —puckered rings of 8 covalently bonded S atoms— are held together by weak van der Waals forces. While it takes 510 kcal/mole to rupture the 8 bonds in the S_8 molecule, only 20.8 kcal/mole are necessary to evaporate sulfur. The close spacing of the four observed lines, which correspond to the four nonequivalent sites I, II, III, IV in the lattice of rhombic sulfur,[4] shows that the effect of the extramolecular surroundings on the field gradient is negligible.

In the evaluation of the molecular field gradient[3] a difficulty is encountered insofar as the S—S—S angle found in the S_8 molecule is 105°, considerably larger than the angle between two pure p orbitals, namely, 90°. The widening of this angle is due to steric effects[5]

evidently, as two S atoms forming a bond to a common partner are not expected to approach each other much closer than double the van der Waals radius of S, namely, 3.70A. The actual approach is 3.4A, which together with the S—S distance of 2.12A for bonded atoms leads to the angle of 105°. Concerning the electronic structure of these bonds two limiting cases will be discussed:

(A) We assume that the S—S—S angle of 105° also is the angle between the axes of the two orbitals originating at an S atom. This necessitates a certain s admixture to the bonding orbitals,[5a] which is determined by the interorbital angle θ and given by the formula[6]

$$a^2 = \sin\theta - 90°/(1 + \sin\theta - 90°),$$

$\psi = as + bp$ denoting a bonding orbital. We obtain $a^2 = 21$ percent. The bond strength of these orbitals would be about 2, as compared to 1.73 for pure p orbitals. However, these hybrids cannot be formed from the $3s^2 3p^4$ configuration of the atomic ground
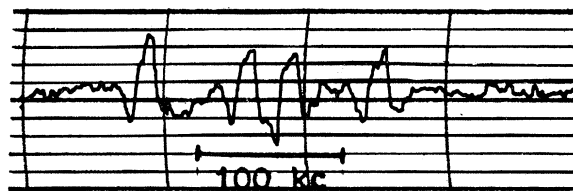

FIG. 1. Nuclear quadrupole resonance spectrum of S^{33} in rhombic sulfur near 22.9 Mc/sec. As the quench frequency of 16 kc/sec is only slightly higher than the line width, main lines, and super-regeneration satellites are not resolved. The time constant in the recording circuit was 16 sec.

[†] Work supported by the U. S. Office of Ordnance Research.
[1] H. G. Dehmelt and H. Krüger, Naturwiss. **37**, 111 (1950) and Z. Physik **129**, 401 (1951); R. V. Pound, Phys. Rev. **79**, 685 (1950).
[2] C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948).
[3] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).
[4] B. E. Warren and S. T. Burwell, J. Chem. Phys. **3**, 6 (1935).
[5] L. Pauling, *Nature of the Chemical Bond* (Oxford University Press, London, 1940), Chap. III, Sec. 13.

[5a] As the energy to promote a $3p$ electron into a $3d$ orbital is of the same order of magnitude as that to promote a $3s$ electron into a $3p$ orbital, $d-p$ hybridization also should be considered. However, it can be seen (compare reference 6) that a small d admixture will not widen but, as opposed to s admixture, reduce the bond angle below 90°. If A^2 denotes the percentage of d admixture of two $d-p$ hybrid bond orbitals one obtains for the reduction of the bond angle ϑ: $\pi/2 - \vartheta \approx \frac{1}{2}A^2$. From the foregoing it appears that the steric effects which we have assumed to cause the widening of the bond angle will tend to suppress d admixture which therefore has been neglected.
[6] Compare R. Hultgren, Phys. Rev. **40**, 891 (1932).

TABLE I. Nuclear quadrupole resonance lines of S^{33} in rhombic sulfur.

Line[a]	Frequency kc/sec
ν^{III}	$22\ 801\pm5$
ν^{IV}	$22\ 866\pm5$
ν^{I}	$22\ 896\pm5$
ν^{II}	$22\ 964\pm5$

[a] The pattern of the bond angles 103°, 105°, 105.6°, 108° in reference 4 for the different lattice sites agrees roughly with that of the lines. Though it is uncertain, if the differences between the bond angles are significant, frequencies have been assigned in opposite sequence as angles, as wider angles correspond to larger s admixture. This would indicate, that increasing the angle from 103° to 108° reduces the coupling constant by only 0.7 percent.

TABLE II. Quadrupole coupling constants and nuclear quadrupole moment of S^{33} and S^{35}.

Isotope	I	$|eQq_{zz}/h|$ cryst S_8 Mc/sec	$|eQq_{zz}/h|$ atom Mc/sec	Q	Q_{Townes} 10^{-24} cm²
S^{33}	$3/2$	45.8	50.4	-0.053	$-0.055\cdots0.103$
S^{35}	$3/2^6$	$\cdots$	35.0	$+0.037$	$+0.038\cdots0.072$

state of S; instead it is necessary first to promote 21 percent of an s electron into a p orbital per bonding orbital, requiring 21 percent of the energy separating the centers of gravity of the levels of the $3s^23p^4$ and $3s3p^5$ configurations. The energy necessary for this promotion comes out to be about 40 kcal/mole, which has to be compared with half the energy of the S−S bond, 32 kcal/mole. Certainly the 14 percent increase in bond strength of the sp hybrid over the pure p orbital cannot compensate for the much too high promotion energy.

(B) We now assume, that the two bonding orbitals of S in covalent molecules are nearly pure p orbitals with the corresponding angle of 90° between their axes. The $X−S−Y$ angle then should be 90° also, in case no repulsion between X and Y is encountered.[6a] Any repulsion between X and Y, on the other hand, will strain the bonds but need not widen the orbital angle though it will widen the $X−S−Y$ angle. This is possible by letting the rigid 90° frame of the two p orbitals pivot around the centers of the regions of overlap with the orbitals of the bond partners.[7] Evi-

dently the restoring forces against this pivoting are rather weak. For example, to widen the H−S−H angle in H_2S from its equilibrium value of 92° to 105° takes only 6 kcal/mole, as calculated from the force constant obtained from vibrational frequencies. As the covalent radius of the H atoms is much smaller than that of S, considerably less will be required in the S_8 molecule.

From the foregoing it appears that the bonding in the S_8 molecule might be nearer to model (B) than (A). Then the field gradient will be nearly axially symmetric and the quadrupole coupling constant[7a] in crystalline S_8 for S^{33} will be two times the mean observed absorption frequency and essentially equal to the atomic coupling constant per unbalanced p electron. A 10 percent higher value has been chosen for the atomic coupling to account for the reduction due to torsional oscillations[1] and a likely s admixture. The field gradient q_{zz} now can be obtained from the doublet separation per p electron for which we use the total splitting of the atomic ^3P ground level, 574 cm^{-1}. With $Z_i=12.5$ one obtains $q_{zz}=13.8\times10^{15}$ cgs. This then leads to the quadrupole moment given in Table II. The value for S^{35} has been calculated using the ratio[8] $Q^{35}/Q^{33}=-0.695$. A factor correcting for the polarization of the inner electron shells by the nuclear quadrupole moment,[9] $C(S)=1.052$, also has been applied.

The author is indebted to Professor Walter Gordy for valuable suggestions and discussions.

[6a] One might think H_2S with the bond angle of 92° to be a good example for this situation. However, according to recent private communications of Professor C. H. Townes and Professor Walter Gordy, the nuclear electric quadrupole hfs of rotational lines of H_2S in the microwave region leads to a large asymmetry of the molecular electric field at the site of the S nucleus, despite the bond angle being 92°. This can be explained by moderate amounts of s and d admixture whose effects cancel (compare reference 5a) with respect to the bond angle but add up to produce the observed electric asymmetry.

[7] Compare the "bent" bonds of C. A. Coulson and W. E. Moffit, J. Chem. Phys. 15, 151 (1947).

[7a] The evaluation of the coupling constant eQq_{zz} is rather insensitive against deviations of the electric field from axial symmetry. Even for the extremely large value of 0.5 for the asymmetry parameter $\epsilon=|q_{zz}/(q_{xx}-q_{yy})|$ e.g., only a reduction of 4 percent of the value calculated for eQq_{zz} in the crystal would result. (Compare e.g., H. Krüger, Z. Physik 130, 371 (1951).)

[8] Cohen, Koski, and Wentink [Phys. Rev. 76, 703 (1949); 81, 948 (1951)] give $eQq_{zz}/h(OCS^{35})=+20.5$ Mc/sec, while $eQ_{zz}/h(OCS^{33})=-29.5$ Mc/sec, see reference 2.

[9] R. Sternheimer, Phys. Rev. 86, 316 (1952).