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Sulfur-33 Nuclear Quadrupole Coupling and the Sulfur Localized Electron Distribution in Ethylene Sulfide

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Abstract: The microwave spectrum of the ^{33}S isotopic species of ethylene sulfide has been observed. The rotational constants are $A = 21{,}966.7 \pm 3.0$ MHz, $B = 10{,}683.65 \pm 0.1$ MHz, and $C = 7948.46 \pm 0.1$ MHz. The ^{33}S nuclear quadrupole coupling constants are $\chi_{aa} = -32.83 \pm 0.05$ MHz, $\chi_{bb} = -16.40 \pm 0.10$ MHz, and $\chi_{cc} = 49.23 \pm 0.15$ MHz. The bonding in the ring compound is discussed in light of the ^{33}S local electronic field gradients. It is concluded that the Walsh localized scheme is more appropriate than the less flexible Coulson–Moffitt scheme.

The electronic structure of small ring compounds and other strained molecular systems is of great interest due to the apparent breakdown of the concept of directed valence. The two standard approaches to describing the molecular orbitals in three-membered rings are due to Walsh[2a] and Coulson and Moffitt.[2b] There has been considerable discussion on which of these two descriptions is a more accurate representation of the bonding.[3,4] In some cases, the two descriptions are equivalent.[4] The present study of the ^{33}S nuclear quadrupole coupling in ethylene sulfide was initiated to determine the asymmetry in the electron density near the sulfur nucleus. This experimental determination of the localized electron asymmetry is extracted from the electronic field gradients at the ^{33}S nucleus. The field gradients are obtained by dividing the ^{33}S nuclear quadrupole coupling constants by the ^{33}S nuclear quadrupole moment. The field gradients are given as the average values of the $\Sigma_i e_i(3x_i^2 - r_i^2)/r_i^5$, $\Sigma_i e_i(3y_i^2 - r_i^2)/r_i^5$, and $\Sigma_i e_i(3z_i^2 - r_i^2)/r_i^5$ operators (all at the ^{33}Snuc leus). The sum over i is over all contributing point charges, e_i. These average values are used to interpret the ^{33}S localized electron density in ethylene sulfide.

Experimental Section

The microwave spectrograph used in this work has been described elsewhere.[5] The microwave spectrum for the naturally occurring ^{34}S (4.25%) and ^{32}S (95.0%) isotopes in ethylene sulfide have been observed before.[6] However, the ^{33}S (0.75%) isotopic species of ethylene sulfide has not been observed until this work. The rotational constants for the ^{33}S species were predicted from the known molecular structure.[6] Four weak transitions showing the ^{33}S nuclear quadrupole coupling were observed and the results are listed in Table I.

The ^{33}S nuclear quadrupole hyperfine structure shown in Table I was fit with the standard first-order theory[7] for a nucleus of spin $^3/_2$. The observed frequencies were fit with three rotational constants and two independent ^{33}S nuclear quadrupole coupling constants with the following results: rotational constants, $A = 21{,}966.7 \pm 3.0$ MHz, $B = 10{,}683.65 \pm 0.1$ MHz, $C = 7948.46 \pm 0.1$ MHz; ^{33}S nuclear quadrupole coupling constants, $\chi_{aa} = -32.83 \pm 0.05$ MHz, $\chi_{bb} = -16.40 \pm 0.10$ MHz, $\chi_{cc} = 49.23 \pm 0.15$ MHz. The a axis bisects the CSC angle and the b axis is also in the molecular plane.[8]

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(7) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(8) We have rechecked the structure given previously and we find the original structure in Table XIV of ref 6 to be remarkably accurate except for a typographical error in the CSC angle. The CSC angle should be 48° 28′.

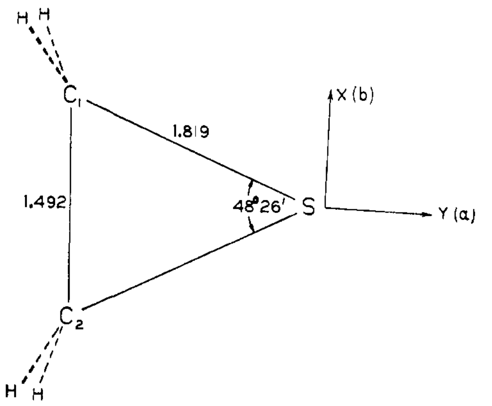

Figure 1. Ethylene sulfide.

Discussion

The interpretation of nuclear quadrupole coupling constants in terms of localized atomic orbitals is a risky proposition. However, within limits, some information about the local electron density may be obtained.

Table I. Observed Transitions in $C_2H_4{}^{33}S$

F–F'	Frequency Obsd	Frequency Calcd	Difference
	0_{00}–1_{01}		
$^3/_2$–$^3/_2$	18625.599	18625.544	0.055
$^3/_2$–$^5/_2$	18633.788	18633.752	0.036
$^3/_2$–$^1/_2$	18640.379	18640.318	0.061
	1_{11}–2_{12}		
$^5/_2$–$^5/_2$	34519.37[a]	34519.427	−0.057
$^3/_2$–$^5/_2$	34523.460	34523.527	−0.067
$^1/_2$–$^3/_2$	34524.920	34524.938	−0.018
$^5/_2$–$^7/_2$	34531.720	34531.734	−0.014
$^3/_2$–$^3/_2$	34532.27[a]	34532.318	−0.048
$^1/_2$–$^1/_2$	34537.215	34537.246	−0.031
	1_{01}–2_{02}		
$^5/_2$–$^5/_2$	36815.911	36815.866	0.045
$^1/_2$–$^3/_2$	36816.305	36816.307	−0.002
$^3/_2$–$^5/_2$	36824.119	36824.073	0.046
$^5/_2$–$^7/_2$	36825.676	36825.677	−0.001
$^1/_2$–$^1/_2$	36826.07[a]	36826.118	0.048
$^3/_2$–$^3/_2$	36831.083	36831.081	0.002
	1_{01}–2_{11}		
$^3/_2$–$^3/_2$	39989.563	39989.558	0.005
$^3/_2$–$^5/_2$	39992.459	39992.487	−0.028
$^5/_2$–$^7/_2$	40000.685	40000.694	−0.009
$^5/_2$–$^5/_2$	40004.77[a]	40004.794	−0.024
$^1/_2$–$^1/_2$	40007.69[a]	40007.612	0.078
$^1/_2$–$^3/_2$	40011.67[a]	40011.712	−0.042

[a] ±0.10 MHz, all other frequencies are ±0.05 MHz. Frequencies were calculated from the following parameters: A = 21,966.7 ± 3.0, B = 10,683.65 ± 0.1, C = 7948.46 ± 0.1 MHz; $\chi_{aa} = -32.83 \pm 0.05$, $\chi_{bb} = -16.40 \pm 0.10$, $\chi_{cc} = 49.23 \pm 0.15$ MHz.

The nuclear quadrupole coupling constant is a product of the electronic field gradient times the nuclear quadrupole moment. The ^{33}S nuclear quadrupole moment has been determined to be $Q = -0.322 \times 10^{-34}$ esu cm^2.[7] Thus in ethylene sulfide, the field gradients divided by the electronic charge are given by (see Figure 1)

$$\begin{aligned}\left(\frac{q_{yy}}{e}\right) = \left(\frac{q_{aa}}{e}\right) = \left\langle 0\left|\frac{\partial^2}{\partial a^2}\left(\frac{V}{e}\right)\right|0\right\rangle = \left\langle 0\left|\frac{\partial^2}{\partial a^2}\sum_i\frac{1}{r_i}\right|0\right\rangle = \\ \left\langle 0\left|\sum_i\frac{3a_i^2 - r^2}{r_i^5}\right|0\right\rangle = -14.10\ \text{Å}^{-3} \\ \left(\frac{q_{xx}}{e}\right) = \left(\frac{q_{bb}}{e}\right) = \left\langle 0\left|\sum_i\frac{3b_i^2 - r_i^2}{r_i^5}\right|0\right\rangle = -7.05\ \text{Å}^{-3} \\ \left(\frac{q_{zz}}{e}\right) = \left(\frac{q_{cc}}{e}\right) = \left\langle 0\left|\sum_i\frac{3c_i^2 - r_i^2}{r_i^5}\right|0\right\rangle = 21.15\ \text{Å}^{-3}\end{aligned} \tag{1}$$

where V is the electrostatic potential at the ^{33}S nucleus and i is a sum over all charges.

We will now approximate the sum over i to include only the charges near the ^{33}S atom in the molecule. This assumption excludes the carbon and hydrogen atoms from consideration. The assumption can be justified on the basis of the $1/r^3$ character of the operators. A single net unit charge at the carbon atom which is further than 1.5 Å from the ^{33}S atom leads to a contribution of less than $1/(1.5)^3 \cong 0.3$ Å^{-3} to the resultant field gradients divided by e as in eq 1. Thus we will assume that the field gradients are caused by some combination of 3s and 3p atomic orbitals at the sulfur nucleus. We will consider an unhybridized model, the Walsh model,[2a] and the Coulson–Moffitt model[2b] of bonding in this ring compound. We will use hydrogenlike radial orbitals for our calculation. The normalized hydrogenlike radial 3p function, given by

$$\phi_{3p}(r) = \frac{4}{9\sqrt{6}}\left(\frac{3\xi}{a_0}\right)^{3/2}\left[\frac{2r\xi}{a_0} - \frac{r^2\xi^2}{a_0^2}\right]e^{-\xi r/a_0} \tag{2}$$

has a node near the nucleus. The corresponding 3p Slater orbital is nodeless. ξ in eq 2 is the orbital exponent similar to the orbital exponent appearing in the Slater orbital. Multiplying eq 2 by the appropriate normalized angular dependence gives the corresponding $3p_x$, $3p_y$, and $3p_z$ functions along the three principal inertial axes. $Y_M{}^1$'s (M = 0, ±1) are the normalized

$$\begin{aligned}\chi_{3p_x} &= \frac{1}{\sqrt{2}}[Y_1{}^1 + Y_{-1}{}^1]\phi_{3p}(r) \\ \chi_{3p_y} &= \frac{1}{\sqrt{2}}[Y_1{}^1 - Y_{-1}{}^1]\phi_{3p}(r) \\ \chi_{3p_z} &= Y_0{}^1\phi_{3p}(r)\end{aligned} \tag{3}$$

spherical harmonics. z is perpendicular to the ring and corresponds to the c axis in eq 1 and $y = a$ bisects the CSC angle in the molecular plane. The molecule and appropriate axes are shown in Figure 1.

Unhybridized Model. The functions for the unhybridized model are given below in Table II.

Table II. Unhybridized Functions

Function	No. of electrons in orbital
χ_{3s}	2 (lone pair)
χ_{3p_z}	2 (lone pair)
χ_{3p_x}	n_x
χ_{3p_y}	n_y

The assumption that we have single bonds (the sulfur atom then has two localized lone pairs) can be justified on the basis of the C–S bond lengths. Methyl mercaptan and dimethyl sulfide, having C–S bond lengths of 1.817 and 1.802 Å, respectively, are both considered to have pure single C–S bonds.[9] The C–S bond length in ethylene sulfide is 1.819 Å,[6] which also appears to be a C–S single bond length.

The field gradients divided by e, as given in eq 1, are related to the above functions by computation of the average values. The results are

$$\left(\frac{q_{zz}}{e}\right) = 21.15 \times 10^{24} = 0.533\left(\frac{\xi}{a_0}\right)^3 - 0.133\left(\frac{\xi}{a_0}\right)^3(n_x + n_y)$$

$$\left(\frac{q_{yy}}{e}\right) = -14.10 \times 10^{24} = 0.266\left(\frac{\xi}{a_0}\right)^3 n_y - 0.133\left(\frac{\xi}{a_0}\right)^3(n_x + 2)$$

$$\left(\frac{q_{xx}}{e}\right) = -7.05 \times 10^{24} = 0.266\left(\frac{\xi}{a_0}\right)^3 n_x - 0.133\left(\frac{\xi}{a_0}\right)^3(n_y + 2) \quad (4)$$

Only two of these equations are linearly independent. Thus we have two equations for the three unknowns, ξ, n_x, and n_y.

One approach to obtain a value of ξ is to assume that the average value of $1/r^3$ for a single 3p electron at the sulfur atom in the molecule is identical with the free-atom value of [10]

$$\left(\frac{1}{r^3}\right)_{\mathrm{av}} = 34.0 \times 10^{24}\ \mathrm{cm}^{-3} \quad (5)$$

The average value of $1/r^3$ with the radial function in eq 2 gives

$$\left(\frac{1}{r^3}\right)_{\mathrm{av}} = \frac{\xi^3}{3a_0^3} \quad (6)$$

Combining eq 5 and 6 gives

$$\xi = 2.47 \quad (7)$$

Substituting $\xi = 2.47$ into eq 4 gives

$$\begin{aligned} n_y &= 1.1 \\ n_x &= 1.3 \end{aligned} \quad (8)$$

Thus eq 3, 7, and 8 define the local sulfur electron density when $(1/r^3)_{\mathrm{av}}$ is the same for a free atom and a molecule. A hydrogenlike radical orbital in eq 2 with $\xi = 2.47$ (eq 7) has a maximum radial density at the same radial distance (0.87 Å) as an SCF optimized Slater orbital ($\xi = 1.827$).[11]

An alternate description is obtained by assuming that $n_x + n_y = 2.0$ which acknowledges the equal electronegativities between the sulfur and carbon atoms. Using this assumption gives

$$\begin{aligned} n_y &= 0.90 \\ n_x &= 1.10 \\ \xi &= 2.27 \\ \left(\frac{1}{r^3}\right)_{\mathrm{av}} &= 26.4 \times 10^{24}\ \mathrm{cm}^{-3} \end{aligned} \quad (9)$$

Thus this latter assumption ($n_x + n_y = 2.0$) leads to an average value of $1/r^3$ which is smaller than the free-atom value. Unfortunately there are no other data to establish firmly whether this is a generally appropriate statement.

Walsh Picture

The Walsh picture is obtained by taking linear combinations of the hydrogenlike orbitals in Table II. The results are shown in Table III.

Table III. Walsh Orbitals

Function	No. of electrons in orbital
$\psi_2 = \frac{1}{\sqrt{3}}\chi_{3s} - \sqrt{\frac{2}{3}}\chi_{3p_y}$	n_1
$\psi_1 = \chi_{3p_x}$	n_2
$\psi_3 = \frac{1}{\sqrt{3}}\chi_{3s} + \frac{1}{\sqrt{6}}\chi_{3p_y} + \frac{1}{\sqrt{2}}\chi_{3p_z}$	2
$\psi_4 = \frac{1}{\sqrt{3}}\chi_{3s} + \frac{1}{\sqrt{6}}\chi_{3p_y} - \frac{1}{\sqrt{2}}\chi_{3p_z}$	2

In this model the lone pairs are contained in two sp^2 orbitals directed away from and perpendicular to the ring (see Figure 1). The other sp^2 orbital is directed toward the center of the ring and will contain a final n_2 number of electrons. The remaining χ_{3p_z} orbital which is perpendicular to the sp^2 plane is available for bonding with a resultant electron population of n_1.

The electronic values of the field gradients in eq 1 with the orbitals in Table III give

$$\left(\frac{q_{xx}}{e}\right) = (-0.089n_1 + 0.267n_2 - 0.355)(\xi/a_0)^3$$

$$\left(\frac{q_{yy}}{e}\right) = (0.178n_1 - 0.133n_2 - 0.089)(\xi/a_0)^3 \quad (10)$$

$$\left(\frac{q_{zz}}{e}\right) = (-0.089n_1 - 0.133n_2 + 0.444)(\xi/a_0)^3$$

Using $\xi = 2.47$ to give the free atom value of $(1/r^3)_{\mathrm{av}} = 34.0 \times 10^{24}\ \mathrm{cm}^{-3}$ in eq 10 gives $n_1 = 0.7$ and $n_2 = 1.3$. Thus the Walsh picture also gives a satisfactory description of the sulfur field gradients in ethylene sulfide.

Coulson and Moffitt Picture. Coulson and Moffitt have proposed a bent bond model for the bonding in cyclopropane.[2b] The S atom wave functions according to the Coulson–Moffitt model are shown in Table IV.

n is the number of electrons in either of the equivalent ψ_1 and ψ_2 hybrid orbitals. A is the hybridization parameter varying from 0 to $1/\sqrt{2}$. This allows the angle between the ψ_1 and ψ_2 hybrids to vary from $\pi/2$ (pure p orbitals) to π (pure sp orbitals). One interesting

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[9] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectry.*, 7, 58 (1961).

[10] R. G. Barnes and W. V. Smith, *Phys. Rev.*, **93**, 95 (1954); C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 1714 (1964).

[11] E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).

Table IV. Coulson–Moffitt Orbitals

Function	No. of electrons in orbital
$\psi_1 = A\chi_{3s} + \frac{1}{\sqrt{2}}\chi_{3p_z} - (\frac{1}{2} - A^2)^{1/2}\chi_{3p_y}$	n (C_1–S bond)
$\psi_2 = A\chi_{3s} - \frac{1}{\sqrt{2}}\chi_{3p_z} - (\frac{1}{2} - A^2)^{1/2}\chi_{3p_y}$	n (C_2–S bond)
$\psi_3 = (\frac{1}{2} - A^2)^{1/2}\chi_{3s} + \frac{1}{\sqrt{2}}\chi_{3p_z} + A\chi_{3p_y}$	2 (lone pair)
$\psi_4 = (\frac{1}{2} - A^2)^{1/2}\chi_{3s} - \frac{1}{\sqrt{2}}\chi_{3p_z} + A\chi_{3p_y}$	2 (lone pair)

choice of A is $A = 1/\sqrt{6}$. With $A = 1/\sqrt{6}$ the functions in Table IV reduce to

$$\psi_1 = \frac{1}{\sqrt{6}}\chi_{3s} + \frac{1}{\sqrt{2}}\chi_{3p_z} - \frac{1}{\sqrt{3}}\chi_{3p_y}$$

$$\psi_2 = \frac{1}{\sqrt{6}}\chi_{3s} - \frac{1}{\sqrt{2}}\chi_{3p_z} - \frac{1}{\sqrt{3}}\chi_{3p_y}$$

$$\psi_3 = \frac{1}{\sqrt{3}}\chi_{3s} + \frac{1}{\sqrt{2}}\chi_{3p_z} + \frac{1}{\sqrt{6}}\chi_{3p_y}$$

$$\psi_4 = \frac{1}{\sqrt{3}}\chi_{3s} - \frac{1}{\sqrt{2}}\chi_{3p_z} + \frac{1}{\sqrt{6}}\chi_{3p_y} \qquad (11)$$

ψ_1 and ψ_2 are sp^5 functions with an angle of 101° 32′. ψ_3 and ψ_4 are the conventional sp^2 functions with an angle of 120° 0′ which are equivalent to ψ_3 and ψ_4 in Table III for the Walsh orbitals.

Returning to Table III, we note that if $n_1 = n_2$, a linear combination of ψ_1 and ψ_2 in Table III will also yield the equivalent sp^5 orbitals in eq 11. This equivalence between orbitals in the Walsh and Coulson–Moffitt schemes is only valid for $n_1 = n_2$. Thus the Coulson–Moffitt equivalent bonding orbitals are more restrictive than the nonequivalent ($n_1 \neq n_2$) Walsh orbitals shown in Table III.

Returning to the general hybrid orbitals in Table IV, we can compute the values of q_{xx}/e, q_{yy}/e, and q_{zz}/e as shown in eq 1. The results are

$$\left(\frac{q_{xx}}{e}\right) = (\tfrac{1}{2}n + A^2n - 1 - 2A^2)\left(\frac{4\xi^3}{15a_0^3}\right)$$

$$\left(\frac{q_{yy}}{e}\right) = (\tfrac{1}{2}n - 2A^2n - 1 + 4A^2)\left(\frac{4\xi^3}{15a_0^3}\right)$$

$$\left(\frac{q_{zz}}{e}\right) = (-n + A^2n + 2 - 2A^2)\left(\frac{4\xi^3}{15a_0^3}\right) \qquad (12)$$

Comparing eq 12 with the experimental results in eq 1 shows that A must be imaginary. From eq 1

$$q_{xx}/q_{yy} \cong \frac{1}{2} \qquad (13)$$

From eq 12 we can write

$$q_{xx}/q_{yy} = \frac{(\frac{1}{2}n + A^2n - 1 - 2A^2)}{(\frac{1}{2}n - 2A^2 - 1 + 4A^2)} = \frac{\frac{1}{2}(n-2)(1+2A^2)}{\frac{1}{2}(n-2)(1-4A^2)} = \frac{1+2A^2}{1-4A^2} \qquad (14)$$

Combining eq 13 and 14 requires that $A^2 = -\frac{1}{8}$. Thus the correct symmetry of the field gradients in ethylene sulfide cannot be obtained with the Coulson–Moffitt combination of 3s and 3p orbitals. The more flexible inequivalent orbitals of Walsh or the unhybridized orbitals appear to be more appropriate for describing the bonding in ethylene sulfide. Using the Walsh model wave functions as given above, a plot was made of the electron density near the S atom. The plot shows that the electron density is spread rather evenly across the ring with a slight maximum pointing into the center of the ring.

The concept of localized bent bonds does not appear to be useful in describing the field gradients in ethylene sulfide. Of course, we could add d orbitals to make the bent bond picture work. However, it seems more appropriate to use our more simple description using the Walsh scheme than increasing the complexity by the addition of d orbitals.

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