

Hyperfine Spectra and Molecular Constants of D₂S¹

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A millimeter wave molecular beam maser has been used to resolve the nuclear hyperfine structure of the $1_{10} \rightarrow 1_{01}$ transition of D₂S at 91.4 Gc/sec. This data, combined with that previously obtained for H₂S and HDS, allows a determination of the molecular constants of hydrogen sulfide. The quadrupole coupling constants for D₂S are $(eQq_J)_{1_{10}} = 17.83 \pm 0.15$ kc/sec and $(eQq_J)_{1_{01}} = -10.82 \pm 0.28$ kc/sec. The components of $\chi_{ii} = eQ_Dq_{ii}$ in its principal axis system are $\chi_{xx} = 149.0$ kc/sec, $\chi_{yy} = -59.8$ kc/sec, and $\chi_{zz} = -89.2$ kc/sec, where the z axis is perpendicular to the plane of the molecule and the x axis is rotated $1^\circ 35'$ from the D-S bond in the direction away from the D-S-D obtuse angle.

INTRODUCTION

D₂S is a light asymmetric molecule with all of its low J rotational transitions falling in the millimeter and submillimeter region of the spectrum. A millimeter wave molecular beam maser has been used to resolve the nuclear hyperfine structure of the $1_{10} \rightarrow 1_{01}$ transition of D₂S at 91.4 Gc/sec. This maser has been described previously by De Lucia and Gordy (1). The observed lines have been assigned and the spectral constants determined. This data, combined with that previously obtained for H₂S and HDS (2-4) allows a determination of the molecular constants of hydrogen sulfide, particularly that of the deuterium quadrupole coupling tensor.

HYPERFINE STRUCTURE THEORY

The 1_{10} and 1_{01} rotational energy levels of D₂S are each split into several hyperfine levels by the interaction of the electric quadrupole and magnetic dipole moments of each of the deuterium nuclei with the electric and magnetic fields produced by the rest of the molecule. The theoretical aspects of this prob-

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lem have been dealt with in several papers, and only the results of this theory will be presented here (2, 5). The coupling scheme most convenient for this problem is

$$\begin{aligned} \mathbf{I}_{D_1} + \mathbf{I}_{D_2} &= \mathbf{I}_D, \\ \mathbf{J} + \mathbf{I}_D &= \mathbf{F} \end{aligned}$$

where \mathbf{I}_{D_1} and \mathbf{I}_{D_2} are the angular momenta of the first and second deuterium nuclei, respectively, and where \mathbf{J} and \mathbf{F} have their usual meanings. Because the two deuterium nuclei occupy identical molecular sites, I_D can only take on the value 1 for the antisymmetrical rotational states, 1_{10} and 1_{01} (6).

A. Spectral Constants

The matrix elements for the electric quadrupole, magnetic dipole, and spin-spin interactions, respectively, in terms of the spectral constants are given by

$$\begin{aligned} W_{\text{quad}} &= \langle I_{D_1} = 1, I_{D_2} = 1, I_D = 1, J = 1, F | \mathbf{q}_1^{(2)} \cdot \mathbf{Q}_1^{(2)} + \mathbf{q}_2^{(2)} \cdot \mathbf{Q}_2^{(2)} | \\ &\quad \cdot I_{D_1} = 1, I_{D_2} = 1, I_D = 1, J = 1, F \rangle \quad (1) \\ &= (-)^{F+1} \frac{15}{2} \begin{Bmatrix} F & 1 & 1 \\ 2 & 1 & 1 \end{Bmatrix} eQq_J, \end{aligned}$$

$$\begin{aligned} W_{\text{mag}} &= \langle I_{D_1} = 1, I_{D_2} = 1, I_D = 1, J = 1, F | \mathbf{m}_1^{(1)} \cdot \mathbf{u}_1^{(1)} + \mathbf{m}_2^{(1)} \cdot \mathbf{u}_2^{(1)} | \\ &\quad \cdot I_{D_1} = 1, I_{D_2} = 1, I_D = 1, J = 1, F \rangle \quad (2) \\ &= (-)^F 6 \begin{Bmatrix} F & 1 & 1 \\ 1 & 1 & 1 \end{Bmatrix} C_J, \end{aligned}$$

and

$$W_{ss} = (-)^F 15 \begin{Bmatrix} F & 1 & 1 \\ 2 & 1 & 1 \end{Bmatrix} \langle JJ | D_0^{(2)} | JJ \rangle. \quad (3)$$

These relations have been specialized to the case $I_{D_1} = I_{D_2} = I_D = 1$. The brackets are Wigner 6 - j symbols and C_J and eQq_J have their usual significance. $D_0^{(2)}$ is defined by $D_0^{(2)} = [(3z^2 - r^2)/r^5] \mu_1 \mu_2 / I_1 I_2$ and can be considered as a spectroscopic constant to be determined, or, as is usually the case, it can be calculated from molecular geometry. It should be noted that the relations for the electric quadrupole energy and the magnetic dipole energy are identical to the case of a single spin 1 nucleus except for the sign of the electric quadrupole energy.

B. Molecular Constants

The spectral constants, which depend upon both the rotational state and the isotopic species, may be expressed in terms of molecular constants, which are

to a good approximation invariant under isotopic substitution and independent of rotational state. The quadrupole spectral constant q_J is given in terms of the traceless symmetric electric field gradient tensor V_{ij} at each nuclear site by

$$q_J = \frac{2J}{2J+3} \sum_g \frac{\langle P_g^2 \rangle}{J(J+1)} V_{gg}, \quad (4)$$

where g refers to the principal axes of the molecular moment of inertia tensor, and P_g is the rotational angular momentum component along the g axis. In most cases the V_{ij} will be nearly symmetric about the bond axis. In a similar manner, the spin-rotation constant is given by

$$C_J = g_I \sum_g \frac{\langle P_g^2 \rangle}{J(J+1)} \Lambda_{gg} B_g, \quad (5)$$

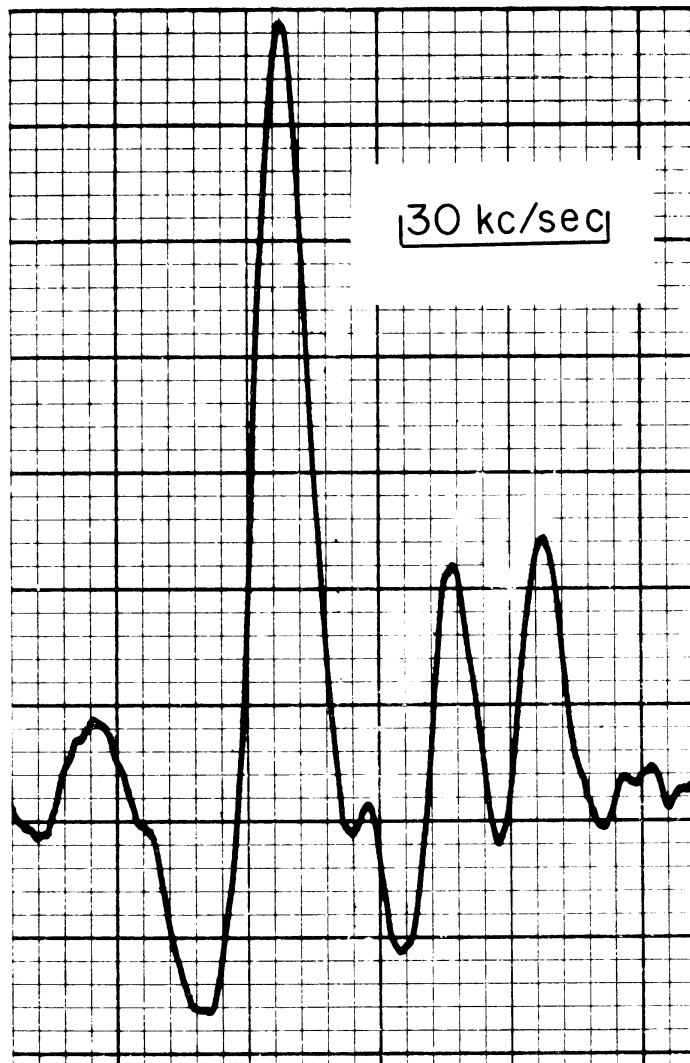


FIG. 1. Hyperfine spectra of the $1_{10} \rightarrow 1_{01}$ transition of D_2S .

TABLE I

Observed ^a (kc/sec)	Calculated ^a (kc/sec)	Difference (kc sec)
36.75	36.44	0.31
21.85	22.16	-0.31
6.66	6.97	-0.31
-7.01	-7.31	0.30
-29.79	-29.79	0.00
	$(eQq_J)_{11c} = 17.83 \pm 0.15$ kc/sec	
	$(eQq_J)_{1c1} = -10.82 \pm 0.28$	
	$(C_D)_{110}{}^b = -1.24$	
	$(C_D)_{101}{}^b = -1.21$	

^a Measured relative to 91 359 121.00 kc/sec.

^b Calculated from H₂S and HDS.

where g_I is the nuclear g -factor, B_g is the rotational constant for the g axis, and Λ is a tensor which relates to the magnetic field produced at the nuclear site by molecular rotation. The product $g_I \Lambda_{gg} B_g$ is the quantity normally referred to as the spin-rotation tensor and is independent of rotational state within a given isotope. The form of Λ_{gg} , in terms of electronic states and nuclear coordinates may be obtained from Townes, (*7*, Eq. (8.37)).

The reflection plane of symmetry in the H₂S molecules implies that Λ have the form

$$\begin{pmatrix} \Lambda_{11} & \Lambda_{12} & 0 \\ \Lambda_{12} & \Lambda_{22} & 0 \\ 0 & 0 & \Lambda_{33} \end{pmatrix},$$

where the coordinate system is that shown in Fig. 2. The tensors are the same for the two hydrogen sites except for the sign of Λ_{12} . The sign for nucleus 1 will be used in what follows. The field gradient tensor has a similar form with the additional requirement that

$$V_{11} + V_{22} + V_{33} = 0. \quad (6)$$

RESULTS

The spectrum of the $1_{10} \rightarrow 1_{01}$ transition of D₂S is shown in Fig. 1. Experimental line width was on the order of 6 kc/sec. Since the magnetic dipole effects are much smaller in D₂S than in either H₂S or HDS, it was felt that a more accurate determination of the electric quadrupole interaction could be made by calculating the deuterium magnetic-dipole interaction energies from the much larger hydrogen magnetic-dipole interactions in H₂S and HDS, and fitting only for the electric-quadrupole interaction. The measured line frequencies, spectral constants, and the calculated line frequencies for D₂S are shown in Table I. Errors quoted are probable errors. Fits which included both the magnetic dipole

TABLE II
OBSERVED AND CALCULATED FREQUENCIES OF HYPERFINE TRANSITIONS OF
HYDROGEN SULFIDE

Transition	Observed (kc/sec)	Calculated from molecular constants (kc/sec)	Difference (kc/sec)
$D_2S(1_{10} \rightarrow 1_{01})^a$			
$F \rightarrow F'$			
$1 \rightarrow 1$	36.75	36.45	0.30
$1 \rightarrow 2$	21.85	22.21	-0.36
$2 \rightarrow 1$	6.66	6.88	-0.22
$2 \rightarrow 2$	-7.01	-7.37	0.36
$0 \rightarrow 1$	-29.79	-29.71	-0.08
$HDS(2_{20} - 2_{21})^b$			
$F_1F \rightarrow F_1'F'$			
$1^1_2 \rightarrow 2^3_2$	91.9	91.69	0.21
$+1^3_2 \rightarrow 2^5_2$			
$3^5_2 \rightarrow 2^3_2$	62.3	61.88	0.42
$+3^5_2 \rightarrow 3^7_2$			
$3^7_2 \rightarrow 2^5_2$	45.8	46.26	-0.46
$+1^1_2 \rightarrow 1^3_2$			
$3^5_2 \rightarrow 1^3_2$	15.6	15.58	0.02
$1^3_2 \rightarrow 3^5_2$	-17.4	-17.40	0.00
$2^5_2 \rightarrow 3^7_2$	-45.6	-45.24	-0.36
$+1^3_2 \rightarrow 1^1_2$			
$2^3_2 \rightarrow 3^5_2$	-62.4	-62.79	0.39
$+3^7_2 \rightarrow 3^5_2$			
$2^3_2 \rightarrow 1^1_2$	-89.5	-89.68	0.18
$+2^5_2 \rightarrow 1^3_2$			
$H_2S(1_{10} \rightarrow 1_{01})^c$			
$F \rightarrow F'$			
$2 \rightarrow 1$	34.613	34.619	-0.006
$1 \rightarrow 0$	16.577	16.585	-0.008
$1 \rightarrow 1$	12.910	12.896	0.014
$2 \rightarrow 1$	-2.852	-2.860	0.008
$1 \rightarrow 2$	-24.596	-24.584	-0.012
$0 \rightarrow 1$	-28.063	-28.067	0.004

^a Measured relative to $\nu_0 = 91\,359\,121.00$ kc/sec.

^b $\nu_0 \approx 11\,283\,830$ kc/sec.

^c Measured relative to $\nu_0 = 168\,762\,762.373$ kc/sec.

and electric quadrupole constants as variables to be determined gave virtually the same spectral constants. These results together with previous measurements on H_2S and HDS have been used to obtain values for the seven independent components of Λ and V . Contributions from the only remaining hyperfine interaction, the spin-spin, have been calculated from geometry assuming only the direct interaction is significant. A fit leaving the spin-spin constants in H_2S

TABLE III
MOLECULAR CONSTANTS

Elements of the quadrupole coupling tensor

$$\chi_{11} = eQ_D q_{11} = 54.2 \pm 1.9 \text{ ke/sec}$$

$$\chi_{22} = eQ_D q_{22} = 35.0 \pm 1.4 \text{ ke/sec}$$

$$\chi_{33} = eQ_D q_{33} = -89.2 \pm 0.8 \text{ ke/sec}$$

$$\chi_{12} = eQ_D q_{12} = 103.9 \pm 1.6 \text{ ke/sec}$$

Elements of the spin-rotation tensor

$$\Lambda_{11} = (-119 \pm 13) \times 10^{-10}$$

$$\Lambda_{22} = (-74 \pm 15) \times 10^{-10}$$

$$\Lambda_{33} = (-247 \pm 28) \times 10^{-10}$$

$$\Lambda_{12} = (125 \pm 2) \times 10^{-10}$$

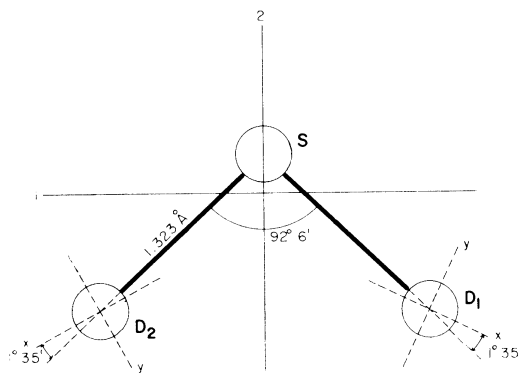


FIG. 2. Molecular geometry of D₂S.

TABLE IV
COMPONENTS OF THE QUADRUPOLE COUPLING TENSOR IN ITS PRINCIPAL
AXIS SYSTEM

$$\chi_{xx} = eQ_D \frac{\partial^2 V}{\partial x^2} = 149.0 \text{ ke/sec}$$

$$\chi_{yy} = eQ_D \frac{\partial^2 V}{\partial y^2} = -59.8$$

$$\chi_{zz} = eQ_D \frac{\partial^2 V}{\partial z^2} = -89.2$$

(where they are by far the largest in magnitude) variable verifies that this assumption is valid (3).

Equations (4) and (5) and the results of the diagonalization of the HDS energy matrix were used to find a set of linear equations which expressed the transition frequencies for all three isotopic species in terms of the molecular constants. A least-squares fit was then performed to find these molecular constants, and Table II shows the results of this fit. The differences between the

experimentally measured line frequencies and the calculated line frequencies shown in this table are within expected experimental uncertainties. Table III lists the molecular constants used to calculate the transition frequencies shown in Table II. It should be noted that there is considerably more redundancy in the fit performed directly between the measured line frequencies and the molecular constants than in the fits between the measured line frequencies and spectral constants of the individual isotopes. It was for this reason that the molecular constants were determined in this manner rather than from the spectroscopic constants. The rather large uncertainties in the spin-rotation tensor are a direct result of the fact that the spin-rotation constants for hydrogen and deuterium in HDS are not quite self-consistent.

The x, y, z principal axis system for χ is rotated $42^\circ 22'$ from the 1, 2, 3, symmetry axis system of D_2S . Figure 2 shows the molecular geometry along with both the symmetry axis system and the principal axis system of the quadrupole coupling tensor. The rotation of $1^\circ 35'$ between the x axis and the D-S bond is similar to that of $1^\circ 20'$ of D_2O (8). The components of χ in the x, y, z principal axis system are shown in Table IV.

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