

Millimeter and Submillimeter Wave Rotational Spectrum and Centrifugal Distortion Effects of D₂S

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The rotational spectrum of D₂S in the ground vibrational state has been studied in the millimeter and submillimeter wavelength region by means of a tunable, high-resolution microwave spectrometer. Sixty-six transitions, 53 of which fall at wavelengths between 1.00 and 0.45 mm have now been measured by microwave techniques. These transitions have been analyzed with a 22 parameter rotation-distortion Hamiltonian which includes distortion effects through P^{10} . Only a partial set of terms in P^8 and P^{10} is necessary, however. The rotational constants, and quartic and sextic distortion constants are (in Mc/sec): $\mathcal{C} = 164\,571.118 \pm 0.045$, $\mathcal{B} = 135\,380.313 \pm 0.045$, $\mathcal{C} = 73\,244.068 \pm 0.071$, $\Delta_J = 13.0763 \pm 0.0026$, $\Delta_{JK} = -41.7800 \pm 0.0066$, $\Delta_K = 29.2170 \pm 0.0113$, $\delta_J = -1.95725 \pm 0.00068$, $\delta_K = 47.2516 \pm 0.0037$, $H_J = 3.783 \times 10^{-3} \pm 0.041 \times 10^{-3}$, $H_{JK} = -3.206 \times 10^{-2} \pm 0.020 \times 10^{-2}$, $H_{KJ} = 6.373 \times 10^{-2} \pm 0.044 \times 10^{-2}$, $H_K = -3.620 \times 10^{-2} \pm 0.075 \times 10^{-2}$, $h_J = -9.84 \times 10^{-4} \pm 0.16 \times 10^{-4}$, $h_{JK} = 2.443 \times 10^{-2} \pm 0.019 \times 10^{-2}$, and $h_K = 8.804 \times 10^{-2} \pm 0.065 \times 10^{-2}$. The analysis of the spectrum is discussed.

I. INTRODUCTION

The recent advances in submillimeter wave rotational spectroscopy and the accompanying theoretical advances in centrifugal distortion theory have provided significant impetus to the study of light asymmetric rotors. In the past, such molecules have eluded an accurate microwave study because of the occurrence of many, if not most, of their rotational transitions at frequencies inaccessible to conventional microwave spectrometers. In addition, inadequacies in the previous formulations of centrifugal distortion theory have handicapped the empirical determination of the distortion constants from observed spectra. The use of a photoconducting indium antimonide detector has made possible the measurement of submillimeter wave transitions as high as 813 Gc/sec as described recently by Helminger, De Lucia, and Gordy (1). As a consequence, it is now feasible to measure microwave lines containing sufficient independent information for an evaluation of the rather large number of distortion constants necessary to characterize the spectra of these light molecules. Furthermore, Watson (2-4) has shown

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how to properly remove the indeterminacy associated with any attempt to calculate the distortion constants of the Hamiltonian of Kivelson and Wilson (5) from spectroscopic data. This is particularly important because use of the planar approximation to remove this indeterminacy gives unsatisfactory results when applied to molecules of this type (6). The theoretical formulation of Watson also explicitly indicates the number of terms to be introduced into the Hamiltonian for each order of distortion; the inclusion of such higher-order distortion effects is necessary for the analysis of the spectrum of these light molecules.

In two previous papers, we have reported analyses of HDS (6) and HDO (7) based exclusively on precision microwave data. Benedict *et al.* have analyzed D₂O (8) using a mixture of microwave and infrared data, and Bellet and Steenbeckeliers have analyzed HDO (9) using a somewhat limited set of microwave data. In this paper, we report an analysis of the microwave spectrum of D₂S. Unlike HDO, D₂O, and HDS, the spectrum of D₂S is unique in that it is almost devoid of low frequency microwave transitions and, as a consequence, very little microwave data has been published on D₂S (10-12) although it has been studied in the infrared region (13-20). The lack of low *J* microwave data has been overcome, as mentioned previously, by employment of a submillimeter wave sweep spectrometer. A total of 66 microwave lines for which the total angular momentum quantum number *J* ranges from 0 to 12 have been measured and assigned. Of the 66 microwave transitions measured only 13 fall below 300 Gc/sec and only 1 falls below 100 Gc/sec.

II. EXPERIMENTAL TECHNIQUES

Submillimeter microwave energy for this experiment was produced by a klystron-driven crystal-harmonic multiplier and detected by an InSb photoconducting detector operating at 1.6°K. Typically, an OKI 55V11 klystron was used as the fundamental klystron. The absorption cell consisted of a copper tube, 1.9 cm in diameter and 30 cm in length. In its present or slightly modified form this tunable microwave spectrometer has been used in recent submillimeter wavelength studies of the rotational spectra of the hydrogen halides (1, 21), the Group V hydrides (22, 23), and the light asymmetric rotors HDS and HDO (6, 7), and has been described in greater detail therein. Lines in the millimeter wavelength region were measured with a similar harmonic source, a more conventional crystal diode detector, and a free space absorption cell described previously (24). The D₂S sample was prepared by the reaction of FeS with dilute D₂SO₄.

III. THEORY

For light asymmetric rotors, such as D₂S, centrifugal distortion effects are extremely important in the interpretation of the observed spectra. The reduced Hamiltonian including distortion effects through P^{10} for an oblate asymmetric rotor has the form

$$\mathfrak{H} = \mathfrak{H}_r + \mathfrak{H}_d^{(4)} + \mathfrak{H}_d^{(6)} + \mathfrak{H}_d^{(8)} + \mathfrak{H}_d^{(10)}, \quad (1)$$

$$\mathfrak{H}_r = \frac{1}{2}(\mathfrak{A} + \mathfrak{B})P^2 + [\mathfrak{C} - \frac{1}{2}(\mathfrak{A} + \mathfrak{B})][P_z^2 - b_o P_-^2], \quad (2)$$

$$\mathfrak{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_-^2 - \delta_K [P_z^2 P_-^2 + P_-^2 P_z^2], \quad (3)$$

$$\begin{aligned} \mathfrak{H}_d^{(6)} = & H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_-^2 \\ & + h_{JK} P^2 [P_z^2 P_-^2 + P_-^2 P_z^2] + h_K [P_z^4 P_-^2 + P_-^2 P_z^4], \end{aligned} \quad (4)$$

$$\begin{aligned} \mathfrak{H}_d^{(8)} = & L_J P^8 + L_{JJK} P^6 P_z^2 + L_{JK} P^4 P_z^4 + L_{KKJ} P^2 P_z^6 + L_K P_z^8 + 2l_J P^6 P_-^2 \\ & + l_{JK} P^4 [P_z^2 P_-^2 + P_-^2 P_z^2] + l_{KJ} P^2 [P_z^4 P_-^2 + P_-^2 P_z^4] \\ & + l_K [P_z^6 P_-^2 + P_-^2 P_z^6], \end{aligned} \quad (5)$$

$$\begin{aligned} \mathfrak{H}_d^{(10)} = & P_J P^{10} + P_{JJK} P^8 P_z^2 + P_{JK} P^6 P_z^4 + P_{KJ} P^4 P_z^6 + P_{KKJ} P^2 P_z^8 + P_K P_z^{10} \\ & + 2p_J P^8 P_-^2 + p_{JJK} P^6 [P_z^2 P_-^2 + P_-^2 P_z^2] + p_{JK} P^4 [P_z^4 P_-^2 + P_-^2 P_z^4] \\ & + p_{KKJ} P^2 [P_z^6 P_-^2 + P_-^2 P_z^6] + p_K [P_z^8 P_-^2 + P_-^2 P_z^8], \end{aligned} \quad (6)$$

where $P^2 = (P_x^2 + P_y^2 + P_z^2)$ is the total angular momentum, $P_-^2 = (P_x^2 - P_y^2)$, $b_o = (\mathfrak{A} - \mathfrak{B}) / (2\mathfrak{C} - \mathfrak{A} - \mathfrak{B})$ is Wang's asymmetry parameter appropriate for a near oblate top, and where \mathfrak{A} , \mathfrak{B} , \mathfrak{C} are related to the usual effective rotational constants A , B , C by the relations

$$\mathfrak{A} = A + 16R_6(C - B) / (B - A), \quad (7)$$

$$\mathfrak{B} = B - 16R_6(C - A) / (B - A), \quad (8)$$

$$\mathfrak{C} = C + 16R_6. \quad (9)$$

In the above, \mathfrak{H}_r is the rigid rotor Hamiltonian and $\mathfrak{H}_d^{(n)}$ are the various distortion Hamiltonians of degree n in the angular momentum. The matrix elements of this Hamiltonian in the symmetric rotor basis are summarized in Table I. Since the energy matrix has only $(K | K)$, $(K | K \pm 2)$ type elements, the Wang transformation gives four separate submatrices for each J (25).

In previous analyses of the rotational spectrum of HDS and HDO, we have employed a rigid rotor basis distortion analysis. Briefly, this procedure makes use of the rigid rotor basis, i.e., the basis in which \mathfrak{H}_r is diagonal, to derive from Eq. (1) a first-order energy expression from which the rotation-distortion constants can be obtained with least-squares techniques. The second- and higher-order centrifugal distortion contributions of \mathfrak{H}_d (the so-called "second-order" effects) are taken into account by use of the constants obtained from the first-order treat-

TABLE I

Matrix Elements for the Angular Momentum Operators in a Symmetric Rotor Basis^a

$$\begin{aligned} (J, K | P_z^{2n} P_z^{2m} | J, K) &= J^n (J+1)^n K^{2m}, \quad n, m = 0, 1, 2, \dots \\ (J, K | P_z^{2n} P_-^2 | J, K \pm 2) &= -\frac{1}{2} J^n (J+1)^n f_{\pm}(J, K) \\ (J, K | P_z^{2n} [P_z^{2m} P_-^2 + P_-^2 P_z^{2m}] | J, K \pm 2) &= -\frac{1}{2} J^n (J+1)^n [K^{2m} + (K \pm 2)^{2m}] f_{\pm}(J, K) \\ f_{\pm}(J, K) &= \{ |J(J+1) - K(K \pm 1)| [J(J+1) - (K \pm 1)(K \pm 2)] \}^{1/2} \end{aligned}$$

^a Phase choice that of G. W. KING, R. M. HAINER AND P. C. CROSS, *J. Chem. Phys.*, **11**, 27 (1943). Angular momentum is in units of \hbar .

ment to construct the complete energy matrix of the Hamiltonian. The energy matrix is subsequently diagonalized and the transition frequencies of the observed lines calculated. The differences between these calculated frequencies and those calculated from the first-order energy expression represent the "second-order" effects of the distortion terms in the Hamiltonian. The observed frequencies are then corrected for these "second-order" effects, a first-order analysis is again carried out, and the procedure is repeated until the calculations converge.

This mode of analysis is very convenient and is applicable to all heavy molecules; it has also been applied successfully to the light molecules HDS and HDO. When, however, the "second-order" effects become large ($\gtrsim 100$ Mc/sec), the convergence of this procedure becomes very slow. It is then convenient to employ an alternative procedure which involves linearization of the problem from the start (26) and is very similar to that used in obtaining the rotational constants from a rigid rotor spectrum (27). Because "second-order" effects are large in D_2S , we have analyzed this molecule using the semirigid rotor basis discussed below.

For convenience, we denote the Hamiltonian of Eq. (1) as

$$\mathfrak{H} = \sum_i T_i \Pi_i, \quad (10)$$

where T_i correspond to the various constants of Eq. (1) which we are interested in evaluating, and the Π_i represent the corresponding quantum mechanical operators. If Eq. (10) is evaluated in the semirigid rotor basis, i.e., the basis in which \mathfrak{H} is diagonal, we have

$$\langle \mathfrak{H} \rangle = E(T_i) = \sum_i T_i \langle \Pi_i \rangle. \quad (11)$$

If the T_i are the correct set of constants, then Eq. (11) represents the true energy of the level. In general, the energy may be expanded in a Taylor series about the approximate parameters (T_i^0), and to first order we have

$$E(T_i) = E(T_i^0) + \sum_i \left(\frac{\partial E}{\partial T_i} \right)_0 \delta T_i. \quad (12)$$

This expression, which is linear in the parameter corrections δT_i , may be used as the basis for a least-squares analysis in which the corrections to the constants are calculated. The derivatives are given by (28)

$$\left(\frac{\partial E}{\partial T_i} \right)_0 = \langle \Pi_i \rangle_0, \quad (13)$$

where the average value on the right is calculated in the semirigid rotor basis employing the T_i^0 .

The procedure for the analysis in the semirigid rotor basis is as follows. Approximate values of the spectral constants T_i^0 are used for the construction of the energy matrix of Eq. (1), and subsequent diagonalization of this matrix yields the $E(T_i^0)$ and the $\langle \Pi_i \rangle_0$. Equation (12) and the least-squares criterion are used in an analysis of the observed transitions for the calculation of the δT_i 's. These

corrections yield an improved approximation to the constants given by

$$T_i = T_i^0 + \delta T_i. \quad (14)$$

The above procedure is then repeated with the improved approximations to the rotation–distortion constants. This numerical iteration procedure is continued until the δT_i 's are negligibly small.

This semirigid rotor basis analysis is employed here on D₂S and has been used at various stages in the analyses of HDS and HDO. Both the rigid rotor basis distortion analysis and the semirigid rotor basis distortion analysis produce the same parameters for each of the latter two molecules and, hence, each procedure serves as a check of the other. In general, when the “second-order” effects are large, the rigid rotor basis tends to be inconvenient because of the number of iterations which are necessary, whereas the semirigid rotor basis has been found to converge very rapidly. Usually, reasonably good approximations to the constants can be obtained from a rigid rotor basis first-order analysis. As additional higher-order distortion constants are subsequently added to the analysis, these constants may be initially equated to zero with success. In fact, with an initial choice of zero for all of the distortion constants, no difficulty was experienced in the convergence of the analysis. This is illustrated in Table II. In both cases, the same final constants were obtained as were obtained with alternate initial constants which were closer to the final results.

IV. CHOICE OF HAMILTONIAN

Of critical importance to the proper analysis of molecules such as D₂S and other light asymmetric rotors is the selection of distortion terms to be retained in the Hamiltonian. This selection is complicated by the rather slow convergence of the power series in the angular momentum as well as by the high statistical correlation among many of the terms. Both the statistical uncertainty σ_i in each of the constants and the correlation coefficients ρ_{ij} among the constants serve as guides in this selection process. These quantities are calculated in the usual manner (6, 26) from the normal equation matrix which is derivable from Eq. (12).

We have found that the following procedure produces a satisfactory Hamiltonian. First, the data set is restricted to transitions which are thought to be largely free of P^{10} effects ($J \lesssim 9$ for D₂S). An analysis is then performed in which all P^4 , P^6 , and P^8 effects are included. In general the error analysis will show that some of the P^8 terms are poorly determined. The least determined of these constants is subsequently omitted and the procedure repeated, with one term eliminated at a time until all of the remaining constants are determined. Toward the final stages of this process it is necessary to examine the standard deviation of the fit in order to judge whether marginally determined constants should be retained. Because of the possible high correlation among some of the constants, it is not always clear in which order the terms should be eliminated. In such situations, inspection of the results of the several alternatives will usually indicate the proper choice.

TABLE II
Semi-Rigid Rotor Basis Distortion Analyses (Mc/sec)^a

Iteration	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K	$\delta\mathcal{C}$	$\delta\mathcal{B}$	$\delta\mathcal{C}$	σ^c
D ₂ S (66 transitions) ^b									
1	13.12049	-42.08801	28.22253	-1.97370	47.67065	-0.358	0.963	-6.138	10.00
2	13.07073	-41.74308	29.20919	-1.95773	47.20557	0.418	-1.077	6.323	0.38
3	13.07631	-41.78028	29.22368	-1.95753	47.24903	-0.050	0.104	-0.149	0.14
4	13.07632	-41.77999	29.21701	-1.95725	47.25157	-0.014	0.011	-0.030	0.12
HDO (53 transitions) ^b									
1	10.84084	34.22088	377.14485	3.65319	62.81535	0.077	-0.512	0.504	0.20
2	10.83745	34.20714	377.07707	3.64712	63.08907	-0.104	0.478	-0.483	0.12
3	10.83749	34.20729	377.07828	3.64713	63.08750	0.003	-0.002	0.003	0.12

^a In both cases a 22 parameter Hamiltonian was employed in the analyses. Only the quartic distortion constants and the changes in \mathcal{C} , \mathcal{B} , \mathcal{C} from each previous approximation are shown.

^b Initial approximation to all distortion constants was zero. Initial approximations to the rotational constants for D₂S were: $\mathcal{C} = 164\,571.122$, $\mathcal{B} = 135\,380.313$, $\mathcal{C} = 73\,244.061$, and for HDO: $\mathcal{C} = 701\,931.526$, $\mathcal{B} = 272\,912.635$, $\mathcal{C} = 192\,055.220$.

^c Standard deviation of the least squares fit.

Next, the remaining lines are introduced into the analysis and various P^{10} terms added to the preliminary Hamiltonian. The selection of these terms is guided by the determinancy of similar terms of lower order as well as by the correlation among the terms. In addition, the reintroduction of some P^8 terms previously eliminated must be considered. This final selection of terms should produce a Hamiltonian which

- (a) fits the data to within experimental uncertainty,
- (b) adequately predicts groups of lines removed from the fit,
- (c) has the minimum number of terms consistent with (a) and (b),
- (d) is consistent with a converging power series.

With regard to (d), this implies, for example, that L_K should be better determined than P_K .

V. ANALYSIS OF THE SPECTRUM

D₂S is an oblate asymmetric rotor, whose spectrum consists entirely of "b" type transitions. Fourteen R-branch and 52 Q-branch transitions have now been measured and assigned. These transitions were assigned primarily on the basis of the distortion analysis. Methods similar to those described for HDO and HDS were used in the analysis of D₂S except that the semirigid rotor basis distortion analysis described in Section III was employed. In addition to a complete set of P^4 and P^6 terms, six P^8 terms and one P^{10} term have been retained which results in a 22-parameter rotational Hamiltonian. The selection of these terms has been discussed in the previous section. All calculations were made with 16 digit floating point arithmetic.

Table III lists the observed and calculated frequencies of the microwave transitions of D₂S. The parameters of Table IV were used for this compilation. The errors listed for the rotation and distortion constants in Table IV are for 95% statistical confidence. The average and standard deviations of the fit are 0.07 and 0.12 Mc/sec, respectively. As a check of the assignments and the Hamiltonian, each of five sets of data (13 transitions per set) was removed from the fit and predicted from an analysis of the remaining lines (6). It was found that all 66 lines were well predicted by this method, and that the rotation and distortion constants obtained from each of the five fits to data subsets were virtually identical with those shown in Table IV.

Because additional higher-order constants will be important at higher J , the predictions of such lines must be viewed with this in mind. Furthermore, because of the correlation among the constants, the addition of higher J transitions or the inclusion of additional distortion constants can be expected to have an effect on the constants. However, this should be significant only for the P^8 or P^{10} distortion coefficients. It is hoped that the P^4 and P^6 distortion coefficients obtained here will be useful in further characterizing the potential function of D₂S. Work along these lines is presently in progress.

The pure rotational spectrum of D₂S in the far-infrared region has been studied by Miller, Leroi and Hard (20). They derived both the ground state rotational constants and the quartic distortion constants τ_{aaaa} , τ_{bbbb} , τ_{aabb} , and τ_{abab} . In Table V we give a comparison of the infrared and microwave results. From the constants of $\mathfrak{C}_d^{(4)}$ given in Table IV, the three taus ($\tau_{\alpha\alpha\alpha}$) and two linear combinations of taus (τ_1, τ_2) may be calculated directly with the relations summarized for convenience in Table VI. This set of constants may be considered equivalent to the original set (note: τ_2 requires a knowledge of A, B, C for its calculation) and is also given in Table V. Three of the distortion constants τ_{aaaa} , τ_{bbbb} , τ_{cccc} , may hence be compared directly with the infrared results. However, if it is desired to extract the individual $\tau_{\alpha\alpha\beta\beta}$ from our constants and to obtain A, B, C from $\alpha, \beta, \mathcal{C}$, the planar relations (see Table VI) must be employed. One procedure would be to use the planar relations and perform a least-squares analysis on the constants Δ_J , etc. Alternately, one of the planar relations can be used to calculate τ_{bbcc} , for example, and then solve τ_1 and τ_2 simultaneously for τ'_{aabb} and τ_{aacc} . The planar relation for τ_{aabb} then gives τ_{abab} from τ'_{aabb} . The results for these and other methods of reduction will, in general, not be quite the same; in fact, significant differences have been found. The latter of the two procedures mentioned here, which requires a minimum number of planar relations, gives the values of τ_{aabb} and τ_{abab} given in Table V. In addition, $R_6 = -2.156$ Mc/sec which yields, from Eqs. (7)–(9),

$$A = 164\,643.9,$$

$$B = 135\,273.0,$$

$$C = 73\,278.6.$$

These are compared with the infrared results in Table V. Unfortunately, in such

calculations, uncertainties are unavoidably introduced and have to be expected when relations for equilibrium constants are applied to effective constants.

Some estimate of the departure from the planarity conditions and hence the effects of vibration can be obtained from

$$\delta_{cd} = \frac{\tau_2}{C} - \tau_1 - \left(\frac{A+B}{C} \right) \tau_{ccc}, \quad (15)$$

Table III. Rotational Transitions of D₂S (Mc/sec).

Transition	Observed Frequency	Calculated Frequency	Distortion Effect ^a	Deviation	Ref. ^b
$1_{1,0} \leftarrow 1_{0,1}$	91 359.12	91 359.15	32.10	-0.03	c, d
$2_{2,0} \leftarrow 2_{1,1}$	128 815.31	128 815.26	133.19	0.05	e
$3_{2,1} \leftarrow 3_{1,2}$	135 591.87	135 591.83	-181.50	0.04	c
$2_{1,1} \leftarrow 2_{0,2}$	194 139.30	194 139.31	-333.64	-0.01	c
$3_{3,0} \leftarrow 3_{2,1}$	195 692.13	195 692.23	243.69	-0.10	c
$3_{1,3} \leftarrow 3_{2,0}$	196 900.84	196 900.75	271.86	0.09	e
$4_{3,1} \leftarrow 4_{2,2}$	201 306.53	201 306.73	413.84	-0.15	c
$1_{1,1} \leftarrow 1_{0,0}$	237 903.80	237 903.63	38.44	0.17	c
$5_{4,1} \leftarrow 5_{3,2}$	250 390.95	250 390.98	1 390.45	-0.03	e
$2_{2,1} \leftarrow 2_{1,2}$	273 879.13	273 879.23	-101.92	-0.05	e
$6_{4,2} \leftarrow 6_{3,3}$	281 788.08	281 788.07	-145.13	0.01	e
$5_{3,2} \leftarrow 5_{2,3}$	290 043.36	290 043.88	-1 554.42	-0.02	c
$4_{4,0} \leftarrow 4_{3,1}$	291 340.25	291 340.13	-428.28	0.12	c
$7_{5,2} \leftarrow 7_{4,3}$	303 863.56	303 863.66	2 666.46	-0.10	e
$4_{2,2} \leftarrow 4_{1,3}$	319 555.99	319 555.91	-1 673.91	0.03	c
$3_{3,1} \leftarrow 3_{2,2}$	321 784.13	321 784.23	-509.48	-0.10	c, e
$6_{2,5} \leftarrow 6_{1,2}$	324 356.04	324 356.05	3 844.27	-0.01	e
$6_{5,1} \leftarrow 6_{4,2}$	335 350.27	335 350.15	2 083.18	0.12	c
$2_{0,2} \leftarrow 2_{1,1}$	346 782.36	346 782.37	-215.93	-0.01	e
$3_{1,2} \leftarrow 3_{0,3}$	351 473.87	351 473.82	-1 039.34	0.05	e

Table III. (continued)

Transition	Observed Frequency	Calculated Frequency	Distortion Effect ^a	Devi- ation	Ref. ^b
$8_{5,3} \leftarrow 8_{4,4}$	374 153.37	374 158.31	-3 495.15	0.00	e
$9_{6,3} \leftarrow 9_{5,4}$	376 492.75	376 492.73	1 994.72	0.02	e
$8_{6,2} \leftarrow 8_{5,3}$	377 560.13	377 560.28	6 284.12	-0.15	e
$2_{1,2} \leftarrow 1_{0,1}$	384 452.14	384 452.20	148.88	-0.06	e
$4_{4,1} \leftarrow 4_{3,2}$	385 315.93	385 315.97	-1 670.67	-0.04	e
$3_{2,2} \leftarrow 3_{1,3}$	387 843.70	387 843.69	-340.90	0.01	e
$5_{5,0} \leftarrow 5_{4,1}$	403 291.63	403 291.62	-2 804.79	0.01	e
$7_{4,3} \leftarrow 7_{3,4}$	405 800.95	405 800.86	-5 642.71	0.09	e
$4_{3,2} \leftarrow 4_{2,3}$	406 857.82	406 857.81	-504.02	0.01	e
$10_{7,3} \leftarrow 10_{6,4}$	424 386.25	424 386.13	10 290.49	0.12	e
$5_{4,2} \leftarrow 5_{3,3}$	440 500.74	440 500.72	-796.49	0.02	e
$5_{2,4} \leftarrow 4_{3,1}$	444 159.43	444 159.43	877.39	0.00	e
$7_{6,1} \leftarrow 7_{5,2}$	447 210.35	447 210.13	982.11	0.17	e
$6_{3,3} \leftarrow 6_{2,4}$	451 575.89	451 575.80	-5 068.49	0.09	e
$4_{2,3} \leftarrow 3_{3,0}$	454 804.75	454 804.82	2.20	-0.07	e
$11_{7,4} \leftarrow 11_{6,5}$	455 365.73	455 365.66	-3 774.53	0.07	e
$5_{5,1} \leftarrow 5_{4,2}$	461 763.49	461 763.54	-4 184.77	-0.05	e
$10_{6,4} \leftarrow 10_{5,5}$	478 255.25	478 255.28	-12 075.68	-0.03	e
$12_{8,4} \leftarrow 12_{7,5}$	479 524.47	479 524.53	10 784.52	-0.06	e
$9_{7,2} \leftarrow 9_{6,3}$	483 402.85	483 403.03	9 623.40	-0.18	e

Table III. (continued)

Transition	Observed Frequency	Calculated Frequency	Distortion Effect ^a	Devi- ation	Ref. ^b
$6_{5,2} \leftarrow 6_{4,3}$	490 325.67	490 325.47	-1 636.40	0.20	e
$5_{2,3} \leftarrow 5_{1,4}$	491 247.75	491 247.77	-3 257.08	-0.02	e
$3_{0,3} \leftarrow 2_{1,2}$	510 025.44	510 025.51	-167.38	-0.07	e
$4_{1,3} \leftarrow 4_{0,4}$	515 114.05	515 114.07	-1 550.00	-0.02	e
$6_{6,0} \leftarrow 6_{5,1}$	516 361.89	516 362.03	-7 642.82	-0.14	e
$11_{8,3} \leftarrow 11_{7,4}$	518 317.29	518 317.23	18 904.38	0.06	e
$3_{1,3} \leftarrow 2_{0,2}$	519 905.23	519 905.33	121.41	-0.10	e
$4_{2,3} \leftarrow 4_{1,4}$	525 317.63	525 317.68	-966.19	-0.05	e
$5_{3,3} \leftarrow 5_{2,4}$	526 701.22	526 701.30	-1 466.57	-0.08	e
$3_{5,4} \leftarrow 3_{4,5}$	530 145.51	530 145.50	-13 865.24	0.01	e
$6_{4,3} \leftarrow 6_{3,4}$	536 003.85	536 003.86	-1 644.69	-0.01	e
$6_{5,1} \leftarrow 6_{5,2}$	546 989.47	546 989.49	-8 716.58	-0.02	e
$7_{6,2} \leftarrow 7_{5,3}$	555 378.25	555 378.22	-3 634.93	0.03	e
$7_{5,3} \leftarrow 7_{4,4}$	557 878.11	557 878.11	-1 544.38	0.00	e
$2_{2,1} \leftarrow 1_{1,0}$	566 972.29	566 972.28	14.86	0.01	e
$6_{7,1} \leftarrow 6_{6,2}$	568 408.12	568 407.80	-3 406.75	0.32	e
$6_{4,4} \leftarrow 6_{3,5}$	586 926.59	586 926.58	-11 241.30	0.01	e
$3_{1,2} \leftarrow 2_{2,1}$	587 620.04	587 620.10	-1 105.40	-0.06	e
$6_{6,3} \leftarrow 6_{5,4}$	595 505.25	595 505.44	-1 538.36	-0.19	e
$10_{8,2} \leftarrow 10_{7,3}$	609 672.97	609 672.98	6 726.69	-0.01	e

Table III. (continued)

Transition	Observed Frequency	Calculated Frequency	Distortion Effect ^a	Deviation	Ref. ^b
⁷ _{3,4} ← ⁷ _{2,5}	630 485.63	630 485.67	-7 363.81	-0.04	e
⁶ _{7,2} ← ⁶ _{3,3}	632 477.80	632 478.00	-7 740.50	-0.20	e
⁴ _{0,4} ← ⁴ _{1,3}	660 418.18	660 418.08	-138.15	0.10	e
⁴ _{1,4} ← ⁴ _{0,3}	662 245.07	662 245.02	-9.37	0.05	e
² _{2,0} ← ² _{1,1}	669 787.00	669 786.94	-366.39	0.06	e
⁵ _{2,4} ← ⁵ _{1,5}	672 337.45	672 337.38	-1 773.46	0.07	e

^a $\nu_{\text{dist}} = \nu_{\text{calc}} - \nu_{\text{r}}(A, B, C)$.

^b The observed frequency is taken from the last reference listed.

^c C. A. Burrus, Ref. 10.

^d F. C. De Lucia and J. W. Cederberg, Ref. 11.

^e Present work.

TABLE IV
Rotational and Distortion Constants of D₂S (Mc sec)^a

$\mathcal{A} = 164\,571.118 \pm 0.045$	
$\mathcal{B} = 135\,380.313 \pm 0.045$	
$\mathcal{C} = 73\,244.068 \pm 0.071$	
$\Delta_J = 13.0763 \pm 0.0026$	$\Delta_{JK} = -41.7800 \pm 0.0066$
$\Delta_K = 29.2170 \pm 0.0113$	$\delta_J = -1.95725 \pm 0.00068$
$\delta_K = 47.2516 \pm 0.0037$	
$H_J = 3.783 \times 10^{-3} \pm 0.041 \times 10^{-3}$	$H_{JK} = -3.206 \times 10^{-2} \pm 0.020 \times 10^{-2}$
$H_{KJ} = 6.373 \times 10^{-2} \pm 0.044 \times 10^{-2}$	$H_K = -3.620 \times 10^{-2} \pm 0.075 \times 10^{-2}$
$h_J = -9.84 \times 10^{-4} \pm 0.16 \times 10^{-4}$	$h_{JK} = 2.443 \times 10^{-2} \pm 0.019 \times 10^{-2}$
$h_K = 8.804 \times 10^{-2} \pm 0.065 \times 10^{-2}$	
$L_{JK} = 2.747 \times 10^{-5} \pm 0.101 \times 10^{-5}$	$L_{JK} = -8.85 \times 10^{-5} \pm 1.07 \times 10^{-5}$
$L_{KKJ} = 7.8 \times 10^{-5} \pm 2.1 \times 10^{-5}$	$l_J = 7.72 \times 10^{-7} \pm 1.02 \times 10^{-7}$
$l_{JK} = -1.750 \times 10^{-5} \pm 0.131 \times 10^{-5}$	$l_K = -5.76 \times 10^{-4} \pm 0.25 \times 10^{-4}$
$\rho_K = 1.95 \times 10^{-6} \pm 0.32 \times 10^{-6}$	

^a The errors quoted are for 95% confidence limits. There is a high positive correlation ($\rho \geq 0.99$) between (H_J, Δ_J), (h_J, δ_J), (L_{JK}, H_K), and (l_J, L_{JK}), and a high negative correlation between (L_{KKJ}, H_K), (L_{KKJ}, L_{JK}), (l_J, h_J) and (l_K, h_K).

TABLE V
Comparison of the Rotational and Quartic Distortion Parameters of D₂S

	Microwave ^a	Microwave ^c	Infrared ^d	Infrared ^e
A	164 643.9 ^b	5.49193 ^b	5.4918	5.484
B	135 273.0 ^b	4.51222 ^b	4.511	4.508
C	73 278.6 ^b	2.44431 ^b	2.4445	2.444
τ_{aaaa}	-67.9633	-0.002267	-0.00213	-0.00211 ^f
τ_{bbbb}	-36.6473	-0.001222	-0.00117	-0.00106 ^f
τ_{cccc}	-2.0533	-0.00006849		-0.00006 ^f
τ_1	10.2042			
τ_2	2.196 $\times 10^5$			
τ_{aabb}	32.42 ^b	0.00108 ^b	0.00113	0.00099 ^f
τ_{abab}	-7.88 ^b	-0.000263 ^b	-0.00036	-0.00026 ^f

^a Calculated from this work. All parameters in units of Mc/sec except τ_2 which has units of (Mc/sec)².

^b Calculated by means of the planar relations. See text.

^c Entries of previous column converted to units of cm⁻¹. Conversion factor 2.997925 $\times 10^4$ (Mc/sec)/cm⁻¹.

^d From Ref. (20). In units of cm⁻¹.

^e From Ref. (17) and (18). In units of cm⁻¹.

^f Calculated from force constants.

TABLE VI
Relations for the Quartic Distortion Coefficients

Alternate tau constants^a

$$\tau_{aaaa} = -4(\Delta_J + \Delta_{JK} + \Delta_K), \quad \tau_{bbbb} = -4(\Delta_J + 2\delta_J), \quad \tau_{cccc} = -4(\Delta_J - 2\delta_J),$$

$$\tau_1 = \tau'_{aabb} + \tau'_{aacc} + \tau'_{bbcc} = -4(\Delta_{JK} + 3\Delta_J),$$

$$\tau_2 = A\tau'_{bbcc} + B\tau'_{aacc} + C\tau'_{aabb} = \left(\frac{B-C}{2}\right) \left[8(\delta_J + \delta_K) - 4\sigma\Delta_J + \tau_1 \left(\frac{B+C}{B-C}\right) \right],$$

$$R_6 = \left(\frac{-1}{32}\right) [4\Delta_J + \tau'_{bbcc}], \quad \sigma = (2A - B - C)/(B - C).$$

Planar relations^b

$$\tau_{aabb} = \frac{1}{2} A_c^2 B_c^2 \left[-\frac{\tau_{aaaa}}{A_c^4} - \frac{\tau_{bbbb}}{B_c^4} + \frac{\tau_{cccc}}{C_c^4} \right],$$

$$\tau_{aacc} = \frac{1}{2} A_c^2 C_c^2 \left[\frac{\tau_{aaaa}}{A_c^4} - \frac{\tau_{bbbb}}{B_c^4} + \frac{\tau_{cccc}}{C_c^4} \right],$$

$$\tau_{bbcc} = \frac{1}{2} B_c^2 C_c^2 \left[-\frac{\tau_{aaaa}}{A_c^4} + \frac{\tau_{bbbb}}{B_c^4} + \frac{\tau_{cccc}}{C_c^4} \right].$$

^a Relations given for a prolate top ($a \leftrightarrow z$, $b \leftrightarrow x$, $c \leftrightarrow y$). For D₂S, which is an oblate top ($a \leftrightarrow y$, $b \leftrightarrow x$, $c \leftrightarrow z$), simply interchange A and C, and a and c. For a planar molecule $\tau_{aacc} = \tau_{aacc}$, $\tau_{bbcc} = \tau_{bbcc}$, $\tau_{aabb} = \tau_{aabb} + 2\tau_{abab}$.

^b Appropriate for both prolate and oblate tops. Molecule in the ab plane.

TABLE VII
Comparison of Infrared Measurements of D₂S with Predictions from a Microwave Analysis (cm⁻¹)

Transition	Infrared measurement ^a	Microwave prediction ^b	Transition	Infrared Measurement ^a	Microwave Prediction ^b	Transition	Infrared measurement ^a	Microwave Prediction ^b
3 _{3,1} ← 2 _{2,0}	30.24	30.239	6 _{5,1} ← 5 _{4,2}	62.09	62.081	9 _{7,3} ← 8 _{6,2}	87.70	87.719
6 _{0,6} ← 5 _{1,5}	31.79	31.820	6 _{6,1} ← 5 _{5,0}	63.78	63.728	9 _{7,2} ← 8 _{6,3}	91.22	91.234
7 _{1,6} ← 7 _{0,7}	32.38	32.499	12 _{1,11} ← 11 _{2,10}	66.03	66.045	9 _{8,2} ← 8 _{7,1}	92.69	92.683
4 _{3,2} ← 3 _{2,1}	35.28	35.270	12 _{2,10} ← 11 _{3,9}	71.00	70.945	11 _{7,5} ← 10 _{6,4}	93.55	93.542
8 _{0,8} ← 7 _{1,7}	41.61	41.576	10 _{3,5} ← 9 _{6,4}	72.29	72.300	8 _{4,4} ← 7 _{3,5}	97.62	97.635
9 _{0,9} ← 8 _{1,8}	46.46	46.453	6 _{3,3} ← 5 _{2,4}	73.78	73.758	10 _{8,2} ← 9 _{7,3}	101.06	101.077
10 _{1,9} ← 10 _{0,10}	47.38	47.347	11 _{3,7} ← 10 _{4,6}	76.25	76.259	10 _{9,2} ← 9 _{8,1}	103.46	103.309
5 _{3,1} ← 4 _{1,0}	52.71	52.763	11 _{3,6} ← 10 _{6,5}	79.65	79.639	10 _{10,1} ← 9 _{9,0}	106.32	106.328
10 _{1,9} ← 9 _{2,8}	56.27	56.299	8 _{6,2} ← 7 _{5,3}	82.03	82.012	11 _{10,2} ← 10 _{9,1}	114.00	113.964
12 _{0,12} ← 11 _{1,11}	61.08	61.133	11 _{6,6} ← 10 _{5,5}	83.03	83.039	12 _{10,2} ← 11 _{9,3}	121.65	121.654
10 _{2,8} ← 9 _{3,7}	61.29	61.256	12 _{3,7} ← 11 _{6,6}	85.41	85.388	12 _{11,2} ← 11 _{10,1}	124.39	124.404

^a Pure rotational measurements of R. E. MILLER, G. E. LEROI, AND T. M. HARD, Ref. (20). Estimated experimental uncertainty is 0.06 cm⁻¹.

^b Predictions are based on the parameters listed in Table IV.

where δ_{cd} is somewhat analogous to the inertial defect, a "centrifugal defect." If all parameters are referred to the vibrationless state, $\delta_{cd} = 0$. For HDS, HDO and D₂S one obtains 2.27, 22.08 and 1.20 Mc/sec, respectively.

In Table VII a comparison is given between the observed infrared spectrum and the spectrum calculated on the basis of the parameters of Table IV. Although in Table VII only about half of the observed lines are listed, the general agreement is representative of all the measured lines. Only in a few cases is the discrepancy as large as the quoted experimental error of 0.06 cm^{-1} .

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