

## Microwave Spectrum and Centrifugal Distortion Effects of HDS

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The rotational spectrum of HDS in the ground vibrational state has been studied by microwave techniques. Twenty-seven new transitions have been measured in the millimeter and submillimeter wavelength region. These have been combined with other microwave measurements on HDS for a centrifugal distortion analysis based entirely on microwave data; it has been necessary to include both P<sup>4</sup> and P<sup>6</sup> distortion effects in the analysis. The results for the effective rotational constants and quartic distortion constants are (in Mc/sec):  $\mathcal{A} = 292\,351.303 \pm 0.135$ ,  $\mathcal{B} = 147\,861.801 \pm 0.054$ ,  $\mathcal{C} = 96\,704.119 \pm 0.054$ ,  $\Delta_J = 2.6134 \pm 0.0015$ ,  $\Delta_{JK} = 28.6933 \pm 0.0097$ ,  $\Delta_K = -11.297 \pm 0.019$ ,  $\delta_J = 0.8554 \pm 0.0008$ , and  $\delta_K = 19.4078 \pm 0.0085$ . Energy levels through  $J = 7$  have been computed for HDS.

### I. INTRODUCTION

The spectra of light asymmetric rotors have long been of interest to molecular spectroscopists. In addition to the usual desire to obtain accurate molecular parameters, such light molecules afford the opportunity to apply centrifugal distortion theory to systems in which the distortion effects are relatively large, even at low  $J$ . In spite of this, few microwave studies of this class of molecules have appeared. This situation is understandable, however, because the small moments of inertia of these molecules cause many of the absorption lines and, in particular, many key low  $J$  lines, to lie at frequencies beyond the reach of conventional microwave spectrometers. As a result, most of the analyses of these molecules have been carried out with data obtained by less precise infrared techniques.

We have constructed a spectrometer that allows us to make measurements as high as 813 Gc/sec ( $\lambda = 0.368$  mm) (1), and with this submillimeter wave spectrometer we have undertaken an analysis of the rotational spectrum of HDS. Within the spectral region now available to us, lie enough absorption lines for a distortion analysis of HDS as well as of a number of other light asymmetric rotor

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molecules. The previously reported work on HDS has been limited to a microwave study of the  $Q$ -branches at centimeter wavelengths by Hillger and Strandberg (2), millimeter wavelength studies by Burrus (3), and studies by Nielsen and Nielsen (4) and by Crosby, Bair and Cross (5) employing infrared techniques. With the present system, measurements can be made with rapidity and accuracy on transitions which fall as high as 750 Gc/sec. This rapidity and ease of measurement is particularly important in problems in which a relatively large number of measurements are necessary. The submillimeter lines measured during the course of this work combined with lower-frequency data allow a complete distortion analysis of HDS based entirely on microwave measurements. Because of the precision of microwave measurements as compared with infrared measurements, the rotational constants as well as the distortion constants of HDS can now be calculated to a high degree of accuracy.

## II. EXPERIMENTAL TECHNIQUES

Turnable, coherent submillimeter wave radiation is produced in this spectrometer by a klystron-driven crystal harmonic generator, as first described by King and Gordy (6). The frequency of this radiation is measured by means of a comparison between the klystron frequency and harmonics of a 5-Mc/sec crystal oscillator which is compared with WWVB. This submillimeter wave energy is directed through the sample cell of the spectrometer by an electroformed horn and teflon lens system. The cell consists of a copper tube 19 mm in diameter and 30 cm in length, with Teflon windows and  $O$ -ring vacuum seals. The output of this cell matches the input light pipe of a 1.6°K InSb photoconducting detector which was obtained from Mullard Ltd. In practice we find this detector to be at least an order of magnitude more sensitive than the usual point-contact detector in the submillimeter region. A diagram of the spectrometer is shown in Fig. 1.

The HDS sample was prepared by mixing equal parts of  $H_2S$  and  $D_2S$  and allowing the hydrogen and deuterium to exchange. The  $D_2S$  was prepared by reacting  $FeS$  and dilute  $D_2SO_4$ . This procedure resulted in a sample which was 25%  $D_2S$ , 50% HDS, and 25%  $H_2S$ . Since the lines measured in this experiment were strong enough to display in real time on an oscilloscope, the isotopic identity of a particular line could be verified by simply verifying that the line disappeared when both  $H_2S$  and  $D_2S$  were admitted successively to the cell rather than the  $D_2S$ -HDS- $H_2S$  mixture.

## III. CENTRIFUGAL DISTORTION THEORY

In the analysis of hydrogen deuterium sulfide significant centrifugal distortion effects were apparent and it has been necessary to include both  $P^4$  and  $P^6$  distortion effects. The theory of centrifugal distortion in asymmetric rotors has been recently discussed by Watson (7-9), and the Hamiltonian for a semirigid prolate

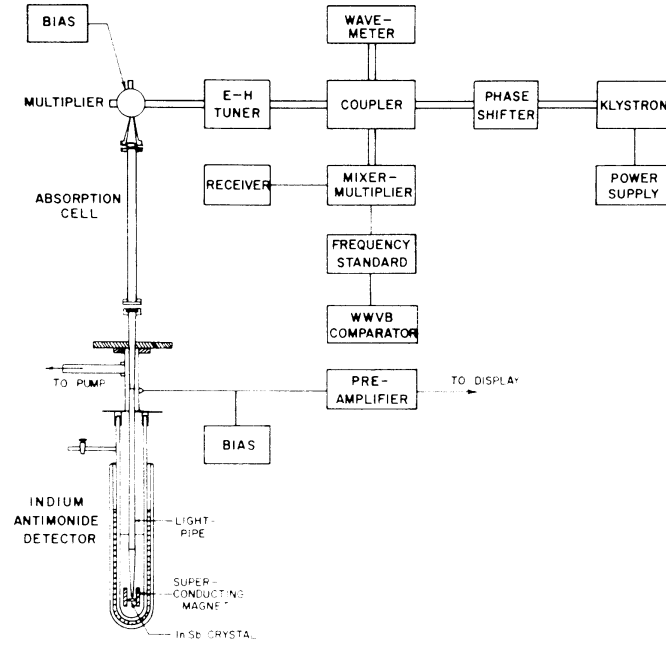


FIG. 1. Block diagram of the spectrometer. Submillimeter microwave energy is produced by a klystron-driven crystal harmonic generator and detected by an InSb photoconducting detector operated at 1.6°K.

rotor may be written as

$$\mathfrak{H} = \mathfrak{H}_r + \mathfrak{H}_d + \mathfrak{H}_d', \quad (1)$$

$$\mathfrak{H}_r = \frac{1}{2}(\mathfrak{B} + \mathfrak{C})P^2 + \left\{ \alpha - \frac{1}{2}(\mathfrak{B} + \mathfrak{C}) \right\} P_z^2 + b_p(P_y^2 - P_x^2), \quad (2)$$

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

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

where  $b_p = (\mathfrak{C} - \mathfrak{B}) / (2\alpha - \mathfrak{B} - \mathfrak{C})$  is Wang's asymmetry parameter,  $P^2 = P_x^2 + P_y^2 + P_z^2$ , and  $\alpha$ ,  $\mathfrak{B}$  and  $\mathfrak{C}$  are the effective rotational constants, which differ from the usual effective constants by an additional centrifugal distortion contribution ( $R_6$ ), i.e.,

$$\alpha = A + 16 R_6, \quad (5)$$

$$\mathfrak{B} = B - 16 R_6 (A - C) / (B - C), \quad (6)$$

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

In the above,  $\mathfrak{H}_r$  is the effective rigid rotor Hamiltonian,  $\mathfrak{H}_d$  and  $\mathfrak{H}_d'$  are the  $P^4$  and  $P^6$  distortion Hamiltonians, respectively. The five quartic distortion coefficients (8) are linear combinations of the  $\tau_{\alpha\beta\gamma\delta}$  (coefficient of  $P_\alpha P_\beta P_\gamma P_\delta$ ) of Wilson and Howard (10). The sextic distortion coefficients are complicated linear combinations of  $\tau_{\alpha\beta\gamma\delta\epsilon\eta}$ .

If the distortion effects are treated as a perturbation on the rigid rotor, the first-order distortion energy may be found by evaluating  $\langle \mathfrak{H}_d \rangle$  and  $\langle \mathfrak{H}_d' \rangle$  in the rigid asymmetric rotor basis. With the aid of the following average-value equations for the angular momentum operators,

$$\langle P_x^2 - P_y^2 \rangle = \sigma[W(b_p) - \langle P_z^2 \rangle], \quad (8)$$

$$\langle P_z^2(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^2 \rangle = 2\sigma[W(b_p)\langle P_z^2 \rangle - \langle P_z^4 \rangle], \quad (9)$$

$$\langle P_z^4(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^4 \rangle = 2\sigma[W(b_p)\langle P_z^4 \rangle - \langle P_z^6 \rangle], \quad (10)$$

the first-order energy expression for the semirigid prolate asymmetric rotor becomes

$$E = E_r + E_d + E_d', \quad (11)$$

$$E_r = \frac{1}{2}(\mathfrak{B} + \mathfrak{C})J(J+1) + [\alpha - \frac{1}{2}(\mathfrak{B} + \mathfrak{C})]W(b_p), \quad (12)$$

$$\begin{aligned} E_d = & -\Delta_J J^2(J+1)^2 - \Delta_{JK} J(J+1)\langle P_z^2 \rangle - \Delta_K \langle P_z^4 \rangle \\ & - 2\delta_{J\sigma} J(J+1)[W(b_p) - \langle P_z^2 \rangle] \\ & - 2\delta_{K\sigma}[W(b_p)\langle P_z^2 \rangle - \langle P_z^4 \rangle], \end{aligned} \quad (13)$$

$$\begin{aligned} E_d' = & H_J J^3(J+1)^3 + H_{JK} J^2(J+1)^2 \langle P_z^2 \rangle + H_{KJ} J(J+1) \langle P_z^4 \rangle \\ & + H_K \langle P_z^6 \rangle + 2h_{J\sigma} J^2(J+1)^2 [W(b_p) - \langle P_z^2 \rangle] \\ & + 2\sigma h_{JK} J(J+1) [W(b_p)\langle P_z^2 \rangle - \langle P_z^4 \rangle] \\ & + 2\sigma h_K [W(b_p)\langle P_z^4 \rangle - \langle P_z^6 \rangle], \end{aligned} \quad (14)$$

where  $\sigma = -1/b_p = (2\alpha - \mathfrak{B} - \mathfrak{C})/(\mathfrak{B} - \mathfrak{C})$ ,  $W(b_p)$  is the Wang reduced energy (see, for example, H. C. Allen, Jr. and P. C. Cross, "Molecular Vib-Rotors," John Wiley and Sons, New York, 1963), and  $\langle P_z^n \rangle$  is the average of  $P_z^n$  in the rigid asymmetric rotor basis. The latter quantities are obtained in conjunction with the diagonalization of the rigid-rotor energy matrix.

In order to obtain the rotational and distortion constants, a least-squares analysis of the observed frequencies was carried out based on Eq. (11). In particular, the constants were fit to the quantities  $(\nu_{\text{obs}} - \nu_r)$ , where  $\nu_r$  is the rigid rotor frequency. In the analysis, linear variations in the rigid-rotor constants were also considered; specifically variations in  $(\mathfrak{B} + \mathfrak{C})/2$ ,  $(\mathfrak{B} - \mathfrak{C})/2$  and  $\alpha - (\mathfrak{B} + \mathfrak{C})/2$  were allowed. The effective rotational constants were subsequently adjusted from their initial values so that the variations in the rigid-

rotor constants were small, e.g., less than 0.1 Mc/sec. In all calculations double-precision (16 digits) arithmetic was employed.

For HDS, a first-order treatment of centrifugal distortion effects is not adequate and higher-order effects have to be considered. These effects were accounted for by an iterative procedure similar to that employed by Pierce *et al.* (11). This entails first analyzing the spectrum by means of Eq. (11) to obtain an approximate set of rotational and distortion constants. These constants are then employed to construct the complete energy matrix of Eq. (1). The form of  $\mathfrak{H}$  in Eq. (1) is particularly convenient since it has only  $(K | K)$  and  $(K | K \pm 2)$  matrix elements in a symmetric top basis. Since  $\mathfrak{H}$  has the Four-group symmetry, the matrix representation in the Wang symmetric-top basis factors into four submatrices like the rigid-rotor energy matrix (12). The energy for a given  $J$  value may be written

$$E = \frac{1}{2}(\mathfrak{B} + \mathfrak{C})J(J + 1) - \Delta_J J^2(J + 1)^2 + H_J J^3(J + 1)^3 + [\alpha - \frac{1}{2}(\mathfrak{B} + \mathfrak{C})]W, \quad (15)$$

where  $W$  is an energy eigenvalue of the reduced energy submatrix  $\mathbf{W}$ , which is composed of  $K$ -dependent matrix elements of  $\mathfrak{H}_r$ ,  $\mathfrak{H}_d$ , and  $\mathfrak{H}_d'$ , in which the original distortion constants have been divided by the factor  $[\alpha - \frac{1}{2}(\mathfrak{B} + \mathfrak{C})]$ . Diagonalization of  $\mathbf{W}$  gives the energy levels of the complete Hamiltonian; by taking energy differences, the transition frequencies are obtained which include the corrections due to centrifugal distortion. The difference in the transition frequency found from Eq. (15) via diagonalization of the complete energy matrix and the frequency computed from the first-order energy expression Eq. (11) gives the second- and higher-order centrifugal distortion effect to the given transition. The observed frequencies are then corrected for these effects and reanalyzed with first-order theory. This procedure thus takes into account higher-order perturbation effects of  $\mathfrak{H}_d$  and  $\mathfrak{H}_d'$  while keeping the analysis for the distortion constants linear in the constants. We have found that about four iterations are required to stabilize the higher-order effects.

#### IV. EXPERIMENTAL RESULTS AND ANALYSIS OF THE SPECTRUM

HDS is a prolate asymmetric rotor with both "a" and "b" type transitions. With the results of this work 45 ground vibrational state transitions have now been measured and assigned. Table I lists the observed microwave transition frequencies of HDS and the transition frequencies calculated by diagonalizing the energy matrix formed using the molecular constants shown in Table II. These constants were calculated by the least-squares procedure discussed in the previous section. Also shown in Table I are the "second-order" corrections which were used in this least-squares fit and the contributions to the transition frequencies due to centrifugal distortion. The average deviation of the fit of the microwave lines is 0.11 Mc/sec while the standard deviation,  $\sigma$ , of the fit is 0.20 Mc/sec. The uncer-

tainties quoted for the constants in Table II are twice the respective standard deviations of the constants, where the standard deviation is  $\sigma_i = \sigma(A_{ii}^{-1})^{1/2}$  with  $\mathbf{A}^{-1}$  the inverse of the normal equation matrix. It is apparent from Table I that the distortion effects are rather large. With heavy molecules, similar size distortion effects are found only at relatively high  $J$ , e.g.,  $J > 30$  (11, 13, 14).

The transitions were assigned primarily on the basis of the distortion analysis

Table I. Rotational Transitions of HDS (Mc/sec)

Transition	Observed Frequency	Calculated Frequency	Distortion Effect <sup>a</sup>	"Second-Order" Effect	Deviation	Ref.
$6_{4,2} \leftarrow 6_{4,3}$	7 935.74	7 935.73	- 214.90	0.62	0.01	b
$11_{6,5} \leftarrow 11_{6,6}$	10 235.31	10 235.13	- 547.00	0.49	-0.35	b
$4_{3,1} \leftarrow 4_{3,2}$	10 361.07	10 361.16	- 156.47	0.30	-0.03	b
$2_{2,0} \leftarrow 2_{2,1}$	11 233.33	11 234.01	- 37.93	0.02	-0.13	b
$9_{5,4} \leftarrow 9_{5,5}$	17 212.31	17 212.32	- 322.34	0.57	0.23	b
$7_{4,3} \leftarrow 7_{4,4}$	27 563.31	27 565.93	- 322.73	0.51	0.35	b
$12_{6,6} \leftarrow 12_{6,7}$	23 342.34	23 342.91	-1172.40	0.35	-0.07	b
$5_{3,2} \leftarrow 5_{3,3}$	40 929.20	40 929.21	- 511.11	0.33	-0.01	b
$10_{5,5} \leftarrow 10_{5,6}$	47 905.33	47 905.07	-1353.34	1.42	0.23	b
$1_{1,0} \leftarrow 1_{1,1}$	51 073.27	51 073.37	- 34.32	0.00	-0.10	b
$3_{2,1} \leftarrow 3_{2,2}$	53 200.33	53 201.01	- 238.37	0.16	-0.03	b
$8_{4,4} \leftarrow 8_{4,5}$	75 551.73	75 552.23	-1337.45	1.22	-0.53	b
$6_{3,3} \leftarrow 6_{3,4}$	110 231.15	110 230.73	-1191.35	0.39	0.39	
$4_{2,3} \leftarrow 4_{2,0}$	110 703.22	110 703.31	- 201.33	-2.13	-0.03	
$5_{3,2} \leftarrow 5_{4,1}$	112 335.45	112 335.43	-2399.37	-5.96	0.02	
$4_{1,4} \leftarrow 4_{2,1}$	135 017.27	135 017.23	1353.40	-1.02	-0.02	
$5_{1,5} \leftarrow 5_{2,2}$	135 354.33	135 354.33	2334.34	-0.13	0.03	
$4_{2,2} \leftarrow 4_{2,3}$	143 034.72	143 034.32	- 769.00	0.26	-0.10	
$2_{1,1} \leftarrow 2_{1,2}$	153 179.13	153 179.33	- 293.71	0.00	-0.17	c
$1_{1,0} \leftarrow 1_{0,1}$	195 553.32	195 553.96	- 38.22	0.00	-0.04	c
$1_{0,1} \leftarrow 1_{0,0}$	244 555.53	244 555.47	- 10.45	0.00	0.11	c
$2_{1,1} \leftarrow 2_{0,2}$	257 731.41	257 731.53	- 375.33	0.08	-0.12	c
$5_{2,4} \leftarrow 5_{3,1}$	303 513.54	303 513.52	1213.30	-3.52	0.02	
$3_{1,2} \leftarrow 3_{1,3}$	304 340.54	304 340.47	- 333.79	-0.03	0.07	c
$10_{4,6} \leftarrow 10_{4,7}$	323 331.43	323 331.42	-4410.30	32.45	0.03	

Table I. (continued)

Transition	Observed Frequency	Calculated Frequency	Distortion Effect <sup>a</sup>	"Second- Order" Effect	Devi- ation	Ref.
$2_{0,2} \leftarrow 1_{1,1}$	333 278.71	333 278.60	- 11.74	-0.08	0.11	c
$3_{1,2} \leftarrow 3_{0,3}$	368 102.22	368 102.30	- 862.28	-0.23	-0.08	
$3_{1,2} \leftarrow 2_{2,1}$	368 550.52	368 550.52	- 338.76	-0.39	0.00	
$1_{1,1} \leftarrow 0_{0,0}$	389 041.08	389 041.06	- 14.36	0.00	0.02	
$8_{3,5} \leftarrow 3_{3,6}$	415 880.03	415 880.18	-4043.48	10.24	-0.15	
$3_{2,1} \leftarrow 3_{1,2}$	417 381.10	417 381.15	- 927.02	0.55	-0.05	
$4_{2,2} \leftarrow 4_{1,3}$	423 571.36	423 571.50	-1840.70	-0.32	-0.14	
$6_{3,3} \leftarrow 5_{4,2}$	431 474.46	431 474.47	-1206.53	-21.41	-0.01	
$2_{1,2} \leftarrow 1_{1,1}$	437 880.83	437 880.80	- 93.36	0.00	0.03	
$2_{2,0} \leftarrow 2_{1,1}$	444 552.85	444 552.78	- 267.72	0.08	0.07	
$6_{2,5} \leftarrow 5_{3,2}$	445 094.65	445 094.66	3178.63	-6.20	-0.01	
$2_{0,2} \leftarrow 1_{0,1}$	477 764.27	477 764.20	- 15.65	-0.08	0.07	
$5_{2,3} \leftarrow 5_{1,4}$	480 508.88	480 508.89	-3015.34	-2.67	-0.01	
$6_{2,4} \leftarrow 5_{2,5}$	480 983.25	480 983.22	-2825.61	1.76	0.03	
$4_{1,3} \leftarrow 4_{0,4}$	532 187.04	532 186.81	-1535.73	-0.35	0.23	
$2_{1,1} \leftarrow 1_{1,0}$	539 986.65	539 986.77	- 302.76	0.00	-0.12	
$2_{1,2} \leftarrow 1_{0,1}$	582 366.42	582 366.39	- 97.27	0.00	0.03	
$3_{0,3} \leftarrow 2_{1,2}$	586 896.20	586 896.32	30.06	-0.16	-0.12	
$6_{2,4} \leftarrow 5_{1,5}$	598 805.17	598 805.12	-4457.60	-4.97	0.05	
$7_{3,4} \leftarrow 7_{2,5}$	628 018.53	628 018.51	-7798.90	-18.52	0.02	

<sup>a</sup> Includes  $P^4$ ,  $P^6$  and "second-order" effects.

<sup>b</sup> Hillger and Strandberg, ref. 2.

<sup>c</sup> Burrus, ref. 3.

and predicted line strengths. In order to further check our assignment, the 45 measured transitions were randomly grouped into nine groups of five members each. Then one group of five transitions was removed from the fit, and the spectral constants and resulting line-frequency predictions were calculated on the basis of the remaining 40 lines. This procedure was repeated for each of the nine groups. The uncertainty,  $\sigma_\nu$ , in each of the line-frequency predictions, was calcu-

TABLE II  
ROTATIONAL AND DISTORTION CONSTANTS OF HDS (MC/SEC)<sup>a</sup>

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$\mathfrak{A} = 292\,351.303 \pm 0.135$	
$\mathfrak{B} = 147\,861.801 \pm 0.054$	
$\mathfrak{C} = 96\,704.119 \pm 0.054$	
$\Delta_J = 2.6134 \pm 0.0015$	$\Delta_{JK} = 28.6933 \pm 0.0097$
$\Delta_K = -11.297 \pm 0.019$	$\delta_J = 0.8554 \pm 0.0008$
$\delta_K = 19.4078 \pm 0.0085$	
$H_{JK} = 1.326 \times 10^{-2} \pm 0.044 \times 10^{-2}$	$H_{KJ} = -2.027 \times 10^{-2} \pm 0.096 \times 10^{-2}$
$H_K = 1.304 \times 10^{-2} \pm 0.104 \times 10^{-2}$	$h_J = 1.07 \times 10^{-4} \pm 0.22 \times 10^{-4}$
$h_{JK} = 5.33 \times 10^{-3} \pm 0.41 \times 10^{-3}$	$h_K = 2.834 \times 10^{-2} \pm 0.134 \times 10^{-2}$

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<sup>a</sup> More significant figures than listed here are required to reproduce exactly the calculations of Table I. The errors are for 95% confidence limits. There is a high positive correlation ( $|\rho| > 0.90$ ) between  $(H_{JK}, h_J)$ ,  $(H_{JK}, h_K)$ ,  $(H_{KJ}, h_{JK})$  and a high negative correlation between  $(h_{JK}, h_J)$  and  $(h_{JK}, h_K)$ .

lated as described by Hamilton (15) from

$$\sigma_v^2 = \sum_{i,j} \sigma_i \sigma_j \rho_{ij} C_i C_j = \sigma^2 \sum_{i,j} A_{ij}^{-1} C_i C_j, \quad (16)$$

where  $\sigma_i$  is the standard error in the  $i$ -th spectral constant, and  $C_i$  the corresponding coefficient in the frequency expression. The correlation coefficients  $\rho_{ij}$  between the  $i$ -th and  $j$ -th constants may be evaluated from the inverse normal equation matrix, i.e.,

$$\rho_{ij} = A_{ij}^{-1} / \sqrt{A_{ii}^{-1}} \sqrt{A_{jj}^{-1}} \quad (-1 \leq \rho_{ij} \leq 1). \quad (17)$$

These are of interest in themselves since they give information on the linear dependence of the constants (15, 16). This procedure revealed that each of the 45 observed lines could be predicted to within the expected theoretical and experimental uncertainty from an analysis which did not include the line itself. In addition it was found that each of the nine subsets of experimental data produced virtually the same set of molecular constants. In the analysis, it has been found that the constant  $H_J$  could not be extracted from the present data. When included in the fit, the error in this constant was approximately three times as large as the constant itself, and the omission of this constant did not affect the fit of the spectrum. If additional higher  $J$  transitions are subsequently measured, it can be expected that small changes in the coefficients of  $P^6$  will occur and that possibly higher-order constants, e.g., coefficients of  $P^8$  will be required to adequately fit the spectrum.

The molecular constants shown in Table II were used to calculate the ground vibrational state energy levels of HDS. These results are shown in Table III.



TABLE III  
ENERGY LEVELS OF HDS (CM<sup>-1</sup>)<sup>a</sup>

0 <sub>0,0</sub>	0.0	4 <sub>3,1</sub>	133.64606 (3)	6 <sub>4,2</sub>	263.96263 (11)
1 <sub>0,1</sub>	8.157491 (3)	4 <sub>4,1</sub>	172.38998 (5)	6 <sub>5,2</sub>	313.48484 (17)
1 <sub>1,1</sub>	12.977011 (5)	4 <sub>4,0</sub>	172.39615 (5)	6 <sub>5,1</sub>	313.49178 (17)
1 <sub>1,0</sub>	14.680635 (5)	5 <sub>0,5</sub>	112.66389 (3)	6 <sub>6,1</sub>	374.8308 (5)
2 <sub>0,2</sub>	24.093987 (7)	5 <sub>1,5</sub>	113.17186 (3)	6 <sub>6,0</sub>	374.8309 (5)
2 <sub>1,2</sub>	27.583140 (8)	5 <sub>1,4</sub>	137.31288 (3)	7 <sub>0,7</sub>	203.38760 (11)
2 <sub>1,1</sub>	32.692652 (9)	5 <sub>2,4</sub>	143.77028 (3)	7 <sub>1,7</sub>	203.47570 (11)
2 <sub>2,1</sub>	47.144941 (14)	5 <sub>2,3</sub>	153.34093 (3)	7 <sub>1,6</sub>	243.15908 (11)
2 <sub>2,0</sub>	47.521335 (14)	5 <sub>3,3</sub>	174.78351 (5)	7 <sub>2,6</sub>	245.27873 (10)
3 <sub>0,3</sub>	47.159892 (13)	5 <sub>3,2</sub>	176.14876 (5)	7 <sub>2,5</sub>	269.11698 (12)
3 <sub>1,3</sub>	49.276750 (13)	5 <sub>4,2</sub>	213.79786 (7)	7 <sub>3,5</sub>	282.25852 (12)
3 <sub>1,2</sub>	59.438461 (14)	5 <sub>4,1</sub>	213.85246 (7)	7 <sub>3,4</sub>	290.06542 (12)
3 <sub>2,2</sub>	71.586201 (17)	5 <sub>5,1</sub>	263.97716 (12)	7 <sub>4,4</sub>	322.12221 (16)
3 <sub>2,1</sub>	73.360795 (17)	5 <sub>5,0</sub>	263.97780 (12)	7 <sub>4,3</sub>	323.04171 (17)
3 <sub>3,1</sub>	100.12977 (3)	6 <sub>0,6</sub>	154.85219 (5)	7 <sub>5,3</sub>	371.4700 (3)
3 <sub>3,0</sub>	100.18301 (2)	6 <sub>1,6</sub>	155.06957 (5)	7 <sub>5,2</sub>	371.5109 (3)
4 <sub>0,4</sub>	76.766238 (18)	6 <sub>1,5</sub>	187.06541 (6)	7 <sub>6,2</sub>	432.3479 (6)
4 <sub>1,4</sub>	77.864487 (18)	6 <sub>2,5</sub>	190.99552 (5)	7 <sub>6,1</sub>	432.3487 (6)
4 <sub>1,3</sub>	94.51808 (2)	6 <sub>2,4</sub>	207.03939 (6)	7 <sub>7,1</sub>	504.8618 (16)
4 <sub>2,3</sub>	103.87577 (2)	6 <sub>3,4</sub>	224.51173 (7)	7 <sub>7,0</sub>	504.8618 (16)
4 <sub>2,2</sub>	108.64690 (2)	6 <sub>3,3</sub>	228.19030 (7)		
4 <sub>3,2</sub>	133.28377 (3)	6 <sub>4,3</sub>	263.69789 (11)		

<sup>a</sup> Standard error (95% confidence limits) in the last digit quoted is enclosed in parentheses. Conversion factor  $2.997925 \times 10^4$  Mc/cm<sup>-1</sup> (Ref. 12).

The uncertainties listed in this table were obtained by the same procedure as that described above for determining the uncertainties in the predicted line frequencies. It should be noted that the uncertainties in transition frequencies derived from uncertainties in the energy levels of Table III are larger than the uncertainties in the frequencies calculated directly. This is to be expected since in the latter case the  $C_i$ 's in Eq. (16) are differences and hence smaller.

It should be pointed out that although a modest increase in the length of the cell of the spectrometer would have made it possible to measure a number of weaker high- $J$  lines, this was unnecessary because the frequency range and sensitivity of the submillimeter wave spectrometer made it possible to measure an adequate number of lines for a microwave distortion analysis using the existing cell of length 30 cm. Several of the low-frequency lines (below 300 Gc/sec) which were measured during this experiment were measured in another spectrometer in this laboratory.

A comparison between the rotational constants of this work and those obtained previously is presented in Table IV. The  $\alpha$ ,  $\beta$ , and  $\mathcal{C}$  determined in this work differ from the  $A$ ,  $B$ , and  $C$  determined in the previous work by an amount on the order of  $R_6$ . This difference, due to the formulation of the distortion problem,

TABLE IV  
COMPARISON OF THE GROUND STATE ROTATIONAL CONSTANTS FOR HDS ( $\text{CM}^{-1}$ )

	Present M.W. work	I.R. <sup>a</sup>	M.W. <sup>b</sup>
$\mathcal{A}$	9.75179	9.743	
$\mathcal{B}$	4.93214	4.922	
$\mathcal{C}$	3.22570	3.232	
$\mathcal{A} - \mathcal{C}$	6.52608	6.511	6.5328
$\mathcal{B} - \mathcal{C}$	1.70644	1.690	1.7061 <sup>c</sup>
$\kappa$	-0.477041	-0.48088	-0.47767

<sup>a</sup> Infrared investigation of Crosby, Bair, and Cross, Ref. 5.

<sup>b</sup> Microwave investigation of Hillger and Strandberg, Ref. 2.

<sup>c</sup> Calculated from  $\kappa$  and  $\mathcal{A} - \mathcal{C}$ .

is small when compared to the experimental difference. A direct comparison of the distortion constants of the previous work and those reported in this paper has not been made because of the different formulation of the distortion theory used in the earlier work.

#### V. PLANAR APPROXIMATION

Since HDS is a planar molecule one could use the relations applicable for planar molecules and reduce the number of quartic distortion constants from five to four. However, since these relations are not strictly correct except in the small oscillations approximation, this can introduce unnecessary errors in the analysis and hence has not been done above. Nevertheless, such an analysis is of interest. Before it was demonstrated by Watson (7) that the quartic distortion effects in asymmetric rotors could be expressed in terms of five rather than six distortion coefficients it was usual practice to employ the planar relations to planar molecules. An analysis using the planar approximations has hence been carried out. In particular, the quartic distortion coefficients in Eq. (1), which are linear combinations of the  $\tau$ 's, have been expressed in terms of four  $\tau$ 's, viz.,  $\tau_{aaaa}$ ,  $\tau_{bbbb}$ ,  $\tau_{aabb}$ ,  $\tau_{abab}$  by means of the planar relations, and the resulting Hamiltonian has been employed to analyze the rotational spectrum. In the planar relations, the effective rotational constants have been used rather than the required equilibrium constants. Also the same number and kind of the coefficients of  $P^6$  have been considered and the "second-order" corrections of Table I have been used to correct the observed frequencies. It has been found that the deviation of the fit goes up rapidly as higher  $J$  transitions are added. The fit is considerably worse than would be expected from experimental errors alone. Two typical analyses are given in Table V. Employing the  $\tau$ 's of Table V, the constants  $\Delta_J$ , etc., have also been calculated. These are compared with the values obtained from the spectrum directly in Table V. The empirical technique of correcting the effective

TABLE V  
COMPARISON OF DISTORTION ANALYSES

	Planar Approximation <sup>a</sup>		Nonplanar Analysis <sup>b</sup>
	$J \leq 5$	$J \leq 12$	$J \leq 12$
$\tau_{bbbb}$	-17.55	-17.70	-17.56
$\tau_{aaaa}$	-79.71	-80.77	-79.90
$\tau_{aabb}$	10.69	10.57	14.27
$\tau_{abab}$	-72.48	-73.63	-75.59
$\Delta_J$	2.59	2.61	2.613
$\Delta_{JK}$	28.42	29.01	28.693
$\Delta_K$	-11.08	-11.43	-11.297
$\delta_J$	0.90	0.91	0.855
$\delta_K$	18.71	19.00	19.408
Av. Dev.	0.76	3.53	0.11

<sup>a</sup> The  $\tau$ 's have been evaluated from the rotational spectrum using the planar relations. The constants  $\Delta_J$ , etc., have been calculated from the  $\tau$ 's.

<sup>b</sup> The  $\Delta_J$ , etc., have been evaluated from the rotational spectrum via Eq. (1). The  $\tau$ 's have been calculated by least squares from  $\Delta_J$ , etc.

$C$  constant such that the inertial defect is zero, interestingly enough, gave a slight improvement of the fit (average deviation was reduced by approximately 15%) with essentially the same constants. Apparently in such molecules with large distortion effects, the planar relations cannot be applied and still fit the data within the experimental error. In the case of heavy molecules with smaller distortion effects the error in applying the planar relations is much smaller at least with regard to the fit.

Alternately, the quartic distortion coefficients listed in Table II may be used to obtain the  $\tau$ 's. Here the planar relations are employed and the five constants are analyzed by the least-squares technique to obtain the four  $\tau$ 's. These results are also listed in Table V, and compare favorably with the  $\tau$ -constants obtained from a direct analysis; the largest discrepancy occurs in  $\tau_{aabb}$ . This analysis like the one above neglects complications due to the fact that effective rotational constants rather than equilibrium constants are employed and that the quartic constants obtained from an analysis of observed frequencies are not equilibrium constants for which the planar relations hold exactly, but effective distortion constants which contain vibrational contributions. In fact, the small oscillations approximations may be particularly bad here, where hydrogen atoms are involved.

#### ACKNOWLEDGMENTS

We are grateful to Professor Walter Gordy for his support and encouragement during this work.

We wish to express our appreciation to C. A. Burrus of the Bell Telephone Laboratories for making his unpublished results available to us, and to William Clark and Michael Garvey for their able assistance in some of the present measurements.

One of us (Paul Helminger) acknowledges support from a grant to the Physics Department, Duke University, Durham, NC, by the Shell Companies Foundation.

RECEIVED: May 24, 1971

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