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MOLECULAR FORCE FIELD AND STRUCTURE OF HYDROGEN SULFIDE: RECENT MICROWAVE RESULTS

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ABSTRACT

Recently, microwave studies of the rotational spectra of hydrogen sulfide and its various isotopic species have been reported. These studies provide accurate rotational constants and, among others, the quartic distortion constants, which depend on the quadratic part of the vibrational potential function. These data are collected and the molecular force field and structure of hydrogen sulfide are considered in light of these recent microwave data. The infrared and microwave data are combined within the theoretical framework of the small oscillations model and the results compare favorably with the true harmonic force field. The IR & MW valence bond force constants of H_2S are (md $Å^{-1}$):

$f_r = 3.988$, $f_\theta = 0.399$, $f_{rr} = -0.017$, $f_{r\theta} = 0.057$.

The results further confirm the usefulness of rotation—vibration data in the determination of force constants, and show that even with large anharmonicity effects a very representative force field can be obtained by combining ground state infrared and microwave data.

Various molecular structures have been evaluated, and the average structures in the ground vibrational state for H_2S and D_2S are found to be:

$\langle r \rangle$	$\langle \theta \rangle$
S—H = 1.3518 Å	HSH = 92.13°
S—D = 1.3474 Å	DSD = 92.11°

A one-dimensional approximation to the anharmonicity effects is applied to determine the equilibrium structure of H_2S from the average structure data. The result is as follows:

$r_e = 1.3362$ Å and $\theta_e = 92.06°$

This bond distance is some 0.0006 Å larger than that obtained by applying the vibrational corrections measured in the infrared region [4].

INTRODUCTION

Hydrogen sulfide and its isotopic variants have been extensively studied over the years in the infrared region under conditions of higher and higher

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resolution. Of the more recent studies [1—6], particular note may be made of the work on H_2S by Edwards et al. [4], and on D_2S by Miller et al. [6]. On the other hand, until recently, these molecules had not been characterized in the microwave region since only a few Q-branch transitions had been measured. The microwave spectra of H_2S [7], D_2S [8] and HDS [9] have now been observed, and numerous rotational transitions, which heretofore have been inaccessible to microwave techniques, have been measured and assigned. This has been possible because of recent advances in submillimeter wave spectroscopy [10].

The analysis of the spectra of these light asymmetric rotors is complicated by the particularly large centrifugal distortion effects. The theoretical treatment of centrifugal distortion given by Watson [11] has been employed in our investigation of these molecules. Two methods of analysis — the rigid rotor basis distortion analysis [9] and the semi-rigid rotor basis distortion analysis [8] — have been described in previous communications. Specific procedures for the analysis of the distortion effects have also been given [8, 9, 12]. Since the series representation of the distortion effects converges very slowly for these light asymmetric rotors, numerous distortion constants have to be included to adequately characterize the microwave spectrum. A systematic method has been described for selecting the appropriate constants to be retained [8, 12] in the Hamiltonian. The method essentially allows the available data to decide which of the many distortion terms are important in the characterization of the spectrum. It is found that the lower order constants are well determined and virtually insensitive to details of the data and reasonable choices of higher-order constants. The information from the two branches of spectroscopy (infrared and microwave) on these molecules are in quite good agreement. In the case of D_2S, for example, the far infrared spectrum was calculated from the microwave constants (some 22 parameters) and compared with the observed [8]. The agreement was well within the quoted experimental error of the infrared data.

The microwave studies furnish accurate rotational constants and, among others, the quartic distortion constants, which depend on the quadratic part of the potential function. In the present communication, the molecular force field and structure of hydrogen sulfide are considered taking cognizance of these recent microwave data. For relatively small molecules, it is well known that the distortion data is particularly useful to supplement the vibrational frequency data and hence, better characterize the potential function [13]. The usual situation, however, is that one is forced to use uncorrected observed vibrational frequencies, etc., and ignore the effects of anharmonicity. Hydrogen sulfide is one of the few molecules for which the anharmonic corrections to the observed vibrational frequencies, which in this case are particularly large, are known. Hence, it is possible to judge directly the merits of the potential function obtained by combination of observed infrared (IR) and microwave (MW) data. The observed vibrational frequencies and distortion constants have been combined within the theoretical framework of the

small oscillations model and the results compare very favorably with the true harmonic force field. Similar calculations and results have been reported recently for water [14]. These results not only confirm the importance of vibration—rotation data in the determination of force constants, but also show that a very representative force field can be obtained.

SUMMARY OF MICROWAVE DATA

The rotational constants and quartic distortion coefficients for the isotopic species of hydrogen sulfide studied are summarized in Table 1. The distortion coefficients listed in Table 1 are linear combinations of the familiar τ-distortion constants. An equivalent and for present purposes more convenient set of five constants, viz., τ_{aaaa}, τ_{bbbb}, τ_{cccc}, τ_1 and τ_2' may be evaluated directly [8] from the spectral constants of Table 1. These latter constants are also given in Table 1. The statistical uncertainties quoted in Table 1 represent 95% confidence limits. Note, however, the uncertainties given for A', B', C' are only estimated errors (see later discussion).

TABLE 1

Rotational and centrifugal distortion constants of hydrogen sulfide (MHz)[a]

	H_2S	D_2S	HDS
$\mathscr{A}$	310182.24±0.51	164571.12±0.05	292351.30±0.14
$\mathscr{B}$	270884.05±0.51	135380.31±0.05	147861.80±0.05
$\mathscr{C}$	141705.88±0.60	73244.07±0.07	96704.12±0.05
Δ_J	49.851±0.038	13.076±0.003	2.613±0.002
Δ_{JK}	−159.696±0.069	−41.780±0.007	28.693±0.010
Δ_K	111.851±0.068	29.217±0.011	−11.297±0.019
δ_J	−6.019±0.005	−1.9573±0.0007	0.8554±0.0008
δ_K	262.17±0.21	47.252±0.004	19.408±0.009
τ_{aaaa}	−247.56±0.16	−67.963±0.012	−80.039±0.085
τ_{bbbb}	−151.25±0.16	−36.647±0.012	−17.297±0.009
τ_{cccc}	−8.03±0.42	−2.053±0.053	−3.610±0.009
τ_1	40.56±0.53	10.204±0.041	−146.134±0.043
τ_2'	0.17±0.22	0.586±0.017	−28.872±0.010
τ_{abab}	−24.8[b]	−7.0[b]	−69.2[b]
	−27.2[c]	−6.2[c]	−67.7[c]
	−22.0[d]	−7.9[d]	−72.0[d]
Ground state rotational constants			
A'	310605.5±10	164642.3±2	292318.5±1
B'	270299.2±10	135266.7±2	147820.2±1
C'	141861.2±1	73284.7±0.2	96761.2±2

[a]Here the statistical correlations between the constants Δ_J, etc. have been ignored in calculating the errors for τ_{aaaa}, etc. Note $\tau_1 = \tau_{bbcc} + \tau_{aacc} + \tau'_{aabb}$, $\tau_2' = (A\tau_{bbcc} + B\tau_{aacc} + C\tau'_{aabb})/(A+B+C)$ and $\tau'_{aabb} = \tau_{aabb} + 2\tau_{abab}$. The rotational constants A', B', C' have been corrected for effects of centrifugal distortion. [b]From planar relations and τ_1. [c]From planar relations and τ_2'. [d]From planar relations and (τ_1, τ_2').

For discussion of the force field of a planar molecule, it is convenient to choose the four independent constants τ_{aaaa}, τ_{bbbb}, τ_{cccc} and τ_{abab}. The first three constants come directly from the analysis of the rotational spectrum, however, τ_{abab} must be extracted from τ_1 and/or τ_2' via the planar relations. In Table 1 the values of τ_{abab} obtained by three different procedures of calculation [14, 15] are given. Because of the effects of vibration, the results of the various calculations are not the same. The spread in values, e.g., for H_2S amounts to some 5 MHz. By reason of the ambiguity in the value of τ_{abab} obtained here, this constant was not considered further in regard to the force field.

Before information on the molecular structure can be obtained, the spectral constants $\mathscr{A}$, $\mathscr{B}$ and $\mathscr{C}$ must be corrected for the contributions of distortion. The ground-vibrational-state rotational constants A', B', C' are related to $\mathscr{A}$, $\mathscr{B}$, $\mathscr{C}$ as follows for an oblate asymmetric top (a↔y, b↔x, c↔z).

$$A' = A + \tfrac{1}{2}\tau_{abab} = \mathscr{A} - 16\,R_6\,(C-B)/(B-A) + \tfrac{1}{2}\tau_{abab} \quad (1)$$

$$B' = B + \tfrac{1}{2}\tau_{abab} = \mathscr{B} + 16\,R_6\,(C-A)/(B-A) + \tfrac{1}{2}\tau_{abab} \quad (2)$$

$$C' = C - \tfrac{3}{4}\tau_{abab} = \mathscr{C} - 16\,R_6 - \tfrac{3}{4}\tau_{abab} \quad (3)$$

where $R_6 = -(4\Delta_J + \tau'_{aabb})/32$ and $\tau'_{aabb} = \tau_{aabb} + 2\tau_{abab}$. These corrections ar particularly important for these light molecules. By means of the planar relations three values of τ'_{aabb} (and τ_{abab}) may be evaluated from τ_1 and τ_2', as outlined previously [14, 15], and these lead therefore to three sets of A', B', C'. The values quoted in Table 1 for the distortion-free rotational constants A', B', C' have been obtained using the values of τ'_{aabb} and τ_{abab} extracted from τ_1 via the planar relations. This gives results which are intermediate between the other two sets of rotational constants. The uncertainties listed represent essentially the spread obtained using the other values of τ'_{aabb} and τ_{abab}. The uncertainties in the derived ground state rotational constants are significantly larger than the experimental uncertainties and this leads to uncertainties in the molecular structure. However, these uncertainties would be significant only if the vibrational corrections were known with greater accuracy.

It may also be noted that the value of τ_2' obtained from the constants of Table 1, particularly that of H_2S, is sensitive to the A, B, C values employed. However, the range of values obtained are well within the quoted statistical uncertainties.

MOLECULAR FORCE FIELD CALCULATIONS

Considerable data on the vibrational frequencies (harmonic and anharmonic) and centrifugal stretching constants are available and various

calculations and comparisons can be made. The pertinent equations and details of the analysis described here have been given elsewhere [14].

(a) Infrared Vibrational Frequency Data

In Table 2, we give first the quadratic force constants in the most general valence bond potential function determined from a weighted least squares analysis of the vibrational frequency data. The vibrational frequency data, which has been used in the calculations of this paper, are summarized in the footnotes of Table 2. The vibrational frequencies of H_2S were taken from Allen and Plyler [16] and for D_2S the harmonic frequencies come from Miller et al. [3], and the observed frequencies come from Miller and Eggers [2] and from Reding and Hornig [17]. The frequencies of HDS have been obtained from the H_2S and D_2S data as suggested by Nibler and Pimentel [18]. The atomic masses and fundamental constants have been taken from Gordy and Cook [19]. The force constants obtained from the harmonic vibrational frequencies represent the so-called harmonic force field associated with the vibrationless state. The constants tabulated here and in other tables are symmetrized force constants consistent with the internal symmetry coordinates: $S_1 = (\delta r_1 + \delta r_2)/\sqrt{2}$, $S_2 = \delta\theta$, $S_3 = (\delta r_1 - \delta r_2)/\sqrt{2}$. The force constants F_{22} and F_{12} have been reduced to md Å^{-1} units by use of the appropriate bond distance. The harmonic force constants of Table 2 are well determined, and since the fit of the data is very good, different weighting does not have a significant effect on the constants. This indicates that the accuracy of the vibrational frequency data is good, and that the theoretical model being employed is satisfactory.

The effective force field for the ground state, obtained by employment of

TABLE 2

Force field from infrared data (H_2S, D_2S, HDS)[a]

	Harmonic frequencies[b]	Observed frequencies[c]		
	(W=1)	I(W=1)	II($W\sim 1/\nu$)	III($W\sim 1/\nu^2$)
F_{11} (md Å^{-1})	4.2731±0.0008	3.786±0.100	3.807	3.846
F_{22} (md Å^{-1})	0.4250±0.0002	0.472±0.042	0.464	0.449
F_{12} (md Å^{-1})	0.064 ±0.010	−0.419±0.131	−0.392	−0.337
F_{33} (md Å^{-1})	4.2960±0.0005	4.000±0.022	4.005	4.012
Av. dev. (cm^{-1})	0.1	5.9	6.1	6.8

[a]The uncertainties quoted throughout for the force constants represent one standard deviation.

[b]Harmonic frequencies used in the analysis are (ω_1, ω_2, ω_3): 2721.9, 1214.5, 2733.4 cm^{-1} for H_2S; 1952.8, 871.8, 1963.9 cm^{-1} for D_2S and 1958, 1057, 2728 cm^{-1} for HDS. Structural parameters are taken as r = 1.336 Å and θ = 92.1°.

[c]Observed frequencies used in the analysis are (ν_1, ν_2, ν_3): 2614.6, 1182.7, 2627.5 cm^{-1} for H_2S; 1896.4, 855.5, 1910 cm^{-1} for D_2S and 1903, 1032, 2621 cm^{-1} for HDS. Structural parameters are taken as r = 1.336 Å and θ = 92.2°.

the observed anharmonic vibrational frequencies, is also given in Table 2. The force constants were adjusted so as to minimize $\Sigma \Delta \nu_i^2 w_i$. Three different kinds of weighting were used. In particular, in (I) all frequencies ν_i were weighted equally $w_i = 1$, in (II) frequencies were weighted inversely proportional to their observed value $w_i \sim 1/\nu_i$, and in (III) $w_i \sim 1/\nu_i^2$. The deviations of the calculated frequencies from the observed frequencies are much larger than the expected experimental uncertainty. The largest discrepancy for unit weighting is about 15 cm^{-1}. This is because of the effects of anharmonicity. The small oscillations model is really not appropriate here where observed frequencies are being employed. Inspection of Table 2 shows that the values of the force constants are sensitive to the weighting chosen. Only the statistical uncertainties (one standard deviation) for unit weighting are quoted and these may be taken as representative. The interaction constant, it will be noted, is somewhat uncertain and negative, while the harmonic frequency data gave a positive value. Analysis III, where the sums of squares of percentage deviations are minimized, gives force constants closest to the harmonic force constants. Here the larger frequencies with the larger anharmonicity effects are weighted less in the analysis.

(b) Microwave Distortion Constant Data

For H_2S-type molecules one can calculate within the small oscillations approximation, the three symmetry force constants of species A_1 directly from the observed distortion constants τ_{aaaa}, τ_{bbbb}, τ_{cccc}. Information on F_{33} of species B_1, which comes from τ_{abab}, is ambiguous as already noted and was not considered. In all calculations involving the distortion constants, the effective rotational constants A', B', C' have been employed. The results of a least squares analysis which makes use of the distortion data of H_2S and D_2S are summarized in Table 3. Also given are the vibrational frequencies predic-

TABLE 3

Force field from microwave distortion data (H_2S, D_2S)[a]

	I(W=1)	II($W \sim 1/\tau$)	III($W \sim 1/\tau^2$)
F_{11} (md Å^{-1})	3.595±0.5	3.626	3.688
F_{22} (md Å^{-1})	0.394±0.01	0.395	0.398
F_{12} (md Å^{-1})	0.067±0.008	0.069	0.074
Av. Dev. (MHz)	0.59	0.79	1.18
H_2S ν_1 (cm^{-1})	2496	2507	2529
H_2S ν_2 (cm^{-1})	1168	1170	1174
D_2S ν_1 (cm^{-1})	1791[b]	1798	1814
D_2S ν_2 (cm^{-1})	839	840	843

[a] Frequencies calculated from corresponding force field. Observed frequencies (cm^{-1}): 2615, 1183; 1896, 855.

[b] Largest discrepancy about 5.5%.

ted from the derived force constants. The data can be fitted reasonably well and a different weighting has only a small effect on the constants. The interaction force constant is positive as found for the harmonic force field, and the data are least sensitive to the stretching constant F_{11}. The calculated frequencies are in reasonable agreement with the observed values with ν_1 of D_2S having the largest discrepancy. The calculated frequencies improve slightly as the larger τ's are weighted less. This weighting favors the D_2S data. In fact, calculations based only on the D_2S data result in somewhat better predictions of ν_1 and ν_2 of D_2S.

(c) Combined Infrared and Microwave Data

It is apparent that for H_2S the observed infrared and microwave data compliment each other and can be profitably combined. Furthermore, it is possible to explore directly how satisfactory the derived force field actually is for this case. In Table 4 we list the force constants most compatible with both spectral regions. The fit of the data indicates the deviations are much larger than the experimental uncertainties since model errors, as expected, dominate the analysis. As we proceed from weighting I through III, the average deviation of the fit rises and the higher vibrational frequencies and largest τ's fit less well. However, different weighting has a relatively small effect on the derived constants. Weighting II which gives a most reasonable distribution of residuals is perhaps to be favored.

A comparison of the best force fields obtained from the various data is given in Table 5. For the IR & MW entry, F_{33} comes from the observed vibrational frequency data analysis. The IR & MW force constants compare most favorably with the harmonic force field. These results indicate that not

TABLE 4

Combined infrared and microwave force field (H_2S, D_2S)[a]

	I(W=1)	II($W\sim 1$/Obs.)	III($W\sim 1$/Obs.^{2})
F_{11} (md Å^{-1})	3.973±0.020	3.971	3.743
F_{22} (md Å^{-1})	0.404±0.005	0.399	0.398
F_{12} (md Å^{-1})	0.091±0.048	0.081	0.073

		$\Delta\tau_{aaaa}$	$\Delta\tau_{bbbb}$	$\Delta\tau_{cccc}$	$\Delta\nu_1$	$\Delta\nu_2$
I	H_2S	−7.1	−7.6	−0.8	−9.9	−0.3
	D_2S	−0.4	−0.7	−0.1	14.4	5.9
II	H_2S	−5.8	−5.3	−0.8	−9.3	7.0
	D_2S	−0.0	−0.1	−0.1	14.6	11.3
III	H_2S	−3.7	−3.1	−0.3	67.2	8.2
	D_2S	0.6	0.5	0.0	69.3	12.2

[a] Δ = (Obs.—Calc.), τ's in MHz, ν's in cm^{-1}.

TABLE 5

Force constants for H_2S[a]

Symmetry force constants	IR(ω_e)[b]	IR(ω_o)[b]	MW[c]	IR(ω_o) & MW[c]
F_{11} (md Å^{-1})	4.2731	3.807	3.626	3.971
F_{22} (md Å^{-1})	0.4250	0.464	0.395	0.399
F_{12} (md Å^{-1})	0.064	−0.392	0.069	0.081
F_{33} (md Å^{-1})	4.2960	4.005		4.005[d]

Valence bond force constants (md Å^{-1})

	f_r	f_θ	f_{rr}	$f_{r\theta}$
IR(ω_e)	4.2845	0.4250	−0.0114	0.045
IR(ω_o)	3.906	0.464	−0.099	−0.277
IR(ω_o)&MW	3.988	0.399	−0.017	0.057

[a]Weighting $\sim 1/\omega$ and $1/\tau$. [b]H_2S, D_2S, HDS data. [c]H_2S, D_2S data. [d]From IR(ω_o) calculation.

only are the force constants better determined by combining both IR and MW data, but even ignoring rather large anharmonicity effects, a very representative force field is obtained.

MOLECULAR STRUCTURE

The various structures which may be calculated for hydrogen sulfide are listed in Table 6. The uncertainty in the distortion effect correction to the rotational constants leads to essentially a negligible uncertainty in the molecular structure. The spread in the effective bond distance obtained from the three sets of A', B' is only about 5×10^{-6} Å, much smaller than that due to the effects of vibration as illustrated by the various r_o structures obtained. It may be observed that the range in the r_o-bond distance in Table 6 decreases as the mass of the principle vibrating atom increases, however, it is not clear whether the bond length increases or decreases with isotopic substitution. The r_s-structure has also been calculated for comparison as well as the average structure [20] for the ground vibrational state. The latter has been evaluated [14] using the IR & MW force field of Table 5. The replacement of H by D leads to a shortening in the average bond length of 0.004 Å. The residual inertial defects for the average moments of inertia are: $\Delta = 0.0005$ amuÅ^2 for H_2S and $\Delta = -0.0004$ amuÅ^2 for D_2S.

Using the IR & MW force field the vibrational part of the inertial defect may be evaluated [21]. The observed values for H_2S and D_2S are, respectively, 0.0657 and 0.0904 amuÅ^2. The calculated inertial defects are 0.0652 for H_2S and 0.0908 amuÅ^2 for D_2S. The agreement between the calculated and observed inertial defects is quite good.

TABLE 6

Molecular structures of hydrogen sulfide[a]

	H_2S		D_2S	
	r(Å)	θ(deg.)	r(Å)	θ(deg.)
Effective structure[b]				
From				
(I_a^o, I_b^o)	1.3363	92.2	1.3362	92.2
(I_a^o, I_c^o)[c]	1.3484	93.2	1.3446	92.9
(I_b^o, I_c^o)[d]	1.3492	91.1	1.3456	91.4
Range	0.0129	2.1	0.0094	1.5
Substitution structure				
	1.3376[e]	91.6[e]	1.3362[f]	92.2[f]
Average structure[g]				
	1.3518	92.13	1.3474	92.11
Equilibrium structure				
	1.3356[h]	92.11[h]	1.3362[i]	92.06[i]

[a] Conversion factor for the moments of inertia 505376 amu Å^2 MHz.
[b] Obtained from different pairs of moments of inertia.
[c] Equivalent to I_a^o, $I_b^o + \Delta$.
[d] Equivalent to I_b^o, $I_a^o + \Delta$.
[e] Calculated from H_2S, HDS data assuming a-coordinate of sulfur is zero and using the center of mass condition.
[f] Calculated from H_2S, D_2S data assuming a-coordinate of sulfur is zero and using the center of mass condition
[g] Calculated from IR&MW force field of Table 5.
[h] Using the vibrational corrections from the infrared study of ref. 4.
[i] One dimensional model calculation.

To evaluate the important equilibrium structure requires a knowledge of the vibrational corrections to the rotational constants A', B', C'. If the infrared results [4] for the vibrational corrections are used, the equilibrium structure calculated (see Table 6) is in agreement with the infrared results obtained previously [4], $r_e = 1.3356$ Å and $\theta_e = 92°07'$.

It is also interesting to evaluate the equilibrium structure from the average structure data assuming a one-dimensional oscillator approximation [14, 22]. For a diatomic molecule, the difference between $\langle r \rangle$ and r_e has the following reduced mass dependence

$$\langle r \rangle - r_e \sim \mu^{-\frac{1}{2}} \tag{4}$$

Making use of the average structure data of H_2S and D_2S in Table 6, and treating the S—H and S—D bonds as one-dimensional oscillators, the equilibrium structure has been calculated via eqn. (4) and is given in Table 6. In

the calculation of θ_e, the same reduced mass dependence has been assumed for $<\theta>$ as for $<r>$. This r_e bond distance is some 0.0006 Å larger than the more accurate value obtained from the infrared study [4].

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