Rotational spectrum of the weakly bonded C₆H₆–H₂S dimer and comparisons to C₆H₆–H₂O dimer

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Two symmetric-top, $\Delta J=1$ progressions were observed for the C₆H₆–H₂S dimer using a pulsed nozzle Fourier transform microwave spectrometer. The ground-state rotational constants for C₆H₆–H₂S are $B=1168.53759(5)$ MHz, $D_J=1.4424(7)$ kHz and $D_{JK}=13.634(2)$ kHz. The other state observed has a smaller B of 1140.580(1) MHz but requires a negative $D_J = -13.80(5)$ kHz and higher order (H) terms to fit the data. Rotational spectra for the isotopomers C₆H₆–H₂³⁴S, C₆H₆–H₂³³S, C₆H₆–HDS, C₆H₆–D₂S and ¹³CC₅H₆–H₂S were also obtained. Except for the dimer with HDS, all other isotopomers gave two progressions like the most abundant isotopomer. Analysis of the ground-state data indicates that H₂S is located on the C₆ axis of the C₆H₆ with a c.m. (C₆H₆)–S distance of 3.818 Å. The angle between the a axis of the dimer and the C_{2v} axis of the H₂S is determined to be 28.5°. The C₆ axis of C₆H₆ is nearly coincident with a axis of the dimer. Stark measurements of the two states led to dipole moments of 1.14(2) D for the ground state and 0.96(6) D for the other state. A third progression was observed for C₆H₆–H₂S which appear to have $K \neq 0$ lines split by several MHz, suggesting a nonzero projection of the internal rotation angular momentum of H₂S on the dimer a axis. The observation of three different states suggests that the H₂S is rotating in a nearly spherical potential leading to three internal rotor states, two of which have $M_j=0$ and one having $M_j=\pm 1$, M_j being the projection of internal rotational angular momentum on to the a axis of the dimer. The nuclear quadrupole hyperfine constant of the ³³S nucleus in the dimer is determined for the two symmetric-top progressions and they are -17.11 MHz for the ground state and -8.45 MHz for the other state, consistent with the assignment to two different internal-rotor states. The ¹⁷O quadrupole coupling constant for the two states of C₆H₆–H₂O were measured for comparison and it turned out to be nearly the same in the ground and excited internal rotor state, -1.89 and -1.99 MHz, respectively. The rotational spectrum of the C₆H₆–H₂S complex is very different from that of the C₆H₆–H₂O complex. Model potential calculations predict small barriers of 227, 121, and 356 cm^{–1} for rotation about a , b and c axes of H₂S, respectively, giving quantitative support for the experimental conclusion that H₂S is effectively freely rotating in a nearly spherical potential. For the C₆H₆–H₂O complex, the corresponding barriers are 365, 298 and 590 cm^{–1}.

I. INTRODUCTION

This study of the benzene–H₂S dimer touches on two broader related aspects of structural chemistry: (1) the “hydrogen bonding” in second row hydrides and (2) their mo-

bility in small clusters. The nature of hydrogen bonding involving the second row hydrides has attracted much interest recently.^{1–3} The greater importance of dispersive forces in HCl dimer relative to first row hydride clusters has been pointed out,³ and as well, electrostatic contributions have been shown to be involved in the potentials of a series of HCl-containing dimers.⁴ There is clearly an interesting juxtaposition of contributing effects at work, and further studies of clusters containing second row hydrides such as H₂S

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TABLE I. Observed and fitted rotational transition frequencies^a for the C₆H₆–H₂S isotopomers in the ground state.

<i>J</i>	Transition <i>J'</i>	<i>K</i>	C ₆ H ₆ –H ₂ S		C ₆ H ₆ –HDS		C ₆ H ₆ –D ₂ S		C ₆ H ₆ –H ₂ ³⁴ S	
			Obs	Res	Obs	Res	Obs	Res	Obs	Res
0	1	0	2337.0688	−0.6	2320.1722	1.3	2288.7175	12.8	2263.2000	−
1	2	1	4674.0516	1.9	4640.2371	−6.2	4577.3141	8.6	4526.3169	1.2
		0	4674.1023	−1.9	4640.3047	−1.2	4577.3690	−2.8	4526.3657	−2.0
2	3	2	7010.7428	0.2	6959.9870	−6.2	6865.5700	4.0	6789.1568	−0.9
		1	7010.9844	0.4	6960.2736	−1.7	6865.8656	1.4	6789.3919	0.5
		0	7011.0687	−1.1	6960.3698	0.4	6865.9641	0.5	6789.4692	−0.1
3	4	3	9346.9499	0.0	9279.1967	0.2	9153.2454	−4.1	9051.5364	−1.0
		2	9347.4958	0.6	9279.8250	1.5	9153.9116	−0.6	9052.0572	0.3
		1	9347.8229	0.5	9280.2018	2.0	9154.3108	1.0	9052.3689	0.4
		0	9347.9316	0.1	9280.3271	1.9	9154.4430	0.6	9052.4730	0.6
4	5	4	11682.4726	−0.8	11597.6281	−1.2	11440.1109	−8.7	11313.2675	1.2
		3	11683.4273	−0.4	11598.7280	1.3	11441.2762	−3.2	11314.1755	0.2
		2	11684.1103	0.9	11599.5129	2.4	11442.1087	0.9	11314.8245	−0.1
		1	11684.5190	0.6	11599.9822	1.5	11442.6067	1.8	11315.2141	−0.1
		0	11684.6549	0.1	11600.1391	1.6	11442.7715	1.0	11315.3440	0.0
5	6	5	14017.1142	−0.6	13915.0563	11.5	13725.9375	−2.4	—	—
		4	14018.5867	−0.6	13916.7654	4.6	13727.7318	2.6	13575.5578	−0.3
		3	14019.7321	−0.4	13918.0777	0.1	13729.1219	0.9	13576.6484	−0.5
		2	14020.5500	−0.5	13919.0181	0.0	13730.1153	0.2	13577.4274	−0.6
		1	14021.0417	0.4	13919.5820	−0.4	13730.7111	−0.5	13577.8954	−0.1
		0	14021.2052	0.3	13919.7702	−0.4	13730.9103	−0.1	13578.0521	0.8
6	7	6	16350.6783	2.3	16231.2884	0.7	—	—	—	—
		5	16352.7748	−0.8	16233.7070	5.1	16013.0293	4.0	—	—
		4	16354.4919	−1.5	16235.6780	1.0	16015.1150	2.1	—	—
		3	16355.8290	−0.5	16237.2165	3.2	16016.7378	1.2	—	—
		2	16356.7840	0.1	16238.3083	−2.3	16017.8958	−0.6	—	—
		1	16357.3571	0.6	16238.9661	−2.9	16018.5902	−2.1	—	—
		0	16357.5479	0.5	16239.1859	−2.6	16018.8224	−1.9	—	—

^aObserved frequencies in MHz and residues in kHz. The standard uncertainties in measured frequencies are 0.1 kHz.

should help highlight similarities and differences in interaction elements, especially with respect to first row hydride clusters.

In these studies the internal dynamics of cluster structures are a sensitive guide to important features of the intermolecular potential surface (IPS). This is evident in the comparative work on the five smallest Ar_{*m*}(H₂O)_{*n*} clusters.^{5–8} The results so far imply that the basic structures found are simply the closest packing of spheres. The knobby water in effect becomes spherical via its high mobility and large amplitude motions in the clusters. Three different dynamic states of the H₂O have been identified in them depending on the IPS: (1) nearly free internal rotor states; (2) tunneling; and (3) coaxial internal rotation about a framework axis.

The benzene–water dimer is an interesting example of the coaxial internal rotor, examined by several groups^{9–13} in sufficient detail for comparison with the H₂S analog. The spectrum of the parent C₆H₆–H₂O consists of at least three progressions that arise due to complex internal rotor states of H₂O. One of the progressions is that of a simple symmetric top and it correlates with the (0_{0,0}) state of H₂O. The other two progressions were believed to come from one $|m|=1$ internal rotor state and fit to the following equation,⁹ with the two progressions assigned to positive and negative values of the product Km :

$$\nu = 2(J+1)\{B - D_{JK}K^2 - D_{Jm}m^2 - D_{JKm}Km - H_{JKm}m^2K^2\} - 4(J+1)^3(D_J - D_{JJm}m^2). \quad (1)$$

However, there were several anomalies with this interpretation. First, the quality of the fit was poor. The $Km = +J$ line was missing from the progression and an odd line appeared near the $m=0$ symmetric-top progression. Recent Stark measurements and the assignment of a K doublet¹⁰ led to a different interpretation. The two progressions were assigned to (1₀₁) and (1₁₁) states of H₂O. Molecular mechanics in cluster (MMC) calculations¹⁴ estimate the barrier for rotation of H₂O about its *a* and *b* axis to be about 365 cm^{−1} and 298 cm^{−1}, respectively. However, the rotation of H₂O about the C₆ axis of benzene has virtually no barrier and a coupling of this motion with the internal rotor states of free H₂O could possibly excite these states. These features appear to be “real” in nature as similar spectral progressions are observed for Rg–C₆H₆–H₂O sandwich trimers,^{10,15} for Rg = Ne, Ar and Kr. In these trimers, the Rg is shielded from the water so it comes as no surprise that they do little more than change the rotational constants. The substitution of H₂S for H₂O should have a direct, more visible effect on the IPS and rotational properties. Nonetheless the two dimers appear to have the same equilibrium geometric structures according to MMC calculations and the IPS differences express themselves primarily as differences in internal dynamics on which we focus.

II. EXPERIMENT

The rotational spectra of the C₆H₆–H₂S dimers were observed with the Balle–Flygare Fourier transform micro-

TABLE II. Observed and fitted rotational transition frequencies^a for the C₆H₆–H₂S isotopomers in the upper state.

<i>J</i>	Transition <i>J'</i>	<i>K</i>	C ₆ H ₆ –H ₂ S		C ₆ H ₆ –D ₂ S		C ₆ H ₆ –H ₂ ³⁴ S	
			Obs	Res	Obs	Res	Obs	Res
0	1	0	2281.2139	–1.2	2261.233	–	2209.101	–
1	2	1	4562.4577	–1.0	4522.4030	20.2	4418.3518	–
2	3	0	4562.7595	0.9	4522.4710	–1.8	4418.6428	–1.1
		2	6843.1581	–0.6	6783.1820	–4.5	6627.0234	1.2
		1	6844.5052	–0.2	6783.5909	–0.9	6628.3307	–0.2
3	4	0	6844.9481	0.4	6783.7267	–0.1	6628.7605	–0.3
		3	9122.7354	–2.8	9043.3695	–11.5	8834.6172	0.8
		2	9125.7495	0.8	9044.2814	–0.1	8837.5407	2.2
		1	9127.5033	1.3	9044.8224	0.6	8839.2409	–0.4
4	5	0	9128.0789	1.2	9045.0031	1.2	8839.7994	–1.0
		4	11400.5962	–2.1	11302.6996	–3.6	11040.5594	–4.8
		3	11405.9436	3.8	11304.2772	–1.8	11045.7466	5.4
		2	11409.5900	0.1	11305.4070	2.4	11049.2813	0.2
		1	11411.7135	–0.3	11306.0820	2.0	11051.3402	–1.6
5	6	0	11412.4110	0.2	11306.3077	2.6	11052.0174	–0.8
		5	13676.0987	–2.7	13560.8840	–5.8	–	–
		4	13684.5316	11.3	13563.3218	0.7	13252.4130	3.5
		3	13690.6938	–4.3	13565.2165	4.4	13258.3875	–2.8
		2	13694.9039	–8.6	13566.5664	3.5	13262.4678	–4.8
		1	13697.3608	–1.0	13567.3731	–0.2	13264.8469	0.7
		0	13698.1682	3.2	13567.6425	–1.0	13265.6287	3.9
		6	15948.5386	–15.7	15817.6712	–6.6	–	–
6	7	5	15960.9438	39.1	15821.1516	6.9	–	–
		4	15970.3092	–6.3	15823.7943	13.1	–	–
		3	15977.1727	–30.4	15826.1923	4.9	–	–
		2	15981.8747	–16.7	15827.7621	–1.2	–	–
		1	15984.6217	9.9	15828.7018	–7.0	–	–
		0	15985.5239	20.7	15829.0143	–9.7	–	–

^aObserved frequencies in MHz and residues in kHz. The standard uncertainties in measured frequencies are 0.1 kHz.

wave spectrometer described in detail elsewhere.¹⁶ The dimers were formed by supersonic coexpansion of “first run neon” (70% Ne and 30% helium) with a few percent each of C₆H₆ and H₂S. The backing pressure was typically 1.5 atm. The benzene was kept in a bubbler at ambient conditions and ≈3% by volume of the carrier gas was bubbled through it. The D₂S was prepared by bubbling H₂S sequentially through 12 small portions of D₂O (sigma) kept in a reflux coil condenser followed by a dry ice trap to remove any D₂O. This method avoided assignment ambiguities by ensuring that there was no significant amount of HDS present when looking for D₂S clusters. Initially, the whole spectral range studied was searched with H₂S and D₂S separately with benzene. This was followed by searches with HDS, which was prepared by bubbling H₂S through a 1:1 mixture of H₂O and D₂O. The previously seen C₆H₆–H₂S/D₂S lines could be observed along with the now stronger and readily assigned C₆H₆–HDS lines.

All uncertainties quoted are $k=1$ (i.e., one standard deviation) in units of the least significant digit shown.

III. RESULTS

A. Search and assignment

The search for transitions of the benzene(Bz)–H₂S dimer was simplified by our earlier work⁹ on Bz–H₂O which found the symmetry axes of Bz and H₂O to be effectively coaxial with a Bz to H₂O c.m. to c.m. separation, R , of 3.329 Å. For Bz–H₂S, the value of R will certainly be larger.

The increase in R for Bz–H₂S was estimated to be between 0.35 Å and 0.65 Å by comparing the R ’s determined for the H₂O and H₂S complexes with Ar and NH₃. These dimers were chosen as providing possible lower (Ar)^{17,18} and upper (NH₃)¹⁹ limits to increase in R . With this in mind, predictions were made for symmetric top Bz–H₂S rotational spectra assuming R would be greater than 3.68 Å. As discussed later in the paper, R was found to be 3.771 Å from the rotational constants. Once the approximate R was determined for the parent isotopomer, spectra were readily predicted and observed for the other isotopomers. This included the ¹³CC₅H₆–H₂S with the mono ¹³C Bz and Bz–H₂³³S, all from natural abundance.

An early search was made for more $\Delta J=1$ progressions arising from excited internal-rotation states as in Bz–H₂O.^{9,10} The B_0 found initially for the parent species was 1168.5 MHz. A more intense symmetric-top progression was found at lower frequencies with a B_0 of 1140.6 MHz, 28 MHz smaller than the B value for the higher frequency progression. Similar pairs of progressions were found for Bz–D₂S and Bz–H₂³⁴S. Only one progression was found for the Bz–HDS species, which was assigned to the ground state on the basis of the rotational and centrifugal constants. The frequencies observed for the two states of the various species are given in Tables I and II, respectively. The rotational and centrifugal distortion constants determined by fitting the experimental frequencies are given in Table III.

The pattern of the two progressions is that of the usual

TABLE III. Rotational constants for the ground and excited states of $C_6H_6-H_2S$ isotopomers.

Constant	$C_6H_6-H_2^{32}S$	C_6H_6-HDS	$C_6H_6-D_2S$	$C_6H_6-H_2^{34}S$
Ground state				
B (MHz)	1168.53759(5)	1160.0884(2)	1144.3555(2)	1131.60287(6)
D_j	1.4424(7)	1.494(3)	1.569(3)	1.369(1)
D_{jk}	13.634(2)	15.676(6)	16.568(9)	12.986(4)
ND ^a	28	28	27	19
SD ^a (kHz)	0.9	3.3	3.6	0.7
Excited state I				
B (MHz)	1140.580(1)	-	1130.6159(4)	1104.5533
D_j (kHz)	-13.80(5)	-	-0.293(5)	-13.56(2)
D_{jk} (kHz)	75.7(1)	-	22.51(1)	73.64(7)
H_j	-15.3(6)	-	-	-15.5(5)
H_{jk}	125(2)	-	-	125(1)
H_{kj}	-275(3)	-	-	-263(3)
ND ^a	28	-	27	19
SD ^b	11.7	-	6.4	2.6

^aNumber of transitions observed

^bStandard uncertainty of the fit. The numbers in parentheses indicate the uncertainty in the least significant digits of the constants determined.

symmetric top, given by Eq. (1) with $m=0$ and $K=0, \pm 1, \pm 2, \dots, \pm J$, the only difference being the negative sign of D_J for the lower state. Moreover, higher order terms, H_{JK} , H_{KJ} and H_J were required for a reasonable fit, implying significant deviations from the semirigid rotor Hamiltonian. However, this state for $Bz-D_2S$ appears to show stark simplicity in comparison with the H_2S analog. The D_J , though negative, is 50 times smaller and there was no need to include any of the H terms to fit the transitions. We designate the higher frequency component as the ground state and the lower frequency component as an excited tunneling/internal rotor state for the following reasons: (1) The only state observed for $Bz-HDS$ has rotational/centrifugal distortion constants similar to that found for the higher frequency $\Delta J=1$ progression and (2) the lower frequency $\Delta J=1$ progression has a negative D_J , which changes dramatically with isotopic substitution.

During the search for the parent isotopomer, a different third progression was identified. In it, the K degeneracy apparently is lifted giving $2J+1$ components for each $J \rightarrow J+1$ transition, of which only some are observed. This progression of lines also requires only Bz and H_2S to appear and it is most likely from the parent isotopomer. This third progression was first noted about 50 MHz above the ground-state $J=1 \leftarrow 2$ transition of the parent at 4674 MHz in the preliminary search for the $Bz-H_2S$ spectrum. Two components were found at 4723.3890 MHz and 4725.0685 MHz of which the latter is stronger. They are very close to $Bz-Ar$ dimer lines,²⁰ causing some initial confusion. But, once this progression was unambiguously assigned to the $Bz-H_2S$ complex, the series of lines could be seen at each J level. They cannot be assigned as the usual K^2 progression or as an $|m|=1$, free rotor K sequence as observed for a CF_3H-NH_3 complex.²¹ The frequencies found for this third progression are listed in Table IV. So far, this progression could not be fit to any model. The highest frequency lines in this progression appear to be a $K=0$ line and they could be fit as a “linear” top. Results of such a fit are included in Table IV. Here

TABLE IV. List of transitions for the “third progression” of the $Bz-H_2S$ rotational spectrum. The highest frequency line in each J could be fitted as $K=0$ lines and the residue is given in the last column.^a

J	J'	K	Observed (MHz)	res (kHz)
0	1	0	2362.2368	-4.8
1	2	0	4725.0685	-3.5
1	2	-	4723.389	
2	3	0	7089.0610	0.8
2	3	-	7085.7701, 7085.5937	
3	4	0	9454.7283	-4.3
3	4	-	9450.1269, 9448.3827	
		-	9444.8943, 9443.0474	
4	5	0	11822.4849	2.4
4	5	-	11814.7653, 11811.9056	
		-	11806.6868, 11808.0235	
		-	11802.5955, 11796.5955	
5	6	0	14192.5885	-5.2
5	6	-	14179.9479, 14176.2811	
		-	14172.1869, 14168.8081	
		-	14163.0541	
6	7	0	16565.0775	1.6
6	7	-	16545.7929, 16541.5649	
		-	16536.3834, 16531.2744	
		-	16526.8881	

^aThe fitted parameters are $B=1181.0715(9)$ MHz, $D_j=-24.7(3)$ kHz and $H_j=-21.8(2)$ Hz. The standard uncertainties in measured frequencies are 0.1 kHz. The numbers in parentheses indicate the uncertainty in the least significant digits of the constants determined.

again, the D_J is negative and it is 17 times larger than that of the ground state. The three progressions are compared in Fig. 1 which gives a stick diagram for the $J=3 \leftarrow 4$ region of the parent dimer along with that of the $Bz-H_2O$ dimer.

In our work on the $Bz-H_2O$ system,⁹ it proved useful to observe the mono- ^{13}C isotopomer at natural abundance. This species is a slightly asymmetric top ($\kappa=-0.95$) for which the $m=0$ internal rotor state was characterized. However, the greater complexity of the higher K transitions in the $|m|=1$ progression made the assignment very difficult for $|m|=1$ lines.²² But, in $Bz-H_2S$, the simpler K^2 sequences observed for the two states suggest that there should be two sets of transitions for mono- $^{13}C-Bz-H_2S$ both having a slightly asymmetric-top spectrum. It was indeed true and the expected $2J+1$ components were observed for each $J \rightarrow J+1$ transition for the two states. The frequencies and their assignments along with the fitted parameters are given in Table V. The centrifugal distortion constants for the two states closely resemble those of the ground and excited states of the parent isotopomer.

B. Hyperfine structure (hfs)

The hfs of $Bz-H_2O$ and $Ar-H_2S$ dimers^{9,18} were useful in augmenting our understanding of their intricate details, and the treatment of it is largely transferable to the hfs of $Bz-H_2S$. The hyperfine interactions most likely to be helpful are those in the H_2S and its isotopomers, namely the proton-proton dipole-dipole interactions and the D and ^{33}S quadrupole interactions. In this event, the Hamiltonians for the sundry isotopic species consist of standard terms from the expressions for rotational, spin-spin and quadrupole interactions:

FIG. 1. Stick diagram of the $J=3 \leftarrow 4$ spectra for $\text{Bz-H}_2\text{O}$ and $\text{Bz-H}_2\text{S}$ complexes. For the latter, three well-resolved progressions are clearly evident. For $\text{Bz-H}_2\text{O}$, there are more lines than what could be fit to 2 progressions.

$$H = H_R + H_{SS} + H_Q.$$

Matrix elements are calculated for the basis set

$$I_1 + I_2 = I \quad \text{and} \quad I + J = F,$$

with subscripts for the one or two nuclei in question. Matrix elements off-diagonal in J and K were ignored, as was the spin-rotation. The spin-spin and nuclear quadrupole hf tensors are designated as D_{gg} and χ_{gg} , respectively, and the

TABLE V. Observed and fitted transition frequencies for the nearly symmetric $^{13}\text{CC}_5\text{H}_6\text{-H}_2\text{S}^{32}\text{S}$ dimer and the resultant rotational constants.

Transition		Observed (MHz) ground state	Res. kHz	Observed (MHz) excited state	Res. kHz
1_{11}	2_{12}	4644.5251	-0.3	4534.4428	6.8
1_{01}	2_{02}	4649.7790	2.7	4539.5823	0.4
1_{10}	2_{11}	4654.9455	1.6	4544.1548	-7.2
2_{12}	3_{13}	6966.6933	-1.2	6802.4519	3.6
2_{02}	3_{03}	6974.5484	0.2	6810.1407	0.0
2_{21}	3_{22}	6974.2740	0.4	6808.4220	-8.5
2_{20}	3_{21}	6974.3189	-3.3	6808.4810	8.7
2_{11}	3_{12}	6982.3216	-0.7	6817.0335	-3.8
3_{13}	4_{14}	9288.7523	0.8	9071.3761	-6.3
3_{31}	4_{32}	9298.3568	0.3	9076.4777	0.0
3_{30}	4_{31}	9298.3568	0.2	9076.4777	-0.0
3_{22}	4_{23}	9298.8614	-0.1	9079.4011	-0.6
3_{21}	4_{22}	9298.9848	1.2	9079.5066	0.6
3_{03}	4_{04}	9299.1800	-0.3	9081.5895	0.1
3_{12}	4_{13}	9309.5878	-0.6	9090.8405	6.2
A		2837(6) MHz		2837 (fixed) ^a	
B		1165.0628(2) MHz		1137.222(3) MHz	
C		1159.8539(2) MHz		1132.359(3) MHz	
D_j		1.425(3) kHz		-13.5(3) kHz	
D_{jk}		13.457(8) kHz		73.9(7) kHz	
$H_j -$				-15(8) Hz	
$H_{jk} -$				115(26) Hz	
$H_k -$				-272(39) Hz	

^aVarying A gives $A = 2747(121)$ and similar residues. The standard uncertainties in measured frequencies are 0.1 kHz. The numbers in parentheses indicate the uncertainty in the least significant digits of the constants determined.

TABLE VI. Hyperfine structure observed for Bz—HDS in the $J=0 \leftarrow 1$ transition.^a

F	F'	Observed (MHz)	Res. (kHz)
1	0	2320.1174	0.2
1	2	2320.1662	−0.5
1	1	2320.2000	0.3

^aThe χ_{aa} from the fit is 110(1) kHz and the line center is 2320.1722(4) MHz. The standard uncertainties in measured frequencies are 0.1 kHz. The numbers in parentheses indicate the uncertainty in the least significant digits of the constants determined.

$g=a,b,c$ coordinates refer to the dimer inertial axes, in which a is usually the benzene six-fold axis. The reported frequencies were fitted with H_R taken to be the semirigid symmetric or near-symmetric top. The analysis is very similar to those reported for the Bz—H₂O and Ar—H₂S dimers. A notable difference is that the dipole–dipole and quadrupole coupling constants, $D_0(\text{H–H})$ and χ_0 (D), are appreciably smaller in H₂S than in H₂O. As usual, it was assumed that the cluster formation does not perturb the monomers appreciably.

It is seen in Tables I and II that two states were found for all symmetric isotopic species, i.e., for the isotopomers other than HDS. The doubling of the states is attributable to a dynamic process interchanging the two identical nuclei, either the two protons or the two deuterons. This might be by tunneling or by “free” rotation of the H₂S or D₂S. Tunneling states have hyperfine constants that are very similar but for “free” rotation the hyperfine constants could be very different.

1. Bz—H₂S

It was noted earlier¹⁸ for Ar—H₂S that the long H—H distance (1.923 Å) in H₂S leads to a D_0 of ~ 35 kHz which is too small for the H₂S dipole–dipole splittings to be well resolved. This difficulty is increased in Bz—H₂S by the weak H—H interactions in Bz, resulting in an unresolved $J=0 \leftarrow 1$ line width of 5 kHz, about triple the normal line width. So, it is not surprising that a careful inspection of the $J=0 \leftarrow 1$ transitions at 2281.214 MHz and 2337.069 MHz for the ground and the excited states of the parent species revealed no hf splittings.

2. Bz—HDS

The hyperfine splitting due to the quadrupole coupling of D in HDS was well resolved in the $J=0 \leftarrow 1$ transitions. Table VI lists the three hyperfine transitions observed which are fitted to a line center and the $\chi_{aa}(D)$, the projection of the D quadrupole interaction tensor on the dimer’s inertial a -axis. The fit gives $\chi_{aa}(D)$ to be 110(1) kHz. For free HDS, the diagonal components of the D quadrupole interaction are 153.7 kHz, −65.3 kHz, and −88.4 kHz for χ_{xx} , χ_{yy} and χ_{zz} , respectively.²³ The principal axis (x) is within 1° of the D—S bond axis. The $\chi_{aa}(D)$ of 110(1) kHz is taken to be the projection of χ_{xx} on to the dimer a axis. With these considerations, the average angle θ between the D—S bond axis and the a inertial axis is obtained by the following relation:

TABLE VII. Nuclear quadrupole coupling constants (MHz) for ³³S and ¹⁷O in Bz—H₂X and Ar—H₂X complexes.^a

	Ar (lower)	Ar (upper)	C ₆ H ₆ (lower)	C ₆ H ₆ (upper)
H ₂ O ^b	−4.222(9)	−1.211(9)	−1.994(1)	−1.890(4)
H ₂ S ^c	−7.849(3)	−17.364(2)	−17.11	−8.45

^aUpper and lower imply higher and lower frequencies. For Ar—H₂S, the lower state is the ground state and for the other three complexes, the upper state is the ground state. The numbers in parentheses indicate the uncertainty in the least significant digits of the constants determined.

^bFor Ar—H₂¹⁷O, the data are from Ref. 26. For Bz—H₂¹⁷O, the three lines for both $J=0 \leftarrow 1$ transitions were fit to the line centers and coupling constants. The line center for the lower state is 3849.4542(5) MHz and that for the upper state is 3873.9092(1) MHz.

^cFor Ar—H₂³³S, the data are from Ref. 18. For Bz—H₂³³S, the coupling constants are determined from the spacing between the two strong lines observed. For the lower states, the transition frequencies are 11226.9598 MHz and 11227.2532 MHz. The upper state transitions were much weaker and the uncertainty in the quadrupole coupling constant could be much larger.

$$\chi_{aa} = (\chi_{xx}/2) \langle 3 \cos^2 \theta - 1 \rangle. \quad (2)$$

This leads to a θ value of 26° compared to 34° for the Bz—HDO complex.⁹

3. Bz—H₂³³S/Bz—H₂¹⁷O

The ³³S and ¹⁷O quadrupole coupling constants in the Bz—H₂X complexes can give some useful information about the dynamic state of the H₂X in the complex. Our earlier work on Bz—H₂O did not include the ¹⁷O isotopomer and it has been observed during this study. For Bz—H₂¹⁷O, the hyperfine constant was determined from the $J=0 \leftarrow 1$ transitions. For Bz—H₂³³S, it was determined from the $J=4 \leftarrow 5, K=0$ transitions, which gives a doublet of comparable intensity.²⁴ The ¹⁷O/³³S hyperfine constants determined from the spectra for Ar—H₂X and Bz—H₂X (X=O or S) are given in Table VII. For Ar—H₂S, the ³³S isotopic spectra clearly revealed that the two observed states have very different nuclear quadrupole coupling constants, consistent with the assignment of the two states to two different internal-rotor states of the complex.¹⁸ Interestingly, it appears that quadrupole hyperfine constants observed for Ar—H₂S and Bz—H₂S are nearly the same (−8 and −17 MHz). In Ar—H₂S, the ground state has a smaller rotational constant than the excited state but for Bz—H₂S it is the opposite. For Bz—H₂¹⁷O, the quadrupole coupling constants for the two states are similar in magnitude (−1.99 and −1.89 MHz) unlike in the other three complexes considered here.

C. Dipole moment

Dipole moments for the two symmetric-top states were measured using the “Stark cage” described in detail in Ref. 10. Analyzing the Stark splittings was straightforward, with the $K \neq 0$ lines showing a first-order splitting dependent on J , K and M_J .²⁴

$$\Delta \nu = 2 \left(\frac{\mu \epsilon}{h} \right) \frac{KM_J}{J(J+1)(J+2)}. \quad (3)$$

TABLE VIII. Electric dipole moment as measured from Stark splitting.^a

K	Ground state	Excited state
$J=4 \leftarrow 5$		
1	$3.80(7) \times 10^{-30}$ C m [1.14(2) D]	$3.0(1) \times 10^{-30}$ C m [0.89(3) D]
2	$3.8(1) \times 10^{-30}$ C m [1.14(4) D]	$3.01(2) \times 10^{-30}$ C m [0.902(7) D]
3	-	$3.05(3) \times 10^{-30}$ C m [0.915(8) D]
$J=5 \leftarrow 6$		
1	-	$3.32(2) \times 10^{-30}$ C m [0.994(7) D]
2	$3.796(3) \times 10^{-30}$ C m [1.138(1) D]	$3.34(3) \times 10^{-30}$ C m [1.00(1) D]
3	$3.79(3) \times 10^{-30}$ C m [1.137(8) D]	$3.34(3) \times 10^{-30}$ C m [1.00(1) D]
4	$3.84(7) \times 10^{-30}$ C m [1.15(2) D]	$3.40(3) \times 10^{-30}$ C m [1.02(1) D]
5	$3.84(3) \times 10^{-30}$ C m [1.15(1) D]	-
$J=6 \leftarrow 7$		
1	-	$3.3(1) \times 10^{-30}$ C m [0.99(3) D]
2	$3.7(1) \times 10^{-30}$ C m [1.12(3) D]	-
3	$3.76(2) \times 10^{-30}$ C m [1.126(5) D]	-
4	$3.87(3) \times 10^{-30}$ C m [1.16(1) D]	-
Average	$3.80(7) \times 10^{-30}$ C m [1.14(2) D]	$3.2(2) \times 10^{-30}$ C m [0.96(6) D]

^aThe standard uncertainty (Type B, $k=1$) covers the variation between different m states. For the excited state it appears like there is a J dependency in a dipole moment with the $J=4 \leftarrow 5$ data slightly different from the rest.

Here, $\Delta\nu$ is the Stark splitting, μ is the electric dipole moment and ε is the applied electric field. The Stark effect on several K transitions in the $J=4 \leftarrow 5$, $5 \leftarrow 6$ and $6 \leftarrow 7$ spectra were analyzed. The results are given in Table VIII. The dipole moment for the ground state is $3.80(7) \times 10^{-30}$ C m [1.14(2) D] and that for the excited symmetric-top state is $3.2(2) \times 10^{-30}$ C m [0.96(6) D].

IV. DISCUSSION

A. Structural analysis

The rotational spectra for all the Bz-H₂S isotopomers (except the mono ¹³C Bz) are observed to be that of a symmetric top. This suggests that the H/D in the H₂S isotopomers do not contribute to the moment of inertia along the a axis of the dimer. This is exactly what was observed in the Bz-H₂O dimer.⁹ There, it was concluded that the H₂O is nearly freely rotating, with a near-zero reduced barrier height, $s = V_6/9F$. Here, $F = A(\text{top}) + A(\text{frame})$, where A is a rotational constant and the torsional potential V_6 is the six fold barrier. In such cases, the effective A rotational constant for the ground state is that of the frame.²⁵ For Bz-H₂O, the excited state appeared to have a spectrum similar to that predicted by internal rotation theory. However, for Bz-H₂S both the observed states have clear symmetric-top spectra. These complications do affect the structural analysis from the rotational constants. Hence, we limit ourselves to only the ground-state rotational constants in deriving structural parameters for the complex.

Due to the similarities in the rotational spectra of the ground-state Bz-H₂O and Bz-H₂S complexes, we follow closely the structural analysis of the former here. The structural parameters considered are the orientation of the H₂S with respect to the benzene ring (the distance, R , between the centers of masses of the two binding partners and the angle β between the C_2 axis of H₂S and the a axis of the dimer) and the average tilt γ of benzene from having its plane perpendicular to the a axis (see Fig. 3 in Ref. 9). The

orientation of H₂S will need another angle to be specified, namely the angle between the plane of the H₂S molecule and the a axis of the dimer. Within our model, this angle is indeterminate.

From the rotational constants of the H₂S, HDS, D₂S and H₂³⁴S isotopomers it is clear that one of the H/D is pointing towards the benzene. The difference in B between H₂S and HDS complexes is ≈ 8 MHz compared to the difference in B between HDS and D₂S of ≈ 16 MHz, i.e., substituting the second H by D leads to a larger change in B which implies that it is further away from the c.m. compared to the first H. Due to the significant differences that arise in the zero point motions on H/D substitution, in general H/D substitution analysis does not give accurate results. However, for the Bz-H₂O complex, these numbers are 38 and 44 MHz, respectively.

With the H₂³⁴S data, the position of the S along the a axis, a_S , is readily determined as $\Delta I_b = \mu_s \times a_S^2$, where ΔI_b is the change in the parent's moment of inertia on ³⁴S substitution and μ_s is the reduced mass for the substitution, $M\Delta m/(M + \Delta m)$.²⁴ This analysis gives a_S to be 2.683 Å. Such an analysis with Bz-HDS, though less reliable, gives a_H to be 1.777 Å. For the Bz-H₂O, due to the symmetric-top nature, we used a modified multiple off-axis substitution analysis with D₂O to get a better estimate of a_H .⁹ Using the same method, a_H is determined to be 1.877 Å for the Bz-H₂S dimer. The difference of 0.806 Å between a_S and a_H in the complex, is the projection of H₂S altitude, 0.918 Å, on to the a axis. This leads to a projection angle β of 28.5° compared to 37° calculated similarly for the Bz-H₂O complex.

A substitution analysis with the mono ¹³C Bz and the parent isotopomers data, can give both a_C and b_C .²⁴ This value of b_C could be used to infer the projection angle γ of the benzene plane. The calculated value of b_C is 1.403 Å, which is slightly larger than that in the free benzene, 1.396 Å. This implies that the C_6 axis of benzene is virtually co-

TABLE IX. Change in B between the ground state and the excited tunneling/internal-rotor states for Ar/Bz- H_2X .^a

H_2X	Bz	Ar
H_2O	13.1	76.1
D_2O	29.7	66.7
H_2^{18}O	11.4	63.9
H_2S	28.0	-44.1
D_2S	13.7	-4.7
H_2^{34}S	27.0	-44.8

^aIn MHz. Bz- H_2O data from Ref. 9; Ar- H_2O from Ref. 26; Ar- H_2S from Ref. 18; Bz- H_2S from this work.

incident with the a axis of the dimer because any tilt would reduce the b_C . The a_C value then is $a(\text{Bz})$, i.e., the distance of Bz on the a axis away from the c.m. of the dimer. It is calculated to be 1.135 Å. With this value, the Bz-S distance is calculated to be 3.818 Å. The a_S value can be converted to $a(\text{H}_2\text{S})$, the distance between the c.m. of the dimer and the c.m. of H_2S using the projection angle β .⁹ The R is given by $a(\text{Bz}) + a(\text{H}_2\text{S})$, and is calculated to be 3.771 Å compared to 3.329 Å for Bz- H_2O .

The dipole moment measured for the ground state of $3.80(7) \times 10^{-30}$ C m [1.14 D] is significantly larger than the 3.26×10^{-30} C m [0.978 D]²³ dipole moment of H_2S . Considering the fact that the H_2S is tilted by 28° from the a axis, the contribution from the monomer is reduced to 2.84×10^{-30} C m [0.85 D]. It implies that there is appreciable polarization in the dimer, $\approx 1.0 \times 10^{-30}$ C m [0.3 D]. It can be compared to the induced polarization of 1.7×10^{-30} C m [0.5 D] in Bz- H_2O .¹⁰ For the excited symmetric-top state, the dipole moment measured is 3.2×10^{-30} C m [0.96 D]. If one assumes that the polarization in this state is similar to that of the ground state, the angle between the C_2 axis of H_2S and the a axis of the dimer is calculated to be about 45° . Structural evaluations based on the rotational constants for the excited symmetric-top state is likely to be affected as this state is perturbed by tunneling/internal rotation. Hence, the geometry predicted by the dipole moment is preferred.

B. Dynamical analysis

The differences in the rotational constant, B , between the two states observed for Ar- H_2X and Bz- H_2X ($X = \text{O/S}$) and its isotopomers are listed in Table IX. For Bz- H_2O , the B for the $|m|=1$ state is that calculated from the $K=0$ state which is unambiguously identified.^{9,10} It offers an interesting summary. For a Bz- H_2O complex, these differences are 13 and 28 MHz for the H_2O and D_2O but for the Bz- H_2S complex, the numbers are almost the same but they are opposite with 28 and 14 MHz for H_2S and D_2S . The H_2^{18}O and H_2^{34}S complexes gave results comparable to the parent isotopomer. Thus, there is a factor of 2 difference between the protonated and deuterated complexes. For comparison, in the Ar- H_2O complex, the difference in B between the two states observed are 76, 67 and 64 for H_2O , D_2O and H_2^{18}O , with the latter two showing similar behavior.²⁶ The situation for Ar- H_2S is more complicated due to the very floppy nature of the IPS,²⁷ and the ground state had a smaller B than the excited rotor state, as implied

TABLE X. Structural data from the experiment and MMC calculations.^a

Parameter	$\text{C}_6\text{H}_6\text{-H}_2\text{S}$		$\text{C}_6\text{H}_6\text{-H}_2\text{O}$	
	Expt.	MMC	Expt.	MMC
$R(\text{\AA})$	3.771	3.938	3.329	3.266
$\beta(^{\circ})$	28.5	47.0	37.0	53.5
$\gamma(^{\circ})$	≈ 0	0	≈ 0	0
Θ	26	0	34	0
Binding energy (cm^{-1})	-	615	-	1303

^a β is the angle between C_2 and the a axis, γ is the tilt angle of the benzene plane from the bc plane and θ is the angle between the OD bond and the a axis in the Bz-HDX complex. R is the c.m.-c.m. distance. MMC parameters are for the equilibrium structure and the experimental parameters are for the ground state vibrationally averaged structure.

by the negative signs in Table X. These assignments are supported by the ^{33}S quadrupole coupling constants reported and they are discussed next.

The ^{33}S nuclear quadrupole coupling constants measured for the two pairs of states of Ar/Bz- H_2S are nearly the same, i.e., the upper state of Bz- H_2S and the lower state of Ar- H_2S (both assigned to the corresponding ground state) have $\chi_{aa} \approx -8$ MHz. Similarly the second state observed for both these complexes have $\chi_{aa} \approx -17$ MHz. It is likely that the internal rotor states involved in these two complexes are related. On the contrary, Ar- H_2O and Bz- H_2O have internal rotor states that are distinctly different. The $\chi_{aa}(^{17}\text{O})$ for the two states in Bz- H_2O were virtually identical (-1.89 MHz and -1.99 MHz) but in Ar- H_2O they were very different (-1.21 and -4.22 MHz). Interestingly, Ar₂-(H_2^{17}O) also gave results nearly identical to that of Ar-(H_2O), giving strong evidence to the similarities of the internal-rotor states of H_2O in the Ar_m-(H_2O) complexes.⁶

For both Bz- H_2X complexes, there was evidence for a third state from the rotational spectra. In the case of a Bz- H_2O complex, the third state is not properly understood yet, but clearly there were more than $2J+1$ lines other than the well-characterized symmetric-top progression. In any case, three progressions were attributed to three different $J=1$ rotational states of H_2O . For Bz- H_2S , there were three clearly identifiable progressions, two of which gave symmetric-top spectra, with no internal angular momentum ($Kl=0$). The third-progression appears to have the K degeneracy split, characteristic of a vibrational/tunneling state with internal angular momentum ($Kl \neq 0$). The roughly 3:1 relative intensities of the two $Kl=0$ sets lead us to assign one of these sets to a triplet H_2S nuclear spin state and the other to a singlet nuclear spin state. The $Kl \neq 0$ state is significantly weaker and only one H_2S nuclear spin component is observed, and its identity is not determined explicitly.

We consider three different internal rotation models to rationalize the observed results. Only one picture, that in which the H_2S subunit is in a nearly spherical potential is consistent with the observations. In all cases, for an ≈ 1 K molecular beam, only internal-rotor states which correlate with the lowest energy monomer state of each of the two spin modifications of H_2S will have a large population. The monomer states of interest are a 0_{00} state with a singlet nuclear spin function and the 1_{01} state with a triplet nuclear

spin function. Because of the M_J degeneracy of the 1_{01} state, two dimer internal-rotor states correlate to this monomer state. One of these states correlates to the $M_j = \pm 1$ component of the monomer 1_{01} state and the other state correlates with the $M_j = 0$ component of the monomer 1_{01} state. Here, we take M_j to be the free-rotor limit projection of the monomer rotational angular momentum j , onto the a inertial axis of the complex.

The first model assumes that Bz-H₂S has a strong hydrogen bond with its C_2 axis nearly coincident with the complex a axis and H₂S has free internal rotation about the a axis. In this case, the 0_{00} monomer state correlates to the lowest energy $m=0$ internal-rotor state while the 1_{01} state correlates to the lowest energy $|m|=1$ internal-rotor state. Here m takes on the role of the internal/vibrational angular momentum l . The $|m|=1$ state is metastable, and collisional relaxation of $|m|=1$ to $m=0$ is nuclear spin forbidden. This is similar to the CF₃H-NH₃ complex in which the $m=0$ state gives a simple symmetric-top spectrum and the $|m|=1$ state gives a progression of lines from $mK = +J$ to $mK = -J$ as expected from Eq. (1).²¹ However, this is contrary to the observation of three distinct progressions. The Bz-H₂O dimer initially appeared to fit this model but the observation of more lines later on showed that it is also more complicated.

The second model assumes that Bz-H₂S is analogous to NH₃-H₂S, with one proton hydrogen bonded to N and internal rotation of the H₂S by motion of the nonbonded H about the N-H-S axis. If one assumes now that there is no interchange tunneling occurs for the H₂S protons, both singlet and triplet spin modifications of H₂S correlate to the same internal rotor state of the complex, i.e., the protons are not equivalent anymore. Thus, one expects to see one intense series with $m=0$. The $|m|=1$ series is estimated to be 9 cm⁻¹ higher in energy, and is no longer metastable with respect to collisional relaxation to $m=0$.

If the interchange of H₂S protons are allowed, as observed in NH₃-H₂S, then the $m=0$ and $|m|=1$ states will each split into a singlet and triplet component. For Bz-H₂S, this accounts for the two $Kl=0$ states, but does not account for the observation of only one $Kl \neq 0$ state. Moreover, the large difference in the B values between the two $Kl=0$ progressions and the observation of very different ³³S quadrupole coupling constants are not reasonable for such a tunneling motion. We note that for NH₃-H₂S, the B values for the symmetric and antisymmetric components of the $m=0$ state are virtually identical, within 1 MHz of each other.¹⁹

The third and most reasonable model assumes that the H₂S is rotating in a nearly spherical potential. This gives rise to three internal-rotor states, ($0_{00}, M_j=0$), ($1_{01}, M_j=0$) and ($1_{01}, M_j=\pm 1$). The two $M_j=0$ states have no internal angular momentum along the a inertial axis and thus give rise to the two $Kl=0$ sets of transitions. The $M_j=\pm 1$ component is associated with the $Kl \neq 0$ set of transitions. The large differences in B between the three sets of transitions is consistent with this picture, since each internal rotor state should have a distinctly different orientation of the H₂S unit within the complex. Moreover, the observation of different hyperfine coupling constants for the ³³S for the two $Kl=0$ states

FIG. 2. A depiction of the MMC equilibrium structure of Bz-H₂S and Bz-H₂O. The optimized geometrical parameters are given in Table X. The benzene plane is taken to define an x - y plane for a discussion of the potential surface, with the y -axis bisecting C-C bonds in the benzene ring. The z coordinate is the H₂X molecule's elevation above the benzene plane. Specifically, it is the distance from the plane to the c.m. (H₂X). The (x, y, z) origin is the center of the benzene molecule (see Figs. 5 and 6).

and the dipole moment measurements described earlier are also consistent with this picture. Neither of these measurements could be made for the third progression. Molecular mechanics in clusters (MMC)¹⁴ calculations on the Bz-H₂S dimer were carried out to explore the IPS and identify differences from that of Bz-H₂O.

V. MMC RESULTS AND DISCUSSION

MMC calculations were carried out not only to find the optimum geometry, shown in Fig. 2, but also to explore the IPS in detail. The parameters used for Bz, H₂S and H₂O have been described in detail in earlier publications.^{7,13} The optimized geometry is given in Table X along with the experimental values. Both Bz-H₂X clusters are predicted to have similar geometries, with one of the hydrogens pointing towards the center of the benzene ring. The equilibrium center-of-mass separation for Bz-H₂O (3.266 Å) is smaller than that of the experimentally determined, vibrationally-averaged value (3.329 Å) while that of Bz-H₂S (3.939 Å) is larger than the experimental value (3.771 Å). This may be due to a relatively larger vibrational sampling of IPS regions where the monomers twist and are more distant. The stabilization energies for Bz-H₂O and Bz-H₂S complexes are 1303 cm⁻¹ and 615 cm⁻¹, respectively, compared to the free monomers.

To look at the mobility of H₂S within the Bz-H₂S complex, the IPS was calculated for rotation of H₂S about its three principal axes. The IPS for the three rotations are depicted in Fig. 3. The barriers for rotation about a , b and c axes of H₂S are 227, 121 and 356 cm⁻¹, respectively. For Bz-H₂O, the corresponding values are larger at 365, 298 and 590 cm⁻¹ (see Fig. 10 in Ref. 10). The optimum inter-

FIG. 3. Intermolecular potential energy, from MMC calculations, for internal rotation of H_2S about its inertial axes in the complex.

molecular separation, R , varies as H_2S is rotated about its' inertial axes and it is shown in Fig. 4. The rotations about a and c axes lead to much larger variation in R , close to $1 \text{ \AA}$ for c rotation. The IPS was then calculated for motion of H_2X along the X and Y directions, i.e., parallel to the benzene plane. Both optimum energy and the Z -coordinate were found for different values of X and Y coordinates. Results are shown in Figs. 5 and 6. The origin is at the center of benzene and the X, Y and Z coordinates refer to the coordinate of the c.m. (H_2X). For both complexes, the optimum geometry is away from $X=0$, showing a multiple minima. However, the barrier for H_2S , at $X=0$, is less than 5 cm^{-1} and that for H_2O is 34 cm^{-1} . The H_2S complex has a very flat potential and varying X from -2 to $+2 \text{ \AA}$ changes the

FIG. 4. Optimum intermolecular separation for $\text{Bz}-\text{H}_2\text{S}$ as a function of the angle of rotation of H_2S about its inertial axes.

FIG. 5. Potential energy as a function of X and Y coordinates of $\text{H}_2\text{S}/\text{H}_2\text{O}$. The benzene plane is parallel to the XY plane.

interaction energy monotonically by about 78 cm^{-1} (59 cm^{-1} for motion along Y). For the H_2O complex, the energy increases by 138 cm^{-1} (173 cm^{-1} for motion along Y). The R reduces by about $0.3 \text{ \AA}$, as the X and Y coordinates vary from 0 to $\pm 2 \text{ \AA}$, as shown in Fig. 6. From the MMC data presented in Figs. 3–6, it appears that the barrier for H_2S is significantly smaller than that for H_2O for all the motions considered above; i.e., the IPS is shallower for $\text{Bz}-\text{H}_2\text{S}$ than for $\text{Bz}-\text{H}_2\text{O}$. The rotation of the nonbonded hydrogen in H_2S about the $\text{S}-\text{H}-\text{Bz}$ axis is likely to be very small, smaller than that found¹⁰ for $\text{Bz}-\text{H}_2\text{O}$, $1-2 \text{ cm}^{-1}$. The MMC results certainly support the possibility that H_2S experiences a nearly spherical potential in the complex, resulting in three internal-rotor states.

FIG. 6. Optimum elevation (Z coordinate for the c.m. $\text{H}_2\text{S}/\text{H}_2\text{O}$) as a function of X and Y .

VI. CONCLUSIONS

Rotational spectra for several isotopomers of the Bz-H₂S complex have been observed using the Balle-Flygare FTMW spectrometer. Three progressions were observed for the parent isotopomer, two of which could be fitted as simple symmetric tops. The ground state has a normal D_J but the other symmetric top has a larger and negative D_J . The third progression has K degeneracy removed in it and also a negative D_J . These three progressions arise from states that are correlated to $(0_{00}, M_J=0)$, $(1_{01}, M_J=0)$ and $(1_{01}, M_J=\pm 1)$ states. The three progressions are well separated in the spectra unlike for Bz-H₂O, which showed an overlap of different rotor states complicating the assignment.

The ground-state rotational constants for the various isotopomers led to R for Bz-H₂S of 3.771 Å compared to 3.329 Å for Bz-H₂O. Substitution analysis gives an angle of 28° between the C₂(H₂S) and C₆(C₆H₆) axes compared to 37° for the H₂O complex. The electric dipole moment for the two symmetric-top states were determined to be 1.14(2) D and 0.99(6) D. The ³³S nuclear quadrupole coupling constants for the two symmetric-top states are very different (−8 and −17 MHz) consistent with the suggestion of two different internal rotor states.

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