

Rotational spectra and structure of the floppy C₂H₄-H₂S complex: bridging hydrogen bonding and van der Waals interactions

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Abstract

This Communication reports the rotational spectrum of a weakly bound C₂H₄-H₂S complex which appears to be a composite of rotational spectra of the hydrogen bonded C₂H₄-H₂O and the van der Waals complex C₂H₄-Ar, reported earlier. Each transition is split in to four with a smaller splitting of about 0.14 MHz and a larger splitting of 1.67 MHz in $(B + C)/2$. Results for D₂S and HDS isotopomers suggest that the smaller splitting is due to C₂H₄ tunneling and the larger splitting is due to internal rotation of H₂S. The equilibrium structure shows S-H···π bonding.

1. Introduction

Intermolecular interactions have attracted enormous interest in the recent decades. Studies on ‘hydrogen bonded’ and ‘van der Waals’ complexes in the gas phase have been leading to important fundamental information about intermolecular potentials [1,2]. The terms ‘hydrogen bonding’, electrostatic interactions and ‘van der Waals interactions’ are loosely and interchangeably used. For example, Dunning [3] does not consider the N₂-HF as hydrogen bonded complex (it is included as an example for electrostatic interaction different from hydrogen bonding) and Bader [4] identifies the Ar-HF as hydrogen bonded complex. According to the IUPAC definition [5], N₂-HF would be hydrogen bonded and Ar-HF is left to the imagination of individuals. The IUPAC definition for hydrogen bond suggests that the two atoms X and Y involved in hydrogen bonding as in X-H···Y are ‘usually (but not necessarily) from the first row of Periodic Table i.e. N, O or F’. IUPAC’s definition also states that hydrogen bonding is best considered as an electrostatic interaction. This may be contrasted with the van der Waals (dispersion) forces leading to the name of van der Waals complexes.

There has been a debate about the similarities and differences between the hydrogen bonded complexes formed by first row (HF, H₂O) and second row (HCl, H₂S) hydrides [6,7]. Tao and Klemperer [6] argue that dispersion plays a more important role in (HCl)₂ than in (HF)₂. On the other hand, Augspurger and Dykstra [7] highlight the importance of electrostatic interactions in a series of HCl complexes. Experimental results on ‘hydrogen bonded complexes’ of second row hydrides can provide useful data for better understanding of weak interactions.

There have been numerous investigations on HF, H₂O and HCl complexes in the gas phase but relatively few H₂S complexes have been investigated. A systematic analysis of the structural parameters of HF, HCl and H₂O complexes led us to define a hydrogen bond radius for these and some other H bond donors [8,9]. Hence, our laboratory has been investigating the rotational spectra of various H₂S complexes, using a pulsed nozzle Fourier transform microwave spectrometer. The S-H group as hydrogen bond donor is important in the amino acid cysteine and its derivatives [10]. This communication discusses the rotational spectrum of C₂H₄-H₂S complex. Ab initio calculations at the MP2/6-311++G** level are reported as well and there is a reasonable agreement between experimental and theoretical structures.

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2. Experimental and computational details

The pulsed nozzle Fourier transform microwave spectrometer used in this study has been described in detail elsewhere [9]. The basic design is that of Balle and Flygare [11] and many of the recent advances [12–14] in design have been implemented. The title complex was formed in a supersonic expansion with Ar as the carrier gas. The back pressure was typically 0.5 atm and the microwave pulse was of 0.5 μ s duration. The identity of the complex was established by ensuring the presence of C₂H₄ and H₂S and also by observing the signal with Helium as carrier gas, with a backing pressure of 1 atm. Strong signals were observed for the C₂H₄–H₂S complex which could be readily seen in a single shot. The C₂H₄–H₂³⁴S transitions could be seen in natural abundance. The HDS/D₂S isotopomers were observed by flowing H₂S through either a H₂O/D₂O mixture or pure D₂O, respectively. All gases have been obtained from Bhoruka Gases Ltd and used as supplied: Ar (99.999%), C₂H₄ (99.9%) and H₂S (99.5%). D₂O (99.5% D) was obtained from Aldrich.

Ab initio calculations have been carried out using GAUSSIAN 98 program suite [15]. The calculations were done at MP2(Full) level with a reasonably larger basis set, 6-311++G**. Initial geometries were chosen with H₂S positioned along both *b* and *c* axes of C₂H₄ and also with H or S pointing towards the center of C₂H₄. Frequency calculations were carried out to ensure that the optimized structure was a true minimum.

3. Results and discussion

3.1. Search and assignment

The rotational constants for C₂H₄–H₂S were predicted both by comparing the rotational constants for several B···HCl and B···H₂S (where B = Ar, C₆H₆ and C₂H₄) complexes and by ab initio calculations. A comparison of several HF/HCl and H₂O/H₂S complexes

indicates that the intermolecular distances are similar. As the masses are close as well, the rotational constants are quite similar for complexes containing these two molecules. For example, the *B* rotational constant for C₆H₆–HCl and C₆H₆–H₂S are 1237.7 MHz [16] and 1168.5 MHz [17], respectively, and that of Ar–HCl and Ar–H₂S are 1678.5 MHz [18] and 1681.4 MHz [19], respectively. Considering these similarities, it was expected that the C₂H₄–H₂S rotational constants would be close to those of C₂H₄–HCl [20] but certainly on the lower side. A search for 1₀₁ → 2₀₂ transition was started at 8950 MHz as the same transition for C₂H₄–HCl occurs at 8951.366 MHz. It turned out to be a long search with the transition finally observed at 7677.8 MHz, very close to that of C₂H₄–Ar (7655.7 MHz) [21].

Each transition is split into four lines with a smaller splitting of <1 MHz and a larger splitting of several MHz. These transitions could be fit independently to a Watson Hamiltonian with only five constants (*A*, *B*, *C*, *D_J* and *D_{JK}*). The rotational transitions observed and the fitted constants for the four progressions are given in Tables 1 and 2, respectively. The rms deviation is an order of magnitude larger (30 kHz) than the experimental uncertainty. However, there is a clear trend in the residues with all the *K* = 0 lines having residues within experimental uncertainties and the two *K_p* = 1 lines showing equal and opposite residues. The C₂H₄–H₂S is a nearly prolate asymmetric top with $\kappa = -0.9912$. A stick diagram of the 1₀₁ → 2₀₂ transitions is shown in Fig. 1 for C₂H₄–H₂S along with those of C₂H₄–H₂O [22,23] and C₂H₄–Ar [21]. The similarity between C₂H₄–H₂S spectrum and a superposition of C₂H₄–H₂O and C₂H₄–Ar is evident. The C₂H₄–D₂S and C₂H₄–H₂³⁴S isotopomers exhibited similar four line pattern. The C₂H₄–HDS showed only two lines with smaller splitting that is identical to C₂H₄–D₂S. The rotational constants for the progression corresponding to L2 in Table 1 for all four isotopomers are given in Table 3. The observed splittings are given in Table 4. The larger splitting can be readily assigned to some internal motion of H₂S, as it is missing for the HDS

Table 1
List of transitions observed for C₂H₄–H₂S complex

Transitions	L1		L2		U1		U2	
	Observed freq. (MHz)	Res. (kHz)						
0 ₀₀ –1 ₀₁	3839.2887	3.6	3839.5289	–1.4	3842.5789	2.4	3842.8441	0.8
1 ₁₁ –2 ₁₂	7567.9895	–49.3	7568.2071	–56.1	7573.8046	–47.7	7574.0447	–49.6
1 ₀₁ –2 ₀₂	7677.8746	–1.2	7678.3620	–1.6	7684.4786	0.3	7685.0082	–3.8
1 ₁₀ –2 ₁₁	7779.9832	51.2	7780.7434	57.3	7788.0750	47.9	7788.9219	48.8
2 ₁₂ –3 ₁₃	11350.9490	–31.9	11351.2883	–29.3	11359.7351	–28.6	11360.0947	–28.5
2 ₀₂ –3 ₀₃	11515.0758	–1.7	11515.8051	2.4	11525.0275	–2.5	11525.8346	3.3
2 ₁₁ –3 ₁₂	11668.8501	30.2	11669.9797	28.4	11681.0539	28.8	11682.3206	29.9
3 ₁₃ –4 ₁₄	15132.6796	48.6	15133.1301	50.0	15144.5033	45.3	15144.9772	46.2
3 ₀₃ –4 ₀₄	15350.1954	0.9	15351.1487	–0.6	15363.5568	1.1	15364.6246	–0.8
3 ₁₂ –4 ₁₃	15556.3646	–48.3	15557.8716	–49.9	15572.7576	–45.5	15574.4373	–46.8

Table 2
Rotational and centrifugal distortion constants for C₂H₄-H₂S complex

Parameters	L1	L2	U1	U2
<i>A</i> (GHz)	26(1)	26(1)	26(1)	26(1)
<i>B</i> (MHz)	1972.64(1)	1972.90(1)	1974.86(1)	1975.14(1)
<i>C</i> (MHz)	1866.70(1)	1866.69(1)	1867.77(1)	1867.75(1)
<i>D_J</i> (kHz)	14.3(5)	14.3(5)	13.2(5)	13.3(5)
<i>D_{JK}</i> (MHz)	1.060(15)	1.061(16)	0.974(14)	0.971(14)
SD (kHz)	34.2	36.2	32.2	33.0

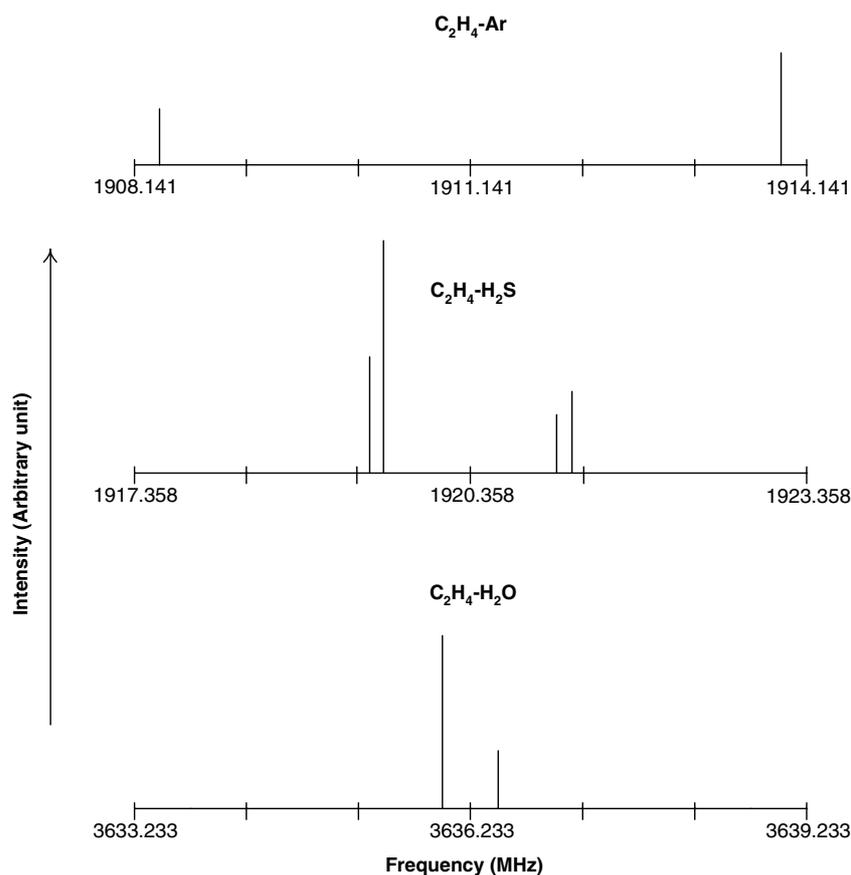


Fig. 1. Stick diagram of $J = 1 \rightarrow 2, K = 0$ transition frequencies for C₂H₄-Ar, C₂H₄-H₂S and C₂H₄-H₂O. The transition frequencies have been divided by $2(J + 1)$ (i.e. 4) in order to plot with the same scale.

Table 3
Rotational and centrifugal distortion constants for C₂H₄-H₂S isotopomers

Parameters	H ₂ S	HDS	D ₂ S	H ₂ ³⁴ S
<i>A</i> (GHz)	26(1)	26(1)	26(1)	26(1)
<i>B</i> (MHz)	1972.90(1)	1964.68(1)	1927.67(1)	1923.11(1)
<i>C</i> (MHz)	1866.69(1)	1859.50(1)	1830.30(1)	1822.05(1)
<i>D_J</i> (kHz)	14.3(5)	11.1(4)	11.8(5)	13.7(5)
<i>D_{JK}</i> (MHz)	1.061(16)	0.882(18)	0.925(13)	1.010(17)
SD (kHz)	34.2	47.8	46.9	33.0

complex. The splitting observed for D₂S is nearly twice that of H₂S, which rules out any tunneling mechanism. The C₆H₆-H₂O complex [24] exhibits similar splitting with the D₂O complex showing a splitting that is

roughly twice that of H₂O. The smaller splitting observed is more intriguing. The fact that it is observed in HDS complex rules out tunneling/internal rotation of H₂S about any other axis. Internal rotation of the hy-

Table 4
Experimental splittings (in MHz) observed in $(B + C)/2$ for $C_2H_4-H_2S$ isotopomers

Isotopomer	1-2	L-U
H_2S	0.14	1.67
$H_2^{34}S$	0.12	1.33
HDS	0.035	-
D_2S	0.035	3.11

drogen away from C_2H_4 about the $S-H \cdots \pi$ bond (see Fig. 2) is unlikely to be the cause, as both HDS and D_2S show identical splitting. Both HDS and D_2S are bonded through D atom and such rotation should involve H or D, respectively, and hence should lead to different splitting. Internal rotation of C_2H_4 about its a -axis, as observed in C_2H_4-Ar complex [21] appears to be the most likely candidate. However, the splitting is dependent on isotopic substitutions on H_2S . It suggests that the internal rotation of C_2H_4 is accompanied by S-H bond contraction, which seems reasonable. Experimental data on substituted C_2H_4 and a detailed analysis of the potential energy surface for the different internal motions would be useful and we are currently working on both these aspects.

3.2. Structure from rotational constants and *ab initio* calculations

The A rotational constant is not well determined in the fit but within the uncertainty, it is identical for all

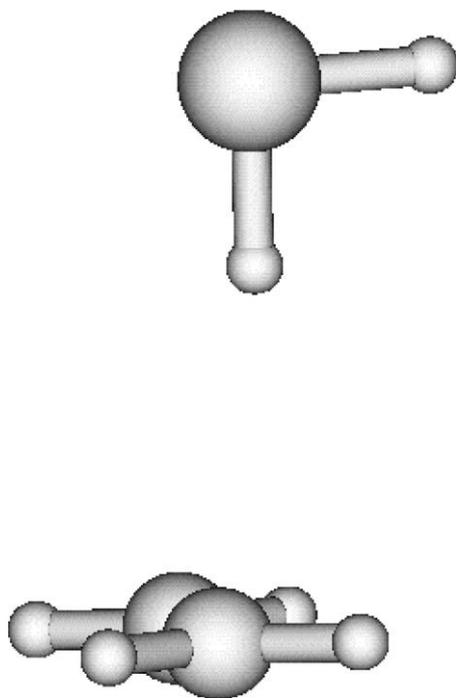


Fig. 2. The equilibrium geometry of $C_2H_4-H_2S$ calculated at MP2/6-311++G** level.

four isotopomers and it is close to the C rotational constant for C_2H_4 . It is similar for the structures determined for all C_2H_4-HX complexes ($X = F$ [25], OH [22,23] and Cl [20]) and *ab initio* results presented here. The H_2S is located on the c -axis of C_2H_4 forming a ‘hydrogen bond’ with the π cloud. However, the B and C rotational constants are reasonably accurate and the c.m.-c.m. separation could be readily determined, assuming the monomer structures are unchanged in the complex. Using parallel axes theorem, one could write the following expressions for moments of inertia about b - and c -axes of the complex

$$I_b(\text{complex}) = I_a(C_2H_4) + I_a(H_2S) + \mu R^2 \quad (1)$$

$$I_c(\text{complex}) = I_b(C_2H_4) + I_c(H_2S) + \mu R^2 \quad (2)$$

Here, μ is the reduced mass of the complex and R is the c.m.-c.m. separation. The H_2S is assumed to be symmetrically bonded to C_2H_4 . The R is calculated to be 4.041(1) and 4.037(1) Å, from Eqs. (1) and (2), respectively. Neglecting the contribution of H_2S (assuming it to be spherical) increases the R by 0.01 Å. As the H_2S term contributes the least to the moments of the complex, consideration of other orientations is unlikely to change the R significantly.

Substitution analysis based on the rotational constants for the various H_2S isotopomers can be used to locate the substituted atom more accurately [26]. From the rotational constants of $C_2H_4-H_2S$, C_2H_4-DHS , $C_2H_4-D_2S$ and $C_2H_4-H_2^{34}S$, the c.m. to atom distances for H (bonded to C_2H_4), S and H (away from C_2H_4) were determined to be 1.034, 1.852 and 2.163 Å, respectively. Though, the D substitution results are less reliable compared to result from ^{34}S substitution, one unambiguous conclusion is that the H_2S is interacting through H with the π cloud. The equilibrium structure calculated at MP2(Full)/6-311++G** level theory is in agreement with this conclusion as shown in Fig. 2. Different initial guesses for the geometry, mentioned earlier, led to this same minimum. The rotational constants from the calculation are $A = 22945$ MHz, $B = 2008$ MHz and $c = 1917$ MHz compared to the experimental values of 26(1), 1972.64(1) and 1866.70(1) MHz, respectively.

Frequency calculations with the structure shown in Fig. 2 revealed that it is a true minimum. Also, a red shift in S-H stretching frequencies was observed. For comparison, S-H stretching frequencies calculated at MP2/6-311++G** level are listed in Table 5 for free H_2S , $Ar-H_2S$, H_2S-H_2S and $C_2H_4-H_2S$. The red-shifts observed in symmetric and asymmetric stretching frequencies are only 1–2 cm^{-1} for $Ar-H_2S$ and for $C_2H_4-H_2S$, they are 11 and 9 cm^{-1} , respectively. Does the small shift observed for $Ar-H_2S$ make it a hydrogen bonded complex? The frequency shifts calculated for $(H_2S)_2$ provide an answer. For H_2S-H_2S , the shifts

Table 5

Comparison of S–H stretching frequencies (in cm^{-1}) of free H_2S , $\text{Ar-H}_2\text{S}$, $\text{H}_2\text{S-H}_2\text{S}^a$ and $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ calculated at MP2(Full) level using 6-311++G**basis set

	S–H symmetric stretching	S–H asymmetric stretching
H_2S	2818	2838
$\text{Ar-H}_2\text{S}$	2817	2836
$\text{H}_2\text{S-H}_2\text{S(a)}$	2817	2836
$\text{H}_2\text{S-H}_2\text{S(d)}$	2806	2830
$\text{C}_2\text{H}_4\text{-H}_2\text{S}$	2807	2829

^a Row 3 has values for acceptor H_2S and row 4 has values for donor H_2S .

Table 6

Binding energy (in kcal/mol) for $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ and $\text{Ar-H}_2\text{S}$ complexes calculated at MP2(Full) level using 6-311++G** basis set

	$\text{C}_2\text{H}_4\text{-H}_2\text{S}$		$\text{Ar-H}_2\text{S}$	
	With BSSE	Without BSSE	With BSSE	Without BSSE
ΔE	-0.8763	-2.1316	0.0679	-0.4198
ΔE_{ZPE}	0.3196	-0.9362	0.2720	-0.2157

ΔE and ΔE_{ZPE} correspond to the zero-point energy uncorrected and zero-point energy corrected binding energies, respectively.

observed for acceptor H_2S are identical to those of $\text{Ar-H}_2\text{S}$ and the shifts observed for donor H_2S are identical to those of $\text{C}_2\text{H}_4\text{-H}_2\text{S}$. The frequency shifts observed in $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ are quite comparable to the experimental shift of 16 cm^{-1} observed in dilute thiophenol solution in benzene [27]. These observations strongly support S–H $\cdots \pi$ interaction in $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ complex. The binding energies calculated for these two complexes are shown in Table 6. Binding energies were corrected for basis set superposition error (BSSE) using the counterpoise method [28] and for zero point energy (ZPE). Not surprisingly, zero point corrections reduce the binding energy for $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ and $\text{Ar-H}_2\text{S}$. The reduction is more for the former as there are six new vibrations in the complex compared to three for $\text{Ar-H}_2\text{S}$. For both complexes, the other vibrational frequencies are very close to those of the monomers. Without BSSE, the ZPE corrected binding energies are -0.22 and $-0.94 \text{ kcal mol}^{-1}$ for $\text{Ar-H}_2\text{S}$ and $\text{C}_2\text{H}_4\text{-H}_2\text{S}$, respectively. The BSSE corrected values come out to be positive for both complexes at this level. Obviously, the counterpoise method for BSSE overcorrects, leading to artificial positive values for binding energy in these two cases.

4. Conclusions

Rotational spectrum of $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ is reported in this Communication. Each transition is split in to 4 components indicating that both C_2H_4 and H_2S exhibit large amplitude tunneling/internal rotation in the complex.

The splitting pattern observed for HDS and D_2S suggests that the larger splitting is due to internal rotation of H_2S and the smaller splitting is due to internal rotation/tunneling of C_2H_4 coupled to S–H stretching motion. The geometry and theoretical vibrational frequency shifts indicate $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ complex to be ‘hydrogen bonded’ like the other $\text{C}_2\text{H}_4\text{-HX}$ ($\text{X} = \text{F}, \text{Cl}, \text{OH}$) complexes. However, the binding energy is small and the intermolecular potential is floppier for $\text{C}_2\text{H}_4\text{-H}_2\text{S}$ than the other $\text{C}_2\text{H}_4\text{-HX}$ complexes. Hence, ethylene tunneling has been experimentally observed in this complex similar to that observed for $\text{C}_2\text{H}_4\text{-Ar}$ and unlike for the other $\text{C}_2\text{H}_4\text{-HX}$ hydrogen bonded complexes mentioned above.

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