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# Rotational spectra, structure, and internal dynamics of Ar–H<sub>2</sub>S isotopomers

H. S. Gutowsky and T. Emilsson

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

E. Arunan

Department of Chemistry, Indian Institute of Technology, Kanpur, 208 016 India

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Several groups have studied the rotational spectra of various isotopomers of the pseudolinear Ar–H<sub>2</sub>S dimer. We have found two additional  $K = 0$  progressions, for Ar–H<sub>2</sub><sup>32</sup>S and Ar–H<sub>2</sub><sup>34</sup>S, which show that the symmetrical isotopomers (with H<sub>2</sub>S or D<sub>2</sub>S) exist in lower and upper states giving progressions with  $\bar{B}$  differing by about 50 MHz. When assigned and analyzed on this basis, the overall spectra are quite similar to those of the Ar–H<sub>2</sub>O analogue where the doubling is caused by 0<sub>00</sub> and 1<sub>01</sub> internal rotor states of the H<sub>2</sub>O or D<sub>2</sub>O. Such states of the H<sub>2</sub>S most likely cause the doubling found in the Ar–H<sub>2</sub>S isotopomers. However, some of the details differ in interesting ways, indicating substantial differences in their potential energy surfaces. The lower states of Ar–D<sub>2</sub><sup>32</sup>S and D<sub>2</sub><sup>34</sup>S have  $\bar{B}$ 's about 28 MHz larger than those for H<sub>2</sub>S, while the isotopomers of the upper states exhibit a more normal decrease of about 12 MHz. Somewhat related to this is the effect of deuteration on the difference in  $\bar{B}$  between lower and upper states. Perdeuteration of Ar–H<sub>2</sub>O decreases  $\Delta\bar{B}$  from 76 to 68 MHz. The corresponding change for Ar–H<sub>2</sub>S is much larger, from 44 to 5 MHz. For the internal rotor model, analysis of the hfs for Ar–H<sub>2</sub>O/D<sub>2</sub>O assigns its upper and lower states to 0<sub>00</sub> and 1<sub>01</sub> rotor states of the water, respectively. But this assignment is reversed in Ar–H<sub>2</sub>S/D<sub>2</sub>S. Also, we have observed and fitted the <sup>33</sup>S quadrupolar hfs for the lower and upper states of Ar–H<sub>2</sub><sup>33</sup>S, finding values for  $\chi_{aa}(\text{}^{33}\text{S})$  of –7.89 and –17.36 MHz. © 1997 American Institute of Physics. [S0021-9606(97)02213-7]

## INTRODUCTION

Our interest in the Ar/H<sub>2</sub>S system was aroused by the remarkably diverse mobility of the water molecules in the five smallest Ar<sub>*m*</sub>–(H<sub>2</sub>O)<sub>*n*</sub> clusters.<sup>1</sup> In the quasilinear<sup>2,3</sup> Ar–H<sub>2</sub>O and the T-shaped<sup>4</sup> Ar<sub>2</sub>–H<sub>2</sub>O, the two H<sub>2</sub>O states observed for each correlate with the 0<sub>00</sub> and 1<sub>01</sub> rotational states of free H<sub>2</sub>O. Moreover, the two dynamic states of the water are virtually the same in the dimer and trimer. In the Ar<sub>3</sub>–H<sub>2</sub>O symmetric top, the H<sub>2</sub>O is a nearly free internal rotor, while in the roughly T-shaped Ar–(H<sub>2</sub>O)<sub>2</sub> and the Ar–(H<sub>2</sub>O)<sub>3</sub> symmetric top the protons interchange via complex tunneling paths probably closely related to those occurring in the water dimer<sup>5</sup> and trimer.<sup>6,7</sup> The different types of water mobility no doubt arise from different as yet largely unexplored features of the potential energy surfaces (PES) for the different clusters.

The importance of water and especially of its hydrogen bonding in proteins warrants better understanding of its dynamics, which is now more accessible to experimental study.<sup>1</sup> It was hoped that a comparative analysis of the dynamics in the closely related Ar/H<sub>2</sub>S system would be a guide to the critical factors present. Such a study involves substitution with a less polar homolog of the monomer exhibiting the mobility. Interactions of sulfur are more dispersive and less electrostatic than those of oxygen. Moreover, compared with H<sub>2</sub>O, the H<sub>2</sub>S is larger, more nearly spherical, and less interactive, all factors which should affect the PES and the mobility of H<sub>2</sub>S in a cluster. These expectations were borne out in the accompanying theoretical paper on the Ar/H<sub>2</sub>S PES by Oliveira and Dykstra.<sup>8</sup>

Enough work had been reported<sup>9–11</sup> on the Ar/H<sub>2</sub>S system to encourage the present study. Rotational transitions of the Ar–H<sub>2</sub><sup>32</sup>S dimer and its D<sub>2</sub>S and HDS isotopic variants were first observed by Viswanathan and Dyke<sup>9</sup> in 1985. They used a molecular beam spectrometer to measure  $J=0 \rightarrow 1$  and  $1 \rightarrow 2$  transitions for one state of each of the three species and resolved the H–H triplet state hfs for  $J=1 \rightarrow 2$  of Ar–H<sub>2</sub><sup>32</sup>S. They also made an unsuccessful search for a possible corresponding singlet state. Additional transitions, including several of Ar–H<sub>2</sub><sup>32</sup>S, were found shortly thereafter by Kukolich *et al.*<sup>10</sup> who suggested the dimers were semirigid without internal rotation. However, both early studies were made before Ar–H<sub>2</sub>O was found to have two internal rotation states analogous to the singlet 0<sub>00</sub> and triplet 1<sub>01</sub> free water states.<sup>2</sup> Now, with the complexities of the Ar–H<sub>2</sub>O as a guide, we find that the previously reported Ar–H<sub>2</sub>S “rigid” dimer is primarily its state with the more intense, triplet H<sub>2</sub>S. But there are also weaker sets of transitions assignable to the dimer with a singlet H<sub>2</sub>S state having a  $\bar{B}$  about 45 MHz smaller than that of the triplet state, requiring reinterpretation of some of the earlier data.

In addition, an extensive study has been described by Lovas *et al.*<sup>11,12</sup> of the complex rotational spectra and structures of the H<sub>2</sub>S–H<sub>2</sub>O and H<sub>2</sub>S–H<sub>2</sub>S dimers and their isotopomers, which were found to be quite similar to those of H<sub>2</sub>O–H<sub>2</sub>O.<sup>5</sup> In the course of that work, which used Ar as a carrier gas, eight  $K=0$  progressions were observed at NIST for Ar–H<sub>2</sub>S and its isotopomers.<sup>12</sup> They include transitions for the two states of Ar–D<sub>2</sub><sup>34</sup>S and the one of Ar–HD<sup>34</sup>S as well as those reported earlier.<sup>9,10</sup> This is an account of our

TABLE I. Observed and fitted<sup>a</sup> rotational transition frequencies for the lower states<sup>b</sup> of Ar-H<sub>2</sub><sup>32</sup>S and Ar-H<sub>2</sub><sup>34</sup>S.

Transition <i>J</i> → <i>J'</i>	Ar-H <sub>2</sub> <sup>32</sup> S		Ar-H <sub>2</sub> <sup>34</sup> S	
	Obs. (MHz)	Res. (kHz)	Obs. (MHz)	Res. (kHz)
0→1	3362.5140	−0.1	3263.2986	−0.1
1→2	6723.7883	−0.1	6525.4029	−0.1
2→3	10 082.5833	0.1	9785.1193	0.7
3→4	13 437.6592	0.1	13 041.2509	−0.3
4→5	16 787.7766	−0.1	16 292.6060	−0.4
5→6	20 131.6968	0.0	19 537.9902	0.3

<sup>a</sup>Rotational constants from the fit are in Table II.<sup>b</sup>In these transitions the H<sub>2</sub>S protons are in the singlet spin state.

encounter with the two states of Ar-H<sub>2</sub>S, which are found to be similar to the corresponding water species, yet substantially different. In fact the behavior exhibited is a “mixture” of an internal rotor and tunneling, indicating a PES more anisotropic to H<sub>2</sub>S dynamics than that of Ar-H<sub>2</sub>O is to H<sub>2</sub>O.

## EXPERIMENT

The spectra were observed with the Balle/Flygare<sup>13</sup> Mark II Fourier transform microwave spectrometer.<sup>14</sup> Its extensive modification has been described.<sup>15</sup> The various Ar-H<sub>2</sub>S dimers were formed by supersonic expansion of argon (Liquid Air) at a backing pressure of 1 atm with ~1% H<sub>2</sub>S (Air Products), using a 900 series valve (General Valve) with a 1 mm diameter pulsed nozzle. The standard deviation of the frequencies reported for well resolved lines is typically less than 0.5 kHz.

In the experiments on Ar-D<sub>2</sub>S it was found to be very valuable to use D<sub>2</sub>S of high isotopic purity to avoid confusion with lines of HDS containing species. This was accomplished by preparing the D<sub>2</sub>S “on the fly,” by bubbling H<sub>2</sub>S sequentially through 12 small portions of D<sub>2</sub>O (Sigma). For the latter, a reflux coil condenser (Chemglass, Inc., Model CG-1216-5) was mounted horizontally with about 0.8 ml of D<sub>2</sub>O loaded into each bottom loop of the coil.

Around 2 ml/min of H<sub>2</sub>S was fed through the assembly and added to a stream of ~200 ml/min of argon. The combined gases were then passed through a trap cooled with dry ice to remove the small amount of D<sub>2</sub>O product present. The D/H ratio in the product was found to be about the same as that in the D<sub>2</sub>O used which was ~1000:1.

The HDS was made by passing H<sub>2</sub>S through a single bubbler containing a 1:1 mixture of D<sub>2</sub>O and H<sub>2</sub>O. All lines found using this mixture were checked against pure H<sub>2</sub>S or D<sub>2</sub>S to insure correct assignment.

## RESULTS

### Assignments and rotational constants

In a search for transitions of the N<sub>2</sub>-H<sub>2</sub>S dimer,<sup>16</sup> with argon as the carrier gas, a single sharp line was found at 3362.5 MHz, requiring H<sub>2</sub>S and Ar but not N<sub>2</sub>. It proved to be the *J*=0→1 transition of a *K*=0 progression (Table I).

TABLE II. Rotational constants determined from transition frequencies reported<sup>a</sup> for several isotopic species and spin states of the Ar-H<sub>2</sub>S dimer.<sup>b</sup>

Species	Lower state <sup>c</sup>		Upper state <sup>c</sup>	
	$\bar{B}$ (MHz)	$D_J$ (kHz)	$\bar{B}$ (MHz)	$D_J$ (kHz)
Ar-H <sub>2</sub> <sup>32</sup> S	1681.3602(1)	51.651(1)	1725.4658(7)	46.63(3)
Ar-H <sub>2</sub> <sup>33</sup> S	1655.8147(1)	50.680(2)	1700.2788(1)	45.03(1)
Ar-H <sub>2</sub> <sup>34</sup> S	1631.7489(1)	49.764(1)	1676.5348(1)	44.17(1)
Ar-D <sub>2</sub> <sup>32</sup> S	1706.5281(6)	36.00(2)	1711.2355(2)	31.82(1)
Ar-D <sub>2</sub> <sup>34</sup> S	1662.4562(4)	34.81(1)	1667.4677(2)	30.31(1)
Single state				
Ar-DH <sup>32</sup> S	1706.2550(9)	44.11(3)		
Ar-DH <sup>34</sup> S	1660.6421(7)	43.08(3)		

<sup>a</sup>As cited in the text.<sup>b</sup>The numbers in parentheses are the standard deviation of the least squares fit.<sup>c</sup>Isotopic species with H<sub>2</sub> and D<sub>2</sub> have lower and upper states corresponding to sym and antisym nonspin wave functions respectively.

Earlier work<sup>9,10</sup> on the Ar/H<sub>2</sub>S system had been interpreted in terms of a simple, semi-rigid Ar-H<sub>2</sub>S dimer, with a strong progression starting at 3450.7 MHz assigned as the only transitions of Ar-H<sub>2</sub><sup>32</sup>S. However, comparison of it with the weaker new progression at systematically lower frequencies led us to assign the two to the upper and lower states respectively of Ar-H<sub>2</sub><sup>32</sup>S (Table II). The doubling of the transitions is similar to that found for Ar-H<sub>2</sub>O and attributed there<sup>2,3</sup> to 0<sub>00</sub> and 1<sub>01</sub> internal rotor states of the H<sub>2</sub>O. Such a doubling was supported by our finding a weak <sup>34</sup>S progression (Table I) starting at 3263.3 MHz and matching a stronger progression beginning at a higher frequency, 3352.9 MHz.<sup>10</sup> The transitions were identified as <sup>34</sup>S by their displacement from the corresponding <sup>32</sup>S transition and by the <sup>34</sup>S/<sup>32</sup>S isotopic abundance.

Although at first we attributed the doubling to internal rotor states,<sup>16</sup> aspects akin to tunneling appeared as more data accumulated. This led us to look more critically at the model employed and to appreciate that its properties are sensitive to the PES for reorientation/rotation, in this case, of the H<sub>2</sub>S. For a low barrier, internal rotor states occur. For somewhat higher barriers, tunneling splittings appear in species with pairs of equivalent nuclei. For high barriers the clusters are semi-rigid or rigid, with well-behaved “covalent” spectra. The changes from one region to another are continuous and dependent on rovibrational coupling so the regions are largely arbitrary, and it is not surprising that nuclear spin statistics and hfs do not readily distinguish between the regions. But they do provide a variety of useful though limited information about the assignments for the observed rotational transitions.

Tunneling is possible only for the homonuclear H<sub>2</sub>S and D<sub>2</sub>S species. With H<sub>2</sub>S the total wave function obeys Fermi-Dirac statistics which require that it be antisymmetric (*a*) to interchange of the protons. For simplicity we take the total wave function as the product of nuclear spin and nonspin or dynamic state parts. Equivalent protons form a singlet *a* spin function (*I*<sub>H</sub>=0) and a triplet symmetric (*s*) spin function

( $I_H=1$ ).<sup>15</sup> In order to obey Fermi–Dirac statistics the  $a$  spin function must be coupled to an  $s$  nonspin function while the  $s$  spin function is coupled to an  $a$  nonspin function. Such a pair of  $a/s$  nonspin functions is provided by tunneling as well as by a range of eligible rotational states of the H<sub>2</sub>S, for which the 0<sub>00</sub> and 1<sub>01</sub> are the lowest energy  $s$  and  $a$  types.

Equivalent considerations apply to the Ar–D<sub>2</sub>S species. The deuterons obey Bose–Einstein statistics, so the total wave function must be symmetric to interchange of the deuterons. Equivalent deuterons form an antisymmetric spin function ( $I_D=1$ ) and two symmetric spin functions ( $I_D=0,2$ ) which have  $a/s$  statistical weights of 3 and 6 respectively. They combine with  $a$  and  $s$  nonspin functions, which may be provided either by tunneling<sup>17</sup> or by excited internal rotor states.

In keeping with this, all of the dimer species observed so far with H<sub>2</sub>S or D<sub>2</sub>S have two sets of  $K=0$  transitions. After Lovas,<sup>12</sup> we designate them as lower and upper states. Also, as a possible mechanistic guide we have tried to establish experimentally the spin functions for each state, thereby learning whether the nonspin function is symmetric or antisymmetric.

With this background in hand we return to the details of the assignment. The transitions in Table I for the lower states of Ar–H<sub>2</sub><sup>32</sup>S/<sup>34</sup>S are single sharp lines while those for  $J=0\rightarrow1$  of the upper states have partially resolved hfs. Also, the upper state transitions are several times more intense. This identifies the lower state as having the proton  $a$  singlet spin function and the upper state the  $s$  triplet spin function. Moreover, it requires that the nonspin function be  $s$  for the lower states of Ar–H<sub>2</sub><sup>32</sup>S/<sup>34</sup>S, and  $a$  for the upper states. In Ar–H<sub>2</sub>O the reverse is true.<sup>2,3</sup>

The doubling found for transitions of Ar–H<sub>2</sub><sup>32</sup>S/<sup>34</sup>S leads to adjustments in the earlier, single state assignments.<sup>9,10</sup> The measurements of Viswanathan and Dyke<sup>9</sup> correspond to the upper state of Ar–H<sub>2</sub>S, the lower state of Ar–D<sub>2</sub>S, and the single state of Ar–DHS, all for the <sup>32</sup>S species. Similarly the new species reported by Kukulich<sup>10</sup> are the upper states of Ar–H<sub>2</sub><sup>34</sup>S and Ar–D<sub>2</sub><sup>32</sup>S. To these Lovas added several <sup>34</sup>S species, the lower and upper states of Ar–D<sub>2</sub><sup>32</sup>S and the single state of Ar–DH<sup>34</sup>S while we did the weak lower states of Ar–H<sub>2</sub><sup>32</sup>S and Ar–H<sub>2</sub><sup>34</sup>S (Table I).

The  $\bar{B}$  and  $D_J$  rotational constants listed in Table II were determined by least squares fitting. The constants for the lower states of Ar–H<sub>2</sub><sup>32</sup>S and Ar–H<sub>2</sub><sup>34</sup>S are based on the data in Table I while those for Ar–H<sub>2</sub><sup>33</sup>S also come from the present work. The others are from the sets of seven transitions for  $J=0\rightarrow1$  to  $6\rightarrow7$  kindly provided by Lovas.<sup>12</sup> The residues are well within the experimental error and the fits are not improved by inclusion of the next higher distortion term,  $H_J$ , except for the upper state of Ar–H<sub>2</sub><sup>33</sup>S.

Only one DHS state was found for Ar–DH<sup>32</sup>S and for Ar–DH<sup>34</sup>S. We might expect two conformers, for example the L-shaped structures Ar–HS–D and Ar–DS–H. But no evidence for more than one form was found. This was also the case for Ar–HDO, and similar arguments apply here.<sup>2</sup> The unlike HD nuclei do not interchange and generate tun-

TABLE III. A comparison of  $\bar{B}$ 's (MHz) and the effects of deuteration for lower and upper states of Ar–H<sub>2</sub>O<sup>a</sup> and Ar–H<sub>2</sub>S isotopomers.

Species	$\bar{B}$	$\bar{B}$	$\Delta\bar{B}(U-L)^c$	$\Delta\bar{B}(H-D)$	
	Lower state <sup>b</sup>	Upper state <sup>b</sup>		$L$	$U$
Ar–H <sub>2</sub> O					
Ar–H <sub>2</sub> <sup>16</sup> O	2912.2	2988.3	76.1		
H <sub>2</sub> <sup>18</sup> O	2721.2	2785.1	63.9		
Ar–D <sub>2</sub> <sup>16</sup> O	2729.1	2795.8	66.7	183.1	192.5
D <sub>2</sub> <sup>18</sup> O	--	--	--	--	--
Ar–H <sub>2</sub> S					
Ar–H <sub>2</sub> <sup>32</sup> S	1681.4	1725.5	44.1		
H <sub>2</sub> <sup>34</sup> S	1631.7	1676.5	44.8		
Ar–D <sub>2</sub> <sup>32</sup> S	1706.5	1711.2	4.7	–25.1	14.3
D <sub>2</sub> <sup>34</sup> S	1662.5	1667.5	5.0	–30.8	9.0

<sup>a</sup>Data for Ar–H<sub>2</sub>O isotopic species are from Ref. 2.

<sup>b</sup>For Ar–H<sub>2</sub>O isotopic species the lower states are  $I_H=1$  or  $I_D=1$  and the upper states are  $I_H=0$  or  $I_D=0,2$ . The assignments are reversed for Ar–H<sub>2</sub>S/D<sub>2</sub>S.

<sup>c</sup>The sign of  $\Delta\bar{B}$  corresponds to  $\bar{B}(I_H=0)-\bar{B}(I_H=1)$ .

neling states. However, the HDS could in principle exist in excited rotational states correlated with the 0<sub>00</sub> and 1<sub>01</sub> states of free HDS. In this event the unlike HD nuclei are uncoupled and relaxation of the 1<sub>01</sub> rotational state to the lower energy 0<sub>00</sub> state is not spin forbidden. On this basis the states observed for Ar–DH<sup>32</sup>S and Ar–DH<sup>34</sup>S could be assigned as 0<sub>00</sub> internal rotor states of the DHS. Support for this assignment is obtained from the numerology of  $D_J$  (Table II). The assignment would give us a deuterium sequence for <sup>32</sup>S of three lower state transitions with  $D_J$ 's of 51.7, 44.1, and 36.0 kHz for Ar–H<sub>2</sub>S, –DHS, and –D<sub>2</sub>S. The  $D_J$  sequence for deuterium substitution in <sup>34</sup>S isotopomers is also reasonable (49.8, 43.1, and 34.8 kHz). So are the  $\bar{B}$  and  $D_J$  sequences for sulfur substitution. For Ar–H<sub>2</sub><sup>*m*</sup>S, with  $m=32, 33, 34$ , an increase in  $\bar{m}$  of one decreases  $\bar{B}$  by 25 MHz for the lower state and 24 MHz for the upper state while  $D_J$  is decreased by 1.0 and 1.8 kHz, respectively. Analogous effects are found for Ar–D<sub>2</sub><sup>*m*</sup>S. However, the  $\bar{B}$  sequences for deuterium substitutions are very unusual.

This brings us to a substantial difference between the Ar–H<sub>2</sub>O and Ar–H<sub>2</sub>S systems. It is seen in Table III which compares the H<sub>2</sub>/D<sub>2</sub> isotopic and lower/upper dependence of  $\bar{B}$  for the two systems. In Ar–H<sub>2</sub><sup>16</sup>O the  $\bar{B}$  for the lower state is 76.1 MHz less than that for the upper state. Dideuteration causes only a small change in  $\Delta\bar{B}$ , decreasing it by 9.4 MHz to 66.7 MHz. In contrast, in Ar–H<sub>2</sub><sup>32</sup>S deuteration changes  $\Delta\bar{B}$  from 44.1 MHz to 4.7 MHz. This ten-fold decrease in  $\Delta\bar{B}$  upon deuteration of Ar–H<sub>2</sub>S is startling when compared with the 10% decrease for Ar–H<sub>2</sub>O. It seems more symptomatic of tunneling than of H<sub>2</sub>/D<sub>2</sub>S rotational excitation. The effect also shows up in a direct comparison of the  $\bar{B}$ 's for the H<sub>2</sub>/D<sub>2</sub> species with S and O in Table III. In the lower state, dideuteration *increases* the  $\bar{B}$  for the <sup>32</sup>S and <sup>34</sup>S species by 25.1 and 30.8 MHz, respectively, while the upper state  $\bar{B}$ 's are *decreased* by 14.3 and 9.0 MHz. The increase in  $\bar{B}$  with deuteration of the lower state is not normal behav-

ior and thereby is indicative of some unusual feature of the PES.

### Hyperfine structure (hfs)

Several varieties of hfs were observed. Those aspects potentially most helpful in revealing the nature of the dimer are the proton-proton dipole-dipole interaction and the deuterium and <sup>33</sup>S quadrupole interactions. The Hamiltonians for the sundry isotopic species of Ar-H<sub>2</sub>S consist of standard terms selected from the expressions for rotational, spin-spin, spin-rotation, and quadrupole interactions,<sup>17-19</sup>

$$H = H_R + H_{SS} + H_{SR} + H_Q, \quad (1)$$

with the hf tensors designated as  $D_{gg}$ ,  $C_{gg}$ , and  $\chi_{gg}$ , respectively. Matrix elements are calculated for the basis set

$$I_1 + I_2 = 1 \quad \text{and} \quad I + J = F, \quad (2)$$

with subscripts for the nuclei in question. Off-diagonal elements generally were ignored as was  $H_{SR}$ . The  $g = a, b, c$  coordinates refer to the inertial axes, in which  $a$  is virtually the Ar to S axis. The reported frequencies were fitted with  $H_R$  taken to be the semirigid rotor contribution

$$H_R = \bar{B}J^2 - D_JJ^4, \quad (3)$$

where  $\bar{B} = (B + C)/2$ . The analysis follows closely that used earlier for the Ar-H<sub>2</sub>O dimer.<sup>2,3</sup> The main difference is that the dipole-dipole and quadrupole coupling constants,  $D_0(\text{H-H})$  and  $\chi_0(\text{D})$ , are appreciably smaller in H<sub>2</sub>S. As usual, it is assumed that cluster formation does not perturb the monomers appreciably.

### Ar-H<sub>2</sub>S

H<sub>2</sub>S has been reported<sup>20</sup> to have an S-H bond distance of 1.352 Å and a bond angle of 92°. The resulting longer H-H distance (1.923 Å) in H<sub>2</sub>S reduces  $D_0$ , from its value of -69 kHz in H<sub>2</sub>O to -35 kHz.<sup>3</sup> The resulting hf splittings are too small for quantitative significance but are helpful in establishing the parity of the nonspin wave functions in the various states. It is seen in Table II that two states were found for all symmetric isotopic species, i.e., with an H<sub>2</sub>S or D<sub>2</sub>S. They are listed as lower or upper frequency states depending on their relative  $B$  values.

Limiting now our consideration to the species with H<sub>2</sub>S, we noted that transitions of the lower states are consistently somewhat weaker (~1/3) than those for the upper states. This is probably why they were missed in the early work. Moreover the low- $J$  transitions of the upper states are broadened by partially resolved  $H_{SS}$  hfs. This is of course consistent with the lower states requiring a singlet proton spin function ( $I_H = 0$ , antisym) and the upper state a triplet function ( $I_H = 1$ , sym). A careful check was made of the  $J = 0 \rightarrow 1$  and  $1 \rightarrow 2$  lower state transitions for Ar-H<sub>2</sub><sup>32</sup>S and Ar-H<sub>2</sub><sup>34</sup>S at the frequencies given in Table I. No evidence of hfs was found at linewidths of 1.5 kHz FWHM.

Several attempts were made to resolve the hfs evident in  $J = 0 \rightarrow 1$  transitions of the upper states. We concentrated on the transition of Ar-H<sub>2</sub><sup>32</sup>S at 3450.74 MHz. However, the hfs extends over only 10-15 kHz and the resolution needed

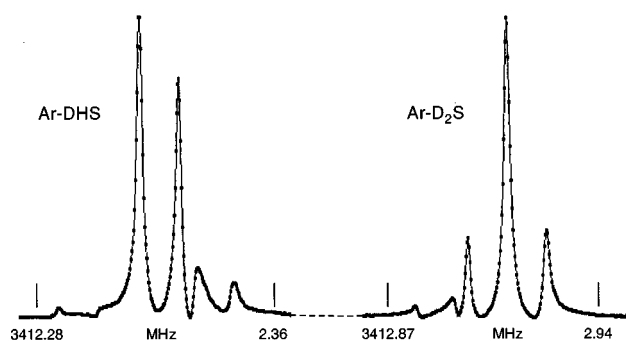


FIG. 1. Hyperfine structure from the deuterium quadrupole interaction, observed with Doppler doubling in the  $J = 0 \rightarrow 1$  transitions for Ar-DHS and for the lower state of Ar-D<sub>2</sub>S. The former is a triplet characteristic of the  $I = 1$  deuterium spin state in DHS while the different intensity distribution for Ar-D<sub>2</sub>S is attributed to the  $I = 0, 2$  spin states of the D<sub>2</sub>S. The line centers and interaction constants ( $\chi_{aa}$ ) obtained by fitting the hfs are given in Table IV.

was too unstable for reproducible measurements. There appeared to be four or possibly five components although just three are predicted.<sup>17</sup> Nonetheless, the observed width of the hfs is compatible with the calculated  $D_0$  of -35 kHz, so we assign  $I_H = 0$  (antisym) and  $I_H = 1$  (sym) spin functions to the lower and upper states. The protons obey Fermi-Dirac statistics so the lower state requires a symmetric nonspin wave function and the upper state an antisymmetric function. This is the reverse of the earlier finding<sup>2,3</sup> for Ar-H<sub>2</sub>O.

### Ar-DHS

As given in Table II only one state was found for dimers with DHS. Their transitions exhibit the quadrupolar hfs characteristic of the  $I = 1$  deuterium nucleus. The triplet structure typical of the  $J = 0 \rightarrow 1$  transition is shown for Ar-DH<sup>32</sup>S in Fig. 1 and fitted in Table IV. The fit gives  $\chi_{aa}(\text{D})$ , the projection on the dimer's inertial  $a$  axis of the deuterium quadrupole interaction tensor to be 62.1 kHz. The quadrupolar

TABLE IV. Analysis of the deuterium hfs observed in the  $J = 0 \rightarrow 1$  transitions of Ar-DH<sup>32</sup>S and of Ar-D<sub>2</sub><sup>32</sup>S.

$F \rightarrow F'$	Frequency (MHz)	Residue (kHz)	Line center (MHz)	$\chi_{aa}(\text{D})$ (kHz)
Single state of Ar-DH <sup>32</sup> S ( $I_D = 1$ )				
1 $\rightarrow$ 0	3412.2937	0.2	3412.3246(3)	62.140(1)
1 $\rightarrow$ 2	3412.3210	-0.5		
1 $\rightarrow$ 1	3412.3404	0.3		
Lower state of Ar-D <sub>2</sub> <sup>32</sup> S ( $I_D = 0, 2$ )				
2 $\rightarrow$ 3	3412.8851	0.0	3412.9000(5)	-85(4)
2 $\rightarrow$ 2	3412.9023	-2.0		
2 $\rightarrow$ 1	3412.9150	0.1		
0 $\rightarrow$ 0	3412.9023	2.3		
Upper state of Ar-D <sub>2</sub> <sup>32</sup> S ( $I_D = 1$ )				
1 $\rightarrow$ 1	3422.3295	a	3422.334	-35
1 $\rightarrow$ 2	3422.3400	a		

<sup>a</sup>Number parameters=number observed.

tensor has been characterized in detail<sup>21</sup> for free HDS and D<sub>2</sub>S, enabling us to learn something about the effective orientation of the HDS in the Ar–DH <sup>32</sup>S dimer.

The diagonal components of the *D* quadrupole interaction in free HDS and D<sub>2</sub>S are 153.7, –65.3, and –88.4 kHz for  $\chi_{xx}$ ,  $\chi_{yy}$ , and  $\chi_{zz}$ , respectively. The principal axis (*x*) is within 1° of the D–S bond axis, *y* is in the plane of the molecule, and *z* is perpendicular to the plane. In D<sub>2</sub>S the *x*, *y* axes are rotated by 43° from the *a*, *b* axes. The asymmetry of the tensor is modest,  $\eta=0.15$ , so for our purposes we treat it as axially symmetric and further assume that it is not perturbed significantly by dimer formation. With these assumptions the projection operator,

$$\chi_{aa} = (\chi_{xx}/2) \langle 3 \cos^2 \theta - 1 \rangle, \quad (4)$$

gives the average angle  $\theta$  between the D–S bond axis and the *a* inertial axis to be 39°. In other words, if the H/D atoms are between the Ar and the S, the D is pointed somewhat more closely at the Ar than is the H. But if the H/D atoms are outside, the reverse applies.

### Ar–D<sub>2</sub>S

Two states were found for the isotopic species of the dimer with two deuterium atoms (Table II). Unlike the Ar–H<sub>2</sub>S species, both the lower and upper states of Ar–D<sub>2</sub>S exhibit hfs, in this case from the deuterium quadrupole interaction. One set of the hfs is to be assigned to the antisymmetric *I<sub>D</sub>*=1 spin function and the other set to the symmetric *I<sub>D</sub>*=0,2 spin functions. The hfs observed for the lower state of the *J*=0→1 transition is included in Fig. 1 where it is compared with the known-to-be *I<sub>D</sub>*=1, *J*=0→1 transition of Ar–HDS. The hf splittings observed for the lower state can be fitted with *I<sub>D</sub>*=1 but the intensities differ substantially and lead us to favor assigning the lower state hfs to *I<sub>D</sub>*=0,2. The assignment and fit on this basis are given in Table IV. The value found for  $\chi_{aa}(D)$  is –85 kHz.

The hfs observed for the *J*=0→1 transition of the upper state is a doublet with a stronger component at higher frequency (3422.3400 Mhz) and a weaker one at lower frequency (3422.3295 Mhz). The doublet can be fitted as either *I<sub>D</sub>*=1 or *I<sub>D</sub>*=0,2 hfs. However, the absence of a third component, presumably the weak *I<sub>D</sub>*=1, *F*=1→0, favors the *I<sub>D</sub>*=1 assignment, as needed. The fit for the latter is listed in Table IV; it gives  $\chi_{aa}(D)$  to be –35 kHz. Accordingly, the value of  $\chi_{aa}(D)$  is very different in lower and upper states, –75 versus –35 kHz. This difference in the two states is strong evidence that tunneling is not the doubling mechanism. If it were, the tunneling should average the  $\chi_{aa}(D)$ 's over the two states and give the same values for both.<sup>22</sup>

Assignment of the hfs for the lower state to the *I<sub>D</sub>*=0,2 symmetric spin functions and that of the upper state to the *I<sub>D</sub>*=1 antisymmetric spin function restricts the parity of the D<sub>2</sub>S internal rotor states. Interchange of equivalent spin-1 nuclei requires a symmetric total wave function, so the symmetric *I<sub>D</sub>*=0,2 spin functions of the lower state must be coupled to a symmetric nonspin function. Similarly the upper

TABLE V. Observed and fitted hfs from the <sup>33</sup>S quadrupole interaction (*I*=3/2) in the low *J* transitions for the lower and upper states of Ar–H<sub>2</sub> <sup>33</sup>S.

<i>J</i> → <i>J'</i> <i>F</i> → <i>F'</i>	Lower state		Upper state	
	Obs. (MHz)	Res. (kHz)	Obs. (MHz)	Res. (kHz)
0→1				
3/2→3/2	3309.8486	–0.1	3396.9054	–0.7
3/2→5/2	3311.8220	0	3401.2485	2.2
3/2→1/2	3313.4011	0.1	3404.7186	–1.5
1→2				
1/2→3/2	6619.6648	1.2	6795.3344	0.5
5/2→5/2	6619.8330	0.5	6795.7037	–1.1
1/2→1/2	6621.6328	–3.9	6799.6719	–1.1
3/2→5/2, 5/2→7/2	6621.8066	0.8	6800.0467	1.4
3/2→3/2	6623.2166	0.7	6803.1467	–1.3
2→3				
1/2→3/2, 3/2→5/2	9929.0190	–1.3	10 195.9308	–1.0
5/2→7/2, 7/2→9/2	9929.5103	1.3	10 197.0077	1.0
3→4				
3/2→5/2, 5/2→7/2	13 233.3737	–1.0	13 590.2890	–0.7
7/2→9/2, 9/2→11/2	13 233.6046	1.0	13 590.7942	0.7
4→5				
5/2→7/2, 7/2→9/2	16 532.7123	–0.7	16 979.9421	–0.8
9/2→11/2, 11/2→13/2	16 532.8491	0.7	16 980.2415	0.7
5→6				
7/2→9/2, 9/2→11/2			20 364.0016	–0.9
11/2→13/2, 13/2→15/2			20 364.2020	0.8

state, with an antisymmetric *I<sub>D</sub>*=1 spin function, must have an antisymmetric nonspin function. This is the reverse of that reported<sup>2,3</sup> for Ar–H<sub>2</sub>O/D<sub>2</sub>O.

The hfs found for Ar–DHS is very similar to that assigned as the lower state of Ar–D<sub>2</sub>S, as may be seen graphically in Fig. 1 for *J*=0→1. This led us to question the species assignment. In particular what we have assigned to Ar–D<sub>2</sub>S might be a second conformer of the mixed dimer,<sup>10</sup> i.e., Ar–HDS, produced by desorption of H<sub>2</sub>S and HDS adsorbed on spectrometer surfaces<sup>23</sup> in earlier experiments or it might be an excited vibrational state.<sup>4</sup> The small separation between the two *J*=0→1 transitions enabled us to make a simple, entertaining, and convincing check of the assignment. The frequency range, including both transitions, was monitored on a display screen (Fig. 1) as the H<sub>2</sub>S in the gas handling system<sup>24</sup> was slowly replaced by and chemically exchanged with D<sub>2</sub>S. At first the signal assigned to Ar–DHS was weak, but grew in strongly, soon reaching a maximum and then almost disappearing. On the other hand the signal assigned to the lower state of Ar–D<sub>2</sub>S was much weaker at first but rapidly grew, reaching an asymptotic maximum with 100% D<sub>2</sub>S.

### Ar–H<sub>2</sub> <sup>33</sup>S

The natural abundance (0.76%) of <sup>33</sup>S is large enough to enable us to observe the transitions of Ar–H<sub>2</sub> <sup>33</sup>S and determine the <sup>33</sup>S, *I*=3/2 hfs. Two states were found readily by interpolation in the results for the <sup>32</sup>S and <sup>34</sup>S species. The hfs obtained for the low *J* (≤6) transitions of the two states is summarized in Table V. These are the *K*=0, *a*-dipole transitions, which depend on  $\chi_{aa}(\text{}^{33}\text{S})$ , where the *a*-axis is

TABLE VI. Line centers and rotational parameters determined via the <sup>33</sup>S hfs for the lower and upper states of Ar-H<sub>2</sub><sup>33</sup>S.

$J \rightarrow J'$	Lower state		Upper state	
	Line center (MHz)	Residue (kHz)	Line center (MHz)	Residue (kHz)
0→1	3311.4271	0.4	3400.3774	-0.2
1→2	6621.6367	-0.5	6799.6730	0
2→3	9929.4150	0.1	10 196.7999	0.2
3→4	13 233.5438	0.2	13 590.6619	-0.1
4→5	16 532.8070	-0.1	15 980.1497	0
5→6	---	---	20 364.1341	0
Parameters determined				
$\chi_{aa}(^{33}\text{S})$ , MHz	-7.894(3)		-17.364(2)	
$B$ (MHz)	1655.8147(1)		1700.2788(1)	
$D_J$ (kHz)	50.680(2)		45.031(2)	
$H_J$ (Hz)	---		-6.47(2)	

essentially the Ar-S line. The data for each state were fitted simultaneously to  $\bar{B}$ ,  $D_J$ , and  $\chi_{aa}(^{33}\text{S})$  via Eqs. (1)–(3). An excellent fit was obtained for the lower state. However, the fit to the line centers of the upper state had an unreasonably large rms deviation of 15 kHz. So a sixth-order centrifugal distortion term ( $H_J$ ) was added and the line centers refitted, with reasonable results. The outcome of the fitting is given in Table VI.

Of particular interest here is the finding that in the lower and upper states of the dimer  $\chi_{aa}(^{33}\text{S})$  is -7.894 and -17.364 MHz, respectively. Also the diagonal elements  $\chi_q$  of the quadrupole coupling in free H<sub>2</sub><sup>33</sup>S have been reported<sup>25</sup> to be -32, -8, and +40 MHz for  $q = x, y, z$ . The S is on the C<sub>2</sub> axis of H<sub>2</sub>S so the inertial and coupling axes are coincident in free H<sub>2</sub>S. Of the coupling axes, we label the C<sub>2</sub> axis as  $y$ , with  $x$  perpendicular to  $y$  in the molecular plane, and  $z$  perpendicular to the plane. One would like to use these results to explore the orientation of the H<sub>2</sub>S in the dimers. However, the one observed quantity  $\chi_{aa}$  is insufficient in itself to determine the orientation of  $\chi_q$  and thereby of the H<sub>2</sub><sup>33</sup>S in the inertial frame<sup>26</sup> of the dimer. In the case of Ar-DHS we were able to assume axial symmetry for  $\chi_q(D)$  and obtain from  $\chi_{aa}(D)$  an approximate average angle of 39° between the D-S bond and the  $a$  inertial axis of the dimer. Even so, the D-S may be pointed at or away from the Ar. But this approach is inapplicable to  $\chi_q(^{33}\text{S})$  because of its large asymmetry,  $\eta=0.6$ , and we are left without a unique indication of the H<sub>2</sub>S orientation.

Nonetheless, it is notable that the lower state value for  $\chi_{aa}$  is -7.9 MHz which is very close to the -8 MHz value of  $\chi_y$  in free H<sub>2</sub><sup>33</sup>S. This may be accidental inasmuch as other orientations can give a  $\chi_{aa}(^{33}\text{S})$  of -8 MHz. But Occam says the simplest and most likely way of having  $\chi_{aa}=-8$  MHz is for the C<sub>2</sub> axis of the H<sub>2</sub>S to be coincident with the  $a$ -axis of a planar C<sub>2v</sub> dimer. Moreover, this is the same orientation as that found for the D<sub>2</sub>S in the lower state of Ar-D<sub>2</sub><sup>32</sup>S. If the dimer is indeed planar, the change in  $\chi_{aa}$  to the upper state value of -17.4 MHz can then be attributed to rotation of the H<sub>2</sub>S by 39° in the dimer plane.

## Effective structure

The doubling of the dimer states by the dynamics of H<sub>2</sub>/D<sub>2</sub>S blurs any simple attempt at a quantitative description of the structure. Especially striking is the large *increase* in  $\bar{B}$  upon deuteration, the change being nearly as large for the mono- as for the di-deutero species (Table II). Nonetheless, an approximate analysis might indicate to us whether on average the H<sub>2</sub>/D<sub>2</sub>S in the dimer favors the S pointed at or away from the argon. One would expect isotopic substitution at the sulfur to have little effect on the dynamic state of the H<sub>2</sub>/D<sub>2</sub>S, and this is borne out by inspection of the rotational constants in Table II. Accordingly we performed a substitution type analysis in which the H<sub>2</sub>/D<sub>2</sub>S is treated as a point mass and the pseudo-diatomic approximation is used.

In this event <sup>32</sup>S/<sup>34</sup>S isotopic substitution leads to the expression

$$\Delta I = \Delta \mu_d R^2, \quad (5)$$

where  $\Delta I$  is the difference in moments of inertia, taken from  $\bar{B}$ ;  $\Delta \mu_d$  is the difference in pseudo-diatomic reduced mass; and  $R$  is the Ar to H<sub>2</sub>S center of mass (c.m.) distance. This tack gives  $R$  to be 4.013 and 3.881 Å for lower and upper states of Ar-H<sub>2</sub>S and 3.821 and 3.795 Å for Ar-D<sub>2</sub>S. For the one state of Ar-DHS, a value of 3.837 was found.

These distances are essentially the Ar-S separation. Comparison of them with hypothetical structures is complicated by the knobby nature of H<sub>2</sub>S. The Ar-SH<sub>2</sub> orientation avoids the hydrogens entirely and provides the closest approach. In it  $R$  would be the sum of Ar and S van der Waals radii, namely 1.93+1.85, or 3.78 Å. The most extended structure is an L-shaped Ar-HSH with a linear Ar-HS. For it  $R$  would be 4.48 Å, made up of the Ar and H radii (1.93 and 1.2 Å) and the H-S bond (1.35 Å). The extended structure is ruled out by the substitution value of ~3.9 Å for  $R$ . However the Ar-SH<sub>2</sub> orientation and a wide range of bent Ar-H<sub>2</sub>S structures are compatible with it.

## DISCUSSION

The experimental findings are an interesting mixture of the familiar and the unexpected. The unusual features are associated mainly with the deuterated species, raising the question of misassignment. Therefore, more care than usual was employed in our work and broader searches were made. Also the extensive work at NIST on the system supports the same overall picture.<sup>11,12</sup> Moreover, our assignments for Ar-HD<sup>32</sup>S and Ar-D<sub>2</sub><sup>32</sup>S agree with those in the molecular beam work.<sup>9</sup>

It is reassuring that the number and type of deuterated states found (Table II) for the Ar-H<sub>2</sub>S/D<sub>2</sub>S system is the same as for Ar-H<sub>2</sub>O/D<sub>2</sub>O..., that is, upper and lower states of Ar-D<sub>2</sub><sup>32</sup>S and of Ar-D<sub>2</sub><sup>34</sup>S, plus a single state for the DHS isotopomers. However, the latter appears to be a lower state progression while those of Ar-DHO and Ar<sub>2</sub>-DHO appear to be upper state.<sup>2,4</sup>

This raises the question of which rotational frequency progressions are for the ground rovibrational state and which are for an excited rovibrational state, presumably the first.

The best available evidence, though somewhat indirect, points to the lower frequency progressions as the ground rovibrational states and the upper progressions as (first) excited states. This is based on Table II, where  $D_J$  for the lower progressions are systematically 5 kHz larger than for the upper progressions. The mono-deutero species Ar-HDS exhibit only single progressions for which the  $D_J$ 's (43.5 kHz) are bracketed by the  $D_J$ 's for the lower progressions of H<sub>2</sub>S or D<sub>2</sub>S (50.7 and 35.4 kHz). Because of this the single progressions of the Ar-DHS species most likely are lower progressions. Two progressions are observed for the dimers with H<sub>2</sub>S or D<sub>2</sub>S because transitions between the two states involved are spin forbidden. However, this is not the case for Ar-HDS which relaxes to the ground rovibrational state<sup>2</sup> thereby assigning it to the lower progressions.

Earlier we noted the large effect of deuteration on  $\Delta\bar{B}$ , the difference in  $\bar{B}$  between upper and lower states (Table III). If the doubling mechanism were tunneling,  $\Delta\bar{B}$  would be directly related to the tunneling splitting and highly sensitive to the mass of the tunneling nuclei. Therefore the large decrease in  $\Delta\bar{B}$  from 44 to 5 MHz upon deuteration of Ar-H<sub>2</sub>S favors a tunneling mechanism. In contrast, deuteration of Ar-H<sub>2</sub>O only reduces  $\Delta\bar{B}$  from 76 to 67 MHz, more in keeping with its internal rotor states.

For Ar-D<sub>2</sub>S a definitive choice could be made between internal rotor and tunneling models if the deuterium hfs were clearly resolved in both lower and upper states. With two internal rotor states the deuterium hfs would be fitted by two different  $\chi_{aa}(\text{D})$ 's. On the other hand, tunneling interchanges the two deuteriums and gives them the same average  $\chi_{aa}(\text{D})$ .

A somewhat modified argument can be based on our finding quite different values of  $\chi_{aa}(^{33}\text{S})$  for the lower and upper states of Ar-H<sub>2</sub><sup>33</sup>S. Tunneling in it would interchange the hydrogens and for D would average their  $\chi_{aa}$ 's but have little or no effect on the <sup>33</sup>S hfs. But different rotational states of the H<sub>2</sub><sup>33</sup>S would project differently on the inertial axes of the dimer and have different  $\chi_{aa}(^{33}\text{S})$ 's, as found. This was also found for Ar-H<sub>2</sub><sup>17</sup>O.<sup>2</sup> All things considered we attribute the doubling of the Ar-H<sub>2</sub>S transitions to internal rotor states and its other unusual features to an unusual PES.<sup>8</sup>

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