Rotational spectra and structures of the $\text{Ar}_3\text{-H}_2\text{O}$ and $\text{Ar}_3\text{-H}_2\text{S}$ symmetric tops

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Rotational spectra of several isotopomers of $\text{Ar}_3\text{-H}_2\text{O}$ and $\text{Ar}_3\text{-H}_2\text{S}$ tetramers were obtained with a Balle–Flygare Fourier transform microwave spectrometer. Both were found to be symmetric tops, the former being an oblate and the latter a prolate one. The rotational constants B , D_J , and D_{JK} were determined to be 1172.1323(1) MHz, 7.199(1) kHz, and $-5.545(2)$ kHz for the H_2O and 819.0385(1) MHz, 3.346(1) kHz, and $+3.145(2)$ kHz for the H_2S containing tetramer. Substitution analysis with the rotational constants of various isotopomers led to an Ar–Ar distance of 3.848 (3.865) Å and an Ar–c.m.(H_2X) distance of 3.675 (4.112) Å for H_2O (H_2S) complexes. The angle between the C_2 axis of the H_2X and the C_3 axis of the tetramer is estimated to be 74° for H_2O and 13° for the H_2S complex. No evidence for any excited tunneling/internal rotor states was found for either of the tetramer. MMC calculations show that the equilibrium geometry has the H_2X positioned above the plane of the Ar_3 with both the protons pointing towards one Ar each. The barrier for the “pseudorotation” in which the protons hop between the argons is determined to be about 6 (8) cm^{-1} only for H_2O (H_2S) making the H_2X moiety very mobile and effectively making both the tetramers symmetric tops. Rigid body diffusion quantum Monte Carlo (RBDQMC) calculations with the MMC potential have been carried out for vibrational analysis.

I. INTRODUCTION

Rotational spectra have been reported for several small clusters^{1–5} in which a tetramer is formed by adding a di- or triatomic molecule to the face of an equilateral Ar_3 trimer. The added species include HF (the first tetramer studied),¹ HCl ,^{2,3} and HCN .⁴ Also, a preliminary account has been⁵ given on $\text{Ar}_3\text{-H}_2\text{O}$, which is treated more fully here and compared with a similar study presented for $\text{Ar}_3\text{-H}_2\text{S}$.

In all five tetramers, the hydrogen end of the added species is closer to the Ar_3 face and the rotational spectrum is clearly that of a symmetric top. Analysis of the hyperfine structure (hfs) caused by the added linear molecule shows them to undergo large amplitude bending vibrations averaging about 40° from the threefold symmetry axis. The rotational spectra of the tetramer containing the diatomic HF and HCl are that of a “normal” symmetric top. However, the spectra of $\text{Ar}_3\text{-HCN}$, with a linear triatomic HCN, exhibit several unusual features.⁴ These were attributed to strong coupling between the radial and bending motions in the $\text{Ar}_3\text{-HCN}$. In fact, such coupling has been observed in all

the $\text{Ar}_m\text{-HCN}$ ($m=1,2,3$) clusters^{6,7} resulting in large centrifugal distortions in the clusters. The origin of this coupling has been explored by molecular mechanics in clusters (MMC) (Ref. 8) calculations of the potential energy surface (PES).

The $\text{Ar}_3\text{-H}_2\text{X}$ tetramers have a nonlinear H_2X as the bonding partner of the Ar_3 . Hence, the symmetric top behavior of the tetramers $\text{Ar}_3\text{-H}_2\text{X}$ may at first seem surprising. But it is consistent with the spectra reported for several heterodimers of benzene. As expected, axial addition to benzene of the linear HF,⁹ HCl ,¹⁰ or HCN (Ref. 4) species generates quite normal symmetric top spectra. The average angle between the symmetry axis of the dimer and the HX bond is about 20° for benzene–HX.⁴ Extensive studies have been made of the benzene–water dimer which also has a ground state symmetric top spectrum.^{11–13} However, the spectrum is more complex, characteristic of two coaxial rotors with a symmetric top frame and a very low effective V_6 barrier.¹⁴ Several internal rotor states were found and they were correlated to the rotational states of free H_2O .¹³ The benzene– H_2S dimer also shows a complex spectra¹⁵ with evidence for ground and excited torsional/internal rotor states.

We have previously reported the rotational spectra of $\text{Ar-H}_2\text{O}$ (Ref. 16) and $\text{Ar}_2\text{-H}_2\text{O}$.¹⁷ In both cases, two internal rotor states of H_2O were found. The $\text{Ar-H}_2\text{S}$ spectrum also showed evidence for two states of H_2S in the dimer.¹⁸

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However, it was very different from that of Ar–H₂O and it showed an anomalous isotopic effect. This paper reports the rotational spectra of the Ar₃–H₂O and Ar₃–H₂S. For both these complexes, evidence for an excited internal rotor state was not found even though the ground state is a symmetric top. Could it be because the barrier for tunneling/internal rotation is much larger in Ar₃–H₂O than in Ar–H₂O or Ar₂–H₂O? Or is it because of the intricate nature of the intermolecular potential surface? MMC calculations have been carried out to determine the equilibrium structure, energy and barrier for internal rotation for both complexes. Following our experience in the Ar–H₂S system,¹⁹ rigid body diffusion quantum Monte Carlo (RBDQMC) calculations using the MMC potential were carried out to estimate the vibrationally averaged rotational constants for comparison with experiment.

II. EXPERIMENT

The microwave spectra of the Ar₃–H₂O and Ar₃–H₂S tetramers were observed with the Balle–Flygare Fourier transform microwave spectrometer described in detail previously.^{20,21} The tetramers were formed by supersonic co-expansion of a few % H₂S (Air products) or H₂O with argon (liquid air) as the carrier gas at 1 atm backing pressure. The optimum microwave pulse required was 3 μ s for Ar₃–H₂O indicating that the dipole moment of the tetramer was much smaller than that of free H₂O. For comparison, the optimum pulse length required for benzene–H₂O was 0.3 μ s and the dipole moment was determined to be ≈ 2.0 D.¹³

For the HDO complex an equivalent mixture of H₂O and D₂O (Sigma) was used. The D₂S was prepared by bubbling H₂S sequentially through 12 small portions of D₂O kept in a reflux coil condenser followed by a dry ice trap to remove any D₂O. This method ensured that there was no significant amount of HDS present when looking for D₂S complexes to avoid assignment ambiguities.

III. RESULTS AND ANALYSIS

A. Ar₃–H₂O tetramer

1. Search and assignment

The rotational spectrum of Ar₃–H₂O was predicted and found readily by assuming its structure would be similar to that of Ar₃–HF (Ref. 1) with the further expectation that it would be a symmetric top as in C₆H₆–H₂O in spite of the asymmetry of the H₂O.^{11,12} This proved to be the case as shown by the transitions in Table I. Their detection requires both Ar and H₂O in the gas mixture. Moreover, only the $K = 3n$ levels appear, where $n = 0, 1, 2, \dots$. This is required for a threefold symmetric top with three interchangeable spin zero ⁴⁰Ar nuclei. Symmetric top transitions were observed from $J = 0 \rightarrow 1$ through $J = 6 \rightarrow 7$ for four isotopic species of water, i.e., H₂O, HDO, D₂O, and H₂¹⁸O.

The transitions for each species were fitted with a non-linear least squares program to the usual expression for a symmetric top,²²

$$\nu_0 = 2B_0(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2. \quad (1)$$

TABLE I. Rotational transition frequencies observed for several isotopic species of the Ar₃–H₂O tetramer in the symmetric top ground state.

Transition $J \rightarrow J'$	K	Ar ₃ –H ₂ O	Ar ₃ –H ₂ ¹⁸ O	Ar ₃ –HDO	Ar ₃ –D ₂ O
0 $\rightarrow$ 1	0	2344.2347	...	2311.8773	2278.7690
1 $\rightarrow$ 2	0	4688.2981	4551.2930	4623.5867	4557.3820
2 $\rightarrow$ 3	0	7032.0160	6826.5442	6934.9700	6835.6799
3 $\rightarrow$ 4	0	9375.2155	9101.3192	9245.8601	9113.5268
	3	9375.6142	9101.6317	9246.2090	9113.8220
4 $\rightarrow$ 5	0	11 717.7242	11 375.4642	11 556.0936	11 390.7630
	3	11 718.2221	11 375.8513	11 556.5360	11 391.1220
5 $\rightarrow$ 6	0	14 059.3688	13 648.8151	13 865.5036	13 667.2324
	3	14 059.9664	13 649.2813	13 866.0325	13 667.6653
6 $\rightarrow$ 7	0	16 399.9756	15 921.2175	16 173.9274	15 942.7842
	3 ^a	16 400.6720	15 921.7583	16 174.5421	15 943.2888
	6	16 402.7705	15 923.3930	16 176.4012	15 944.7875

^aThis transition is split into a doublet for all the isotopomers and frequencies given in this row are the averages of doublets split by 10.5 kHz.

The rms deviation of the fitting was ≤ 1 kHz for the H₂O and H₂¹⁸O but slightly larger for HDO and D₂O due to the unresolved quadrupole coupling from D. The results obtained for B_0 , D_J , and D_{JK} , and the rms deviation of the fit are listed in Table II. The moment of inertia about the symmetry axis of the tetramer should be closer to that of the I_c for free Ar₃. Comparing the B_0 of the parent isotopomer (1172.1323 MHz) with the C rotational constant of Ar₃ given in Table II (859.86 MHz) shows that the Ar₃–H₂O is an oblate top. Moreover, the D_{JK} is negative, as expected for the oblate symmetric top.²²

It should be noted that the $K = 3$ component of the $J = 6 \rightarrow 7$ transition is a symmetrical doublet with a small splitting of 10.5 kHz in all four isotopic species. A similar but larger splitting was found for Ar₃–HCN starting from the

TABLE II. Rotational constants determined by fitting Eq. (1) to the symmetric top transitions observed for several isotopic species of Ar₃–H₂O (Table I) and of Ar₃–H₂S (Table IV).

Species	B_0 (MHz)	D_J (kHz)	D_{JK} (kHz)	σ^a (kHz)
Ar ₃ –H ₂ ¹⁶ O	1172.1323(1)	7.199(1)	–5.545(2)	0.8
Ar ₃ –H ₂ ¹⁸ O	1137.8760(1)	6.595(1)	–4.318(3)	0.9
Ar ₃ –HD ¹⁶ O	1155.9513(3)	6.847(4)	–4.907(8)	2.6
Ar ₃ –D ₂ ¹⁶ O	1139.3953(3)	6.378(4)	–3.997(8)	2.7
Ar ₃ –H ₂ ³² S	819.0385(1)	3.346(1)	3.145(2)	0.8
Ar ₃ –H ₂ ³⁴ S	799.8039(1)	3.247(1)	3.216(6)	0.4
Ar ₃ –HD ³² S	813.2486(1)	3.160(2)	5.045(4)	1.9
Ar ₃ –D ₂ ³² S	808.7339(3)	3.108(3)	9.006(8)	4.3
Ar ₃ –HF ^b	1188.2123(2)	6.846(3)	–5.753(6)	
Ar ₃ –HCl ^c	843.8974(1)	2.333(2)	1.818(6)	
Ar ₃ –HCN ^d	886.4878(1)	10.374(2)	173.156(7)	
Ar ₃ –Ne ^e	1139.0830(1)	9.052(2)	–1.525(8)	
Ar ₃ ^f	859.86 ^g	...	...	

^aStandard deviation of the fit in kHz.

^bReference 1.

^cReference 2.

^dReference 4.

^eReference 29.

^fReference 28.

^gFor Ar₃, theoretical estimate for the rotational constant C is given for comparison. If Ar₃–HX has a larger B it will be an oblate and if not it will be a prolate top. Except for Ar₃–HCN, which also has unusual centrifugal distortion constants, all the tetramers satisfy this condition.

TABLE III. Observed and fitted deuterium hyperfine structure in the $J=0 \rightarrow 1$, $K=0$ transitions of $\text{Ar}_3\text{-HDO}$.^a

$F \rightarrow F'$	Obs. (MHz)	Res. (kHz)
$1 \rightarrow 0$	2311.8468	0.3
$1 \rightarrow 2$	2311.8724	-0.7
$1 \rightarrow 1$	2311.8896	0.3

^aThe line center is 2311.8773(5) MHz and the χ is 83(2) kHz.

$J=4 \rightarrow 5$ transitions. For the $J=6 \rightarrow 7$ transition, the splitting was 46 kHz and it was strongly dependent on J .⁴ The cause of this splitting is a minor centrifugal distortion term that appears in the Hamiltonian of a symmetric top.²³⁻²⁵ Obviously, this distortion in the $\text{Ar}_3\text{-H}_2\text{O}$ is much smaller than that in $\text{Ar}_3\text{-HCN}$.

2. Hyperfine interactions

There are two weak but detectable hyperfine interactions in the isotopic species of water studied as the $\text{Ar}_3\text{-H}_2\text{O}$ tetramer. For the H_2^{16}O and H_2^{18}O isotopomers, there is the proton-proton magnetic dipole-dipole interaction with a $D_0(\text{H-H})$ of -69.1 kHz in free H_2O .¹⁶ Then there is the deuterium nuclear quadrupole coupling in the HDO and D_2O isotopomers with $\chi_0(\text{D})$ cited to be 315 kHz for free HDO and 330 kHz in free D_2O .²⁶ Two aspects of the resulting hfs are particularly useful here. It is an indicator of the nuclear spin statistics and symmetry for any internal dynamic states of the water, i.e., tunneling or internal rotation. Also, the effective magnitude of the interaction depends on the angular orientation of H_2O along the inertial axes of the tetramer.

Except for the $J=6 \rightarrow 7$, $K=3$ doublets, the transitions found for the tetramers with H_2^{16}O and H_2^{18}O do not have any hfs. Careful checks were made of the $J=0 \rightarrow 1$ transitions under high resolution conditions with a FWHM of ~ 2 kHz. They were found to be clean, sharp singlets. The absence of the hfs suggests that the H_2O protons are in a singlet spin state with $I_{\text{H}}=0$ and thus are indistinguishable, which constrains the H_2O to states obeying Fermi-Dirac statistics. This may be accomplished by combining the singlet and triplet ($I_{\text{H}}=1$) states respectively, with antisymmetric and symmetric tunneling or internal rotor states of the H_2O , thereby generating two states and two sets of transitions. For example in $\text{Ar-H}_2\text{O}$ (Refs. 16, 27) and $\text{Ar}_2\text{-H}_2\text{O}$,¹⁷ the antisymmetric singlet proton state is coupled to the symmetric 0_{00} rotational state of the H_2O and the symmetric triplet proton state is coupled to the antisymmetric 1_{01} rotational state. However no other states were detected for $\text{Ar}_3\text{-H}_2\text{O}$ in an extensive search in spite of their predicted threefold greater intensity. MMC calculations of the intermolecular potential surface provide some important clues and they are discussed in the next section.

Transitions of $\text{Ar}_3\text{-HDO}$ and $\text{Ar}_3\text{-D}_2\text{O}$ exhibit the quadrupole hfs characteristic of the $I=1$ deuterium nuclei. It is most readily identified and assigned in the $J=0 \rightarrow 1$ transitions. The best results were obtained for the triplet structure of the $J=0 \rightarrow 1$ transition at 2311.8767 MHz of $\text{Ar}_3\text{-HDO}$ which gives $\chi_{aa}(\text{D})=83$ kHz. Table III lists the hyperfine

TABLE IV. Rotational transition frequencies observed for several isotopic species of the $\text{Ar}_3\text{-H}_2\text{S}$ tetramer in the symmetric top ground state.

Transition $J \rightarrow J'$	K	$\text{Ar}_3\text{-H}_2\text{S}$	$\text{Ar}_3\text{-H}_2^{34}\text{S}$	$\text{Ar}_3\text{-HDS}$	$\text{Ar}_3\text{-D}_2\text{S}$
$1 \rightarrow 2$	0	3276.0478	3199.1112	3252.9328	3234.8400
$2 \rightarrow 3$	0	4913.8706	4798.4730	4879.2114	4852.0700
$3 \rightarrow 4$	0	6551.4521	6397.600	6505.2601	6469.0777
	3	6551.2256	6397.3677	6504.8927	6468.4300
$4 \rightarrow 5$	0	8188.7124	...	8131.0051	8085.7868
	3	8188.4291	...	8130.5550	8084.9700
$5 \rightarrow 6$	0	9825.5704	9594.8409	9756.3716	9702.1222
	3	9825.2308	9594.4942	9755.8253	9701.1499
$6 \rightarrow 7$	0	11 461.9475	...	11 381.2829	11 318.0090
	3	11 461.5515	...	11 380.6484	11 316.8789
	6	11 460.3620	...	11 378.7380	11 313.4621
$7 \rightarrow 8$	0	13 097.7624	...	13 005.6643	12 933.3726
	3 ^a	13 097.3121	...	13 004.9351	12 932.0851
	6	13 095.9527	...	13 002.7600	12 928.1980

^aThe $K=3$ lines did not show any resolvable doubling up to the $J=7 \rightarrow 8$ transitions.

components and the quadrupole coupling constant estimated. It can be compared to 315 kHz in the free HDO. The difference is usually attributed to the projection of OD bond on to the c axis of the tetramer,¹² assuming that the electric charge distribution in D is not significantly perturbed following the complex formation with Ar_3 . With this assumption the projection angle, β , between the OD bond and the dimer c axis is calculated according to the following relation:

$$\chi_{aa}(\text{D}) = \frac{1}{2}\chi_0(\text{D})\langle 3 \cos^2 \beta - 1 \rangle. \quad (2)$$

The β thus calculated was 44° , compared to 34° for the benzene-HDO complex.¹²

B. $\text{Ar}_3\text{-H}_2\text{S}$

1. Search and assignment

The similarity of rotational constants between $\text{Ar}_n\text{-HF}$ and $\text{Ar}_n\text{-H}_2\text{O}$ proved very useful in finding the latter clusters. It was natural to expect that the $\text{Ar}_3\text{-H}_2\text{S}$ would have a rotational constant in the vicinity of that of the HCl counterpart. The expectation turned out to be true and the B rotational constant for $\text{Ar}_3\text{-H}_2^{32}\text{S}$ is ~ 819 MHz compared to ~ 844 MHz for the HCl analog.² Predicting the transitions for the other isotopomers was straightforward and soon H_2^{34}S , HDS, and D_2S containing tetramers were found. Table IV lists all the transitions found for the $\text{Ar}_3\text{-H}_2\text{S}$ system. Table II includes the rotational constants B , D_J , and D_{JK} for the four isotopomers along with those of the H_2O analogs. The rms deviation of the fit is included in Table II and they were within our experimental uncertainty. The D_{JK} is positive for this tetramer as it is a prolate symmetric top. One intriguing observation is that the D_{JK} for $\text{Ar}_3\text{-D}_2\text{S}$ (9.0 kHz) is about three times larger than that of the $\text{Ar}_3\text{-H}_2\text{S}$ (3.1 kHz). For the $\text{Ar}_3\text{-H}_2\text{O}$ and $\text{Ar}_3\text{-D}_2\text{O}$, the D_{JK} s differ by 28% only. Table II lists the rotational and centrifugal distortion constants of the other $\text{Ar}_3\text{-HX}$ tetramers that have been studied previously for comparison.

FIG. 1. Structure of the $\text{Ar}_3\text{-H}_2\text{X}$ tetramer. R is the distance between the c.m. of the Ar_3 and H_2X . The angles θ , ϕ , and χ define the orientation of H_2X . The abc axes shown in the figure are appropriate for the $\text{Ar}_3\text{-H}_2\text{S}$, oblate top. For the $\text{Ar}_3\text{-H}_2\text{O}$, the symmetry axes a and c are interchanged.

2. Hyperfine interactions

The smaller B for $\text{Ar}_3\text{-H}_2\text{S}$ implied that the $J=0 \rightarrow 1$ transition is below our spectrometer limit. However, $J=7 \rightarrow 8$ could be observed. The $K=0, 3$, and 6 lines were cataloged. The $K=3$ lines did not show any evidence for doubling even up to the $J=7 \rightarrow 8$ transition. Also, none of the rotational transitions observed for $\text{Ar}_3\text{-H}_2\text{S}$ showed any hfs. For $\text{Ar}_3\text{-D}_2\text{S}$, most of the lines were broadened due to the D quadrupole interactions but the splittings were not well resolved for any meaningful analysis. For $\text{Ar}_3\text{-HDS}$, the $J=0 \rightarrow 1$ line could not be observed and the hfs from the higher J, K levels were difficult to analyze. The $K=3$ transition of the $J=3 \rightarrow 4$ showed fairly resolved three line pattern with the splitting of 5.1 and 12.2 kHz. These could be assigned to the $\Delta F = +1$ transitions from $F''=4, 3$, and 2 and the hyperfine coupling constant was estimated to be 42 kHz. In the HDS monomer the value is 154 kHz (Ref. 18) and application of Eq. (2) gives an angle 44° between the OD axis and the a axis of the tetramer. This angle happens to be the same as that found for $\text{Ar}_3\text{-HDO}$. The similarity may be fortuitous as the inertial analysis, which is discussed in the next section, seems to indicate that the average orientations of H_2O and H_2S with respect to the symmetry axis of the tetramer are very different.

C. Structure of the tetramers

From the symmetric top spectrum and also the fact that only $K=3n$ ($n=0,1,2$) levels were observed, it is obvious that the Ar_3 forms an equilateral triangle with the H_2X species along the C_3 axis. It also implies that the H_2X has an effective spherical geometry. Figure 1 shows the structure of the tetramers. In order to specify the structure fully, the following parameters are needed: $R = \text{c.m.}-\text{c.m.}$ separation between the Ar_3 and H_2X ; $r = \text{the Ar}-\text{Ar}$ distance; $\theta = \text{the}$

angle between the C_2 axis of the H_2X and the C_3 axis of the complex. Two more angles ϕ and χ as defined in Fig. 1 are needed to specify the orientation of the asymmetric H_2X with respect to Ar_3 . From the experimental rotational constants, we estimate three of these parameters R , r , and θ as described in this section. MMC calculations have been carried out to determine the equilibrium structure and the results are described in the next section.

From the rotational constants of the $^{18}\text{O}(^{34}\text{S})$ isotopomer along with the parent isotopomer, the distance between the O (S) and c.m. of the tetramer could be determined from the following equation:²²

$$\Delta I = \mu_s a_x^2, \quad (3)$$

where ΔI is the change in moments of inertia following the substitution, $\mu_s = M \Delta m / (M + \Delta m)$, is the reduced mass for substitution and a_x is the distance of the substituted atom from the c.m. along the symmetry axis. (For $\text{Ar}_3\text{-H}_2\text{O}$ the symmetry axis is c and for $\text{Ar}_3\text{-H}_2\text{S}$ it is a . However, for convenience we will use a_x to denote the distance between atom X and the c.m. of the tetramer along the symmetry axis.) For $\text{Ar}_3\text{-H}_2\text{O}$, a_O is calculated to be $2.563 \text{ \AA}$ and for $\text{Ar}_3\text{-H}_2\text{S}$, a_S is calculated to be $2.744 \text{ \AA}$. Application of Eq. (3) for D substitution is less valid because of the large changes in zero point motion between H and D containing species. Also, the D's are not located on the symmetry axis. However, we can get an upper bound for the a_H by using Eq. (3) from the rotational constants of $\text{Ar}_3\text{-D}_2\text{O}(\text{D}_2\text{S})$. The a_H is calculated to be $2.499(1.989) \text{ \AA}$. The differences, $\Delta a_H = a_x - a_H$, for the tetramer and free H_2X can be used to estimate the average projection angle, θ , between the symmetry axes of H_2X and the tetramer. For free H_2O , $\Delta a_H = 0.595 \text{ \AA}$ and for free H_2S , it is $0.919 \text{ \AA}$. From these values, θ is calculated to be 84° and 34° for H_2O and H_2S complexes, respectively.

A more detailed substitution analysis could be done for D_2X by the multiple substitution off the axis method²² as was carried out for the "symmetric top" benzene-water dimer.¹² In this case,

$$\Delta I_b = \Delta m b_H^2 + [2 \Delta m M / (M + 2 \Delta m)] a_H^2, \quad (4)$$

where $b_H^2 + \Delta a_H^2 = r(\text{XH})^2$ and Δm is the difference in mass between H and D. These relations yield values of $a_H = 2.404(1.850) \text{ \AA}$ and $\Delta a_H = 0.160(0.895) \text{ \AA}$ for the $\text{H}_2\text{O}(\text{H}_2\text{S})$ complexes. These values lead to a projection angle θ of 74° and 13° , significantly smaller than the upper bounds estimated above. These θ values and a_x are used to determine $a(\text{H}_2\text{X})$, the distance between the c.m. (H_2X) and the c.m. of the tetramer. The $a(\text{H}_2\text{X})$, thus calculated are 2.545 and $2.691 \text{ \AA}$ for the H_2O and H_2S complexes, respectively. According to the first moment condition the following relation holds:

$$a(\text{Ar}_3) \times m(\text{Ar}_3) = a(\text{H}_2\text{X}) \times m(\text{H}_2\text{X}). \quad (5)$$

Of course, $a(\text{Ar}_3) + a(\text{H}_2\text{X})$ gives R , the c.m.-c.m. distance between the two units. It is determined to be 2.928 and $3.454 \text{ \AA}$ for the H_2O and H_2S complexes, respectively. These val-

TABLE V. Geometry of the $\text{Ar}_3\text{-HX}$ tetramers determined from the rotational constants (distances in Å and the angle in degs).

Complex	$R(\text{Ar-Ar})$	$R(\text{Ar-HX})^a$	θ^b
Ar_3^c	3.811	...	...
$\text{Ar}_3\text{-Ne}^d$	3.826	3.610	...
$\text{Ar}_3\text{-HF}^e$	3.835	3.519	41
$\text{Ar}_3\text{-HCl}^f$	3.851	3.978	37
$\text{Ar}_3\text{-HCN}^g$	3.85 ^{g,l}	3.47	45
$\text{Ar}_3\text{-H}_2\text{O}^h$	3.848	3.675	~74
$\text{Ar}_2\text{-H}_2\text{O}^i$	3.822	3.687	...
$\text{Ar-H}_2\text{O}^j$	...	3.691	~81
$\text{Ar-H}_2\text{S}^k$	...	4.013	...
$\text{Ar}_3\text{-H}_2\text{S}^h$	3.865	4.112	~13

^aThe distance between Ar and the c.m. of the bonding partner to Ar_3 .

^bThe angle between the C_3 axis of the complex and the symmetry axis of the HX. For the HX species the angle was determined from the quadrupole coupling constant of X and for the H_2X , it was determined by inertial analysis described in the text.

^cReference 28.

^dReference 29.

^eReference 1.

^fReference 2.

^gReference 4.

^hThis work.

ⁱReference 17.

^jReference 27.

^kReference 18.

^lFixed at $\text{Ar}_3\text{-HCl}$ value.

ues could be used to estimate r , the Ar–Ar distance and Ar–c.m.(H_2X) distances using parallel axis theorem to define I_b of the tetramer as given below,

$$I_b(\text{Ar}_3\text{-H}_2\text{X}) = I_b(\text{Ar}_3) + I_s(\text{H}_2\text{X}) + \mu_D R^2. \quad (6)$$

Here, $I_s(\text{H}_2\text{X})$, is the moment of inertia of H_2X about the b axis of the tetramer. The symmetric top nature of the tetramer encourages us to use an average value for $I(\text{H}_2\text{X})$, i.e., $(I_a + I_c)/2$. It should be emphasized that the light tops H_2X have moments of inertia between 1–3 amu Å², which is the smallest of all the four terms in Eq. (6). Its effect on R or r is important in the second or third decimal only. We neglect the tilt of Ar_3 . In Eq. (6), except for $I_b(\text{Ar}_3)$, all other terms are known and it is solved to get $I_b(\text{Ar}_3) = 2 \times m_{\text{Ar}} \times (r/2)^2$. The Ar–Ar distance, r , is calculated to be 3.848 and 3.865 Å for H_2O and H_2S complexes, respectively. From these values, the Ar–c.m.(H_2X) distance is calculated as 3.675 and 4.112 Å.

Table V compares the structural parameters of some $\text{Ar}_n\text{-HX}$, where $n = 1, 2$ or 3 for $\text{HX} = \text{HF}, \text{HCl}, \text{HCN}, \text{H}_2\text{O}$, and H_2S and Ar_3 (Ref. 28) and $\text{Ar}_3\text{-Ne}$.²⁹ The Ar–Ar distance is fairly constant in all the $\text{Ar}_3\text{-HX}$, varying from 3.826 Å in $\text{Ar}_3\text{-Ne}$ to 3.865 Å in $\text{Ar}_3\text{-H}_2\text{S}$. This can be compared to the theoretical estimate of 3.811 Å in the free Ar_3 .²⁸ All the Ar–Ar distances differ in the second decimal only and are within 3.84(3) Å. The Ar–HX distance shows a clear trend between first row and second row hydrides. For the first row hydrides such as HF, HCN, H_2O and even Ne, the distance observed is 3.6(1) Å. For the second row hydrides, HCl and H_2S , it is about 4.0(1) Å. The Ar– H_2O and Ar–Ne distances are very close differing only in the second decimal. Table II includes the rotational constants for several $\text{Ar}_3\text{-HX}$ and $\text{Ar}_3\text{-Ne}$ tetramers. For $\text{Ar}_3\text{-D}_2\text{O}$ and $\text{Ar}_3\text{-Ne}$

FIG. 2. (A) The global minimum structure of $\text{Ar}_3\text{-H}_2\text{O}$ obtained by MMC calculations. The structure represents one of the three minima. (B) The transition structure connecting two of the minima. It is only 6 cm^{-1} above the minimum compared to a zero point vibrational energy of 174 cm^{-1} . $\text{Ar}_3\text{-H}_2\text{S}$ has similar global minimum and transition structures and the energy difference is 8 cm^{-1} .

(D_2O and Ne both having a mass of about 20 amu), the rotational constants happen to be nearly identical. The angle between the symmetry axes of the tetramer and HX is about 40° for the linear HX. However, for H_2O it is much larger at around 74° implying that the Ar_3 and H_2O planes may be nearly parallel. For H_2S , the average tilt is calculated to be only 13°.

IV. MMC AND RBDQMC CALCULATION RESULTS

Calculations were carried out to determine the optimum geometry of the two tetramers. The model potentials used for the clusters' potential surfaces followed the molecular mechanics for clusters (MMC) scheme⁸ in expressing the interaction as a sum of the classically evaluated electrical interaction energy plus Lennard-Jones or 6–12 terms among different monomer sites. The electrical interaction is the sum of the permanent moment interaction and polarization energy based on the dipole and quadrupole polarizabilities of the monomers, whereas the 6–12 terms are treated with adjustable parameters. The parameters for the 6–12 potentials are those obtained previously for argon,⁸ water,⁸ and H_2S .¹⁹ Back polarization, which is usually included in MMC evaluations was found to be very unimportant and therefore was not included.

The structure of the global minimum is shown in Fig. 2. It has the H_2O above the plane of the Ar_3 , with the two H pointing towards two of the argons. This structure has only a plane of symmetry and the two Ar–Ar distances were 3.761 and 3.777 Å. The Ar–c.m.(H_2O) distances were 3.405 and 3.496 Å. Both these distances were significantly smaller than

FIG. 3. Potential energy curves for $\text{Ar}_3\text{-H}_2\text{O}$ as a function of θ . The lower and upper curves are for $\phi=0$ and 180° , respectively. The difference between the two curves at any given θ gives the barrier to rotation about ϕ . (θ and ϕ are defined in Fig. 1.)

the distances estimated from the rotational constants, as was found earlier in MMC calculations on $\text{Ar}_2\text{-H}_2\text{O}$ system.¹⁷ Obviously it is one of the three equivalent minima and any one among the three pair of the argons could be connected to the two hydrogens. A transition state was located that connects two of the minima. It has one hydrogen hooked on to an argon and the other pointing in between the other two argons, as shown in Fig. 2. The difference in energy between the minima and the transition state was a mere 6 cm^{-1} . The water could exhibit pseudorotation over the plane of the argons, in which one hydrogen is bonded to an argon and the other hops from the second to third argon followed by the first hydrogen hopping from the first to second argon and so on. For $\text{Ar}_3\text{-H}_2\text{S}$, very similar minimum and transition structures were found and the energy difference was again very small at 8 cm^{-1} .

For $\text{Ar}_3\text{-H}_2\text{O}$, the equilibrium value of θ was found to be 15° compared to the experimental estimate of 74° . Hence, it was decided to calculate the barrier for the pseudorotation as a function of θ . Calculations were done with θ fixed in 5° increments from 0 to 180° . All the other parameters were optimized except for ϕ . Figure 3 shows the total energy of $\text{Ar}_3\text{-H}_2\text{O}$ as a function of θ . The transition structure discussed above turns out to be the optimum structure for $\theta = 0^\circ$. The lower curve is the energy calculated for $\phi = 0^\circ$

when both the hydrogens are pointing toward two argons. The upper curve is for $\phi = 180^\circ$ when both hydrogens are pointing away from the two argons, corresponding to the highest energy structure for a given θ . The difference between the two curves gives the barrier for rotation about ϕ for a given value of θ . It varies from 0 to 30 cm^{-1} for various values of θ . Figure 3 suggests that the H_2O is likely to exhibit some kind of a swinging motion with both θ and ϕ varying. This is very different from internal rotation about an axis from which a ground ($m=0$) and an excited ($m=1$) states could be expected having different spin states of H_2X . This is obviously a consequence of the equilibrium geometry and more importantly the asymmetric interaction of only two of the three argons with the two hydrogens.

The experimentally determined structural parameters (both distances and angles) are significantly different from the MMC equilibrium structure. In order to make a more reasonable comparison with the experimentally determined “average” structures, quantum Monte Carlo calculations were carried out for averaging the rotational constants over all the vibrational modes. Vibrational analysis was carried out with the MMC potential via rigid body diffusion quantum Monte Carlo (RBDQMC) calculations. Our implementation³⁰ follows Anderson’s diffusion quantum Monte Carlo (DQMC) approach³¹ which exploits an equivalence of the differential equation for diffusion and the time-dependent differential Schrödinger equation on replacing the time variable, t , in the Schrödinger equation by an imaginary time variable, $\tau = it$. Monte Carlo (MC) techniques used to obtain a numerical solution of the diffusion equation are used to simulate the solution of the modified Schrödinger equation via pseudo particles, “psips,” that propagate (diffuse) in randomized, discrete steps in imaginary time τ . A short time step of 4.0 a.u. (time) [1.0 a.u. (time) or $1.0\text{ } h/(2\pi E_h) = 2.41888 \times 10^{-17}\text{ s}$] was used in the calculations on $\text{Ar}_n\text{-H}_2\text{O}$. The number of psips was 7000, and the energy and property evaluations were performed through 30 cycles of 8000 time steps each. These were carried out following an equilibration sequence of 19 000 time steps of decreasing size and an overall duration of $1.1 \times 10^6\text{ a.u.}$ The rms deviations of the energies for the 30 cycles from the average of the 30 cycle energies were around 0.4 cm^{-1} . The diffusion simulation yielded weights for each psip that reflect the vibrational state probability densities³² and rotational constants were calculated as an average by descendant weighting of

TABLE VI. MMC and RBDQMC results.^a

Cluster	Equilibrium energy	Ground state energy	ZPE ^b	$\langle A+B \rangle/2$ Calc.	$\langle A+B \rangle/2$ Expt.	Deviation %
$\text{Ar}_3\text{-H}_2\text{O}$	-932	-758	174	1221	1172	4.2
$\text{Ar}_3\text{-D}_2\text{O}$	-932	-765	167	1199	1139	5.3
$\text{Ar}_3\text{-H}_2\text{S}^c$	-870	-668	202	793	819	-3.2
$\text{Ar}_3\text{-D}_2\text{S}^c$	-870	-682	188	783	808	-3.1
$\text{Ar}_4\text{-H}_2\text{O}$	-1242	-1026	216	759	...	...
$\text{Ar}_4\text{-D}_2\text{O}$	-1242	-1033	209	757	...	...

^aThe energies are in cm^{-1} and the rotational constants are in MHz.

^bZero point energy in cm^{-1} .

^cResults for $\text{H}_2\text{S/D}_2\text{S}$ clusters were reported previously. The rotational constants given are $\langle B+C \rangle/2$ for these complexes (Ref. 33).

the inverses of the principal moments of inertia.

The results of the calculations are given in Table VI. The values of the zero point energies (ZPE) reinforce the view that the barriers for pseudorotation or swinging in $\text{Ar}_3\text{-H}_2\text{X}$ species are relatively small in that the available energy for vibrational excursion is much more than the energy to overcome the barriers. Results for $\text{Ar}_4\text{H}_2\text{O/D}_2\text{O}$ illustrate the diminishing effect of deuterium substitution with increasing cluster mass (increasing numbers of argons) and provide predictions for future searches for these clusters. The rotational constants from RBDQMC calculations differ from the experimental rotational constants by 3%–5%. For the $\text{Ar-H}_2\text{S}$ dimer RBDQMC calculations could reproduce the experimental rotational constants to within 1%. The larger error in $\text{Ar}_3\text{-H}_2\text{S}$ indicates that the Ar-Ar pair and possibly three-body interactions are not adequately represented in the MMC potential.

V. CONCLUSIONS

The rotational spectrum of $\text{Ar}_3\text{-H}_2\text{O}$ and $\text{Ar}_3\text{-H}_2\text{S}$ tetramers were obtained with a Balle-Flygare FT microwave spectrometer. Both these complexes give a simple symmetric top spectra and due to the spin statistics of the zero spin ^{40}Ar atoms only $K=3n$ ($n=0,1,2$) were observed. Inertial analysis leads to Ar-Ar distances of 3.843 and 3.865 Å in the H_2O and H_2S complexes, respectively. The $\text{Ar-c.m.}(\text{H}_2\text{X})$ distance was determined to be 3.675 and 4.112 Å. The average angle between the C_2 axis of H_2X and the symmetry axis of the tetramer is estimated to be 74° and 13° for the H_2O and H_2S complexes, respectively. No evidence for an excited internal rotor/torsional state was found for both tetramers. MMC calculations indicate that the global minimum has the H_2X above the plane of the Ar_3 with both the protons pointing towards one Ar each. The barrier to “pseudorotation” of H_2X above the Ar_3 plane is estimated to be very small at $6(8)\text{ cm}^{-1}$ for $\text{H}_2\text{O}(\text{H}_2\text{S})$. However, the pseudorotation of H_2X is some kind of a swinging motion and not rotation about some axis possibly explaining the absence of internal rotor excited states.

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