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 $\text{H}_2\text{O}$ and 819.0385(1) MHz, 3.346(1) kHz, and $+3.145(2)$ kHz for the $\text{H}_2\text{S}$ containing tetramer. Substitution analysis with the rotational constants of various isotopomers led to an $\text{Ar}–\text{Ar}$ distance of 3.848 Å and an $\text{Ar}$-c.m.($\text{H}_2\text{X}$) distance of 3.675 (4.112) Å for $\text{H}_2\text{O}$ ($\text{H}_2\text{S}$) complexes. The angle between the $C_m$ axis of the $\text{H}_2\text{X}$ and the $C_3$ axis of the tetramer is estimated to be $74^\circ$ for $\text{H}_2\text{O}$ and $13^\circ$ for the $\text{H}_2\text{S}$ 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 $\text{H}_2\text{X}$ positioned above the plane of the $\text{Ar}_3$ with both the protons pointing towards one $\text{Ar}$ 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 $\text{H}_2\text{O}$ ($\text{H}_2\text{S}$) making the $\text{H}_2\text{X}$ 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\textsuperscript{1–5} in which a tetramer is formed by adding a di- or triatomic molecule to the face of an equilateral $\text{Ar}_3$ trimer. The added species include HF (the first tetramer studied),\textsuperscript{1} HCl,\textsuperscript{2,3} and HCN.\textsuperscript{4} Also, a preliminary account has been\textsuperscript{5} 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 $\text{Ar}_3$ 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 $40^\circ$ 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 $\text{Ar}_3$–HCN, with a linear triatomic HCN, exhibit several unusual features.\textsuperscript{4} These were attributed to strong coupling between the radial and bending motions in the $\text{Ar}_3$–HCN. In fact, such coupling has been observed in all the $\text{Ar}_m$–HCN ($m = 1,2,3$) clusters\textsuperscript{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 $\text{H}_2\text{X}$ as the bonding partner of the $\text{Ar}_3$. 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,\textsuperscript{9} HCl,\textsuperscript{10} or HCN (Ref. 4) species generates quite normal symmetric top spectra. The average angle between the symmetry axis of the dimer and the $\text{HX}$ bond is about $20^\circ$ for benzene–$\text{HX}$.\textsuperscript{4} Extensive studies have been made of the benzene–water dimer which also has a ground state symmetric top spectrum.\textsuperscript{11–13} However, the spectrum is more complex, characteristic of two coaxial rotors with a symmetric top frame and a very low effective $V_0$ barrier.\textsuperscript{14} Several internal rotor states were found and they were correlated to the rotational states of free $\text{H}_2\text{O}$.\textsuperscript{13} The benzene–$\text{H}_2\text{S}$ dimer also shows a complex spectra\textsuperscript{15} with evidence for ground and excited torsional/internal rotor states.

We have previously reported the rotational spectra of $\text{Ar}$–$\text{H}_2\text{O}$ (Ref. 16) and $\text{Ar}_2$–$\text{H}_2\text{O}$.\textsuperscript{17} In both cases, two internal rotor states of $\text{H}_2\text{O}$ were found. The $\text{Ar}$–$\text{H}_2\text{S}$ spectrum also showed evidence for two states of $\text{H}_2\text{S}$ in the dimer.\textsuperscript{18}
However, it was very different from that of Ar–H$_2$O and it showed an anomalous isotopic effect. This paper reports the rotational spectra of the Ar$_3$–H$_2$O and Ar$_3$–H$_2$S. 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 Ar$_3$–H$_2$O than in Ar–H$_2$O or Ar$_2$–H$_2$O? 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–H$_2$S system, 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 Ar$_3$–H$_2$O and Ar$_3$–H$_2$S tetramers were observed with the Balle–Flygare Fourier transform microwave spectrometer described in detail previously. [2] The tetramers were formed by supersonic co-expansion of a few % H$_2$S (Air products) or H$_2$O with argon (liquid air) as the carrier gas at 1 atm backing pressure. The optimum microwave pulse required was 3 µs for Ar$_3$–H$_2$O indicating that the dipole moment of the tetramer was much smaller than that of free H$_2$O. For comparison, the optimum pulse length required for benzene–H$_2$O was 0.3 µs and the dipole moment was determined to be $\approx$2.0 D. [3]

For the HDO complex an equivalent mixture of H$_2$O and D$_2$O (Sigma) was used. The D$_2$O was prepared by bubbling H$_2$S sequentially through 12 small portions of D$_2$O kept in a reflux coil condenser followed by a dry ice trap to remove any D$_2$O. This method ensured that there was no significant amount of HDS present when looking for D$_2$O complexes to avoid assignment ambiguities.

III. RESULTS AND ANALYSIS

A. Ar$_3$–H$_2$O tetramer

1. Search and assignment

The rotational spectrum of Ar$_3$–H$_2$O was predicted and found readily by assuming its structure would be similar to that of Ar$_3$–HF (Ref. 1) with the further expectation that it would be a symmetric top as in C$_6$H$_6$–H$_2$O in spite of the asymmetry of the H$_2$O. [11,12] This proved to be the case as shown by the transitions in Table I. Their detection requires both Ar and H$_2$O in the gas mixture. Moreover, only the $K = 3n$ levels appear, where $n = 0, 1, 2, \ldots$ This is required for a threefold symmetric top with three interchangeable spin zero $^{40}$Ar nuclei. Symmetric top transitions were observed from $J = 0 \rightarrow 1$ through $J = 6 \rightarrow 7$ for four isotopic species of water, i.e., H$_2$O, HDO, D$_2$O, and H$_2^{18}$O.

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

$$v_0 = 2B_0(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2.$$  (1)


| Table I. Rotational transition frequencies observed for several isotopic species of the Ar$_3$–H$_2$O tetramer in the symmetric top ground state. |
|---|---|---|---|---|
| Transition | $J \rightarrow J$ | $K$ | Ar$_3$–H$_2$O | Ar$_3$–H$_2^{18}$O |
| 0 $\rightarrow$ 1 | 0 | 2344.2347 | $\cdots$ | 2311.8773 |
| 1 $\rightarrow$ 2 | 0 | 4688.2981 | 4551.2930 | 4623.5867 |
| 2 $\rightarrow$ 3 | 0 | 7032.0160 | 6826.5442 | 6934.9700 |
| 3 $\rightarrow$ 4 | 0 | 9375.2155 | 9101.3192 | 9245.8601 |
| 4 $\rightarrow$ 5 | 3 | 11717.7242 | 11375.4642 | 11556.0936 |
| 5 $\rightarrow$ 6 | 3 | 14059.3688 | 13684.8151 | 13865.5036 |
| 6 $\rightarrow$ 7 | 0 | 16399.9756 | 15921.2175 | 16173.9274 |

The rms deviation of the fitting was $\approx$1 kHz for the H$_2$O and H$_2^{18}$O but slightly larger for HDO and D$_2$O 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 $I_3$ for free Ar$_3$. Comparing the $B_0$ of the parent isotopomer (1172.1323 MHz) with the C rotational constant of Ar$_3$ given in Table II (859.86 MHz) shows that the Ar$_3$–H$_2$O 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 Ar$_3$–HCN starting from the

| Table II. Rotational constants determined by fitting Eq. (1) to the symmetric top transitions observed for several isotopic species of Ar$_3$–H$_2$O (Table I) and of Ar$_3$–H$_2$S (Table IV). |
|---|---|---|---|---|
| Species | $B_0$ (MHz) | $D_J$ (kHz) | $D_{JK}$ (kHz) | $\sigma^*$(kHz) |
| Ar$_3$–H$_2$O | 1172.1323(1) | 7.199(1) | $-5.454(5)$ | 0.8 |
| Ar$_3$–H$_2^{18}$O | 1137.8760(1) | 6.595(1) | $-4.318(3)$ | 0.9 |
| Ar$_3$–HDO | 1155.9513(3) | 6.847(4) | $-4.907(8)$ | 2.6 |
| Ar$_3$–D$_2$O | 1139.3953(3) | 6.378(4) | $-3.997(8)$ | 2.7 |
| Ar$_3$–H$_2$S | 819.0385(1) | 3.346(1) | $-3.145(2)$ | 0.8 |
| Ar$_3$–HDS | 799.8039(1) | 3.247(1) | $-3.216(6)$ | 0.4 |
| Ar$_3$–HD$_2$S | 813.2486(1) | 3.160(2) | $-5.045(4)$ | 1.9 |
| Ar$_3$–D$_2$H$_2$S | 808.7339(3) | 3.108(3) | $-9.006(8)$ | 4.3 |
| Ar$_3$–HF | 1188.2123(2) | 6.846(3) | $-5.753(6)$ | 0.8 |
| Ar$_3$–HCN | 843.8974(1) | 2.332(3) | $-1.818(6)$ | 0.8 |
| Ar$_3$–HCN$^-$ | 886.4878(1) | 10.374(2) | $-173.156(7)$ | 0.8 |
| Ar$_3$–Ne | 1139.0830(1) | 9.072(2) | $-1.529(8)$ | 0.8 |
| Ar$_3$ | 859.86 | $\cdots$ | $\cdots$ | $\cdots$ |

$a$ Standard deviation of the fit in kHz.

$^a$Reference 1.

$^b$Reference 2.

$^c$Reference 4.

$^d$Reference 29.

$^e$Reference 28.

$^f$For Ar$_3$–HCN which also has unusual centrifugal distortion constants, all the tetramers satisfy this condition.
J = 4 → 5 transitions. For the J = 6 → 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.\(^7\)–\(^9\) Obviously, this distortion in the Ar\(_3\)–H\(_2\)O is much smaller than that in Ar\(_3\)–HCN.

2. Hyperfine interactions

There are two weak but detectable hyperfine interactions in the isotopic species of water studied as the Ar\(_3\)–H\(_2\)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\(_2\)O.\(^10\) Then there is the deuteron nuclear quadrupole coupling in the HDO and D\(_2\)O isotopomers with \(\chi_0(\text{D})\) cited to be 315 kHz for free HDO and 330 kHz in free D\(_2\)O.\(^26\) Two aspects of the resulting hfss are particularly useful. 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\(_2\)O 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 hfss. 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 hfss suggests that the H\(_2\)O protons are in a singlet spin state with \(I_{\text{H}} = 0\) and thus are indistinguishable, which constrains the H\(_2\)O 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\(_2\)O, thereby generating two states and two sets of transitions. For example in Ar–H\(_2\)O (Refs. 16, 27) and Ar\(_2\)–H\(_2\)O,\(^17\) the antisymmetric singlet proton state is coupled to the symmetric \(0_{00}\) rotational state of the H\(_2\)O and the symmetric triplet proton state is coupled to the antisymmetric \(1_{01}\) rotational state. However no other states were detected for Ar\(_3\)–H\(_2\)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 Ar\(_3\)–HDO and Ar\(_3\)–D\(_2\)O exhibit the quadrupole hfss 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 Ar\(_3\)–HDO which gives \(\chi_{aa}(\text{D}) = 83\) kHz. Table III lists the hyperfine 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, \(\beta\), between the OD bond and the dimer \(c\) axis is calculated according to the following relation:

\[
\chi_{aa}(D) = \frac{1}{2}\chi_0(D)(3\cos^2 \beta - 1).
\]

The \(\beta\) thus calculated was 44°, compared to 34° for the benzene–HDO complex.\(^12\)

B. Ar\(_3\)–H\(_2\)S

1. Search and assignment

The similarity of rotational constants between Ar\(_3\)–HF and Ar\(_3\)–H\(_2\)S proved very useful in finding the latter clusters. It was natural to expect that the Ar\(_3\)–H\(_2\)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 Ar\(_3\)–H\(_2\)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\(_2\)\(^{16}\)S, H\(_2\)\(^{18}\)S, HDS, and D\(_2\)S containing tetramers were found. Table IV lists all the transitions found for the Ar\(_3\)–H\(_2\)S system. Table II includes the rotational constants \(B, D_j,\) and \(D_{JK}\) for the four isotopomers along with those of the H\(_2\)O 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 Ar\(_3\)–D\(_2\)S (9.0 kHz) is about three times larger than that of the Ar\(_3\)–H\(_2\)S (3.1 kHz). For the Ar\(_3\)–H\(_2\)O and Ar\(_3\)–D\(_2\)O, the \(D_{JK}\)s differ by 28% only. Table II lists the rotational and centrifugal distortion constants of the other Ar\(_3\)–HX tetramers that have been studied previously for comparison.

\[\begin{array}{cccccc}
\text{Transition} & \text{\(J' - J\)} & \text{\(K\)} & \text{Ar\(_3\)–H\(_2\)S} & \text{Ar\(_3\)–H\(_2\)\(^{18}\)S} & \text{Ar\(_3\)–D\(_2\)S} \\
\hline
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 & 6397.6000 & 6505.2601 & 6469.0777 \\
4 \rightarrow 5 & 0 & 6551.2256 & 6397.3677 & 6504.8927 & 6468.4300 \\
5 \rightarrow 6 & 0 & 9825.5704 & 9594.8409 & 9756.3716 & 9702.1222 \\
6 \rightarrow 7 & 0 & 11 461.9475 & \cdots & 11 381.2829 & 11 318.0090 \\
7 \rightarrow 8 & 0 & 13 097.7624 & \cdots & 13 005.6643 & 12 933.3726 \\
8 & 0 & 13 097.3121 & \cdots & 13 004.9351 & 12 932.0851 \\
9 & 6 & 13 095.9527 & \cdots & 13 002.7600 & 12 928.1980 \\
\end{array}\]

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

\(\text{\(^*\)The } K = 3 \text{ lines did not show any resolvable doubling up to the } J = 7 \rightarrow 8 \text{ transitions.}\)
angle between the $C_2$ axis of the $H_2X$ and the $C_3$ axis of the complex. Two more angles $\phi$ and $\chi$ 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 $\theta$ 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 $^{18}O(^{34}S)$ 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:

$$\Delta I = \mu_s a_s^2,$$

where $\Delta I$ 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 $a_s$ is the distance of the substituted atom from the c.m. along the symmetry axis. 

For $Ar_3-H_2O$, the symmetry axis is $c$ and for $Ar_3-H_2S$ 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 $Ar_3-H_2O, a_O$ is calculated to be 2.563 Å and for $Ar_3-H_2S, a_S$ is calculated to be 2.744 Å. 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 $Ar_3-D_2O(D_2S)$. The $a_H$ is calculated to be 2.499(1.989) Å. 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, $\langle \theta \rangle$ between the symmetry axes of $H_2X$ and the tetramer. For free $H_2O$, $\Delta a_H = 0.595$ Å and for free $H_2S$, it is 0.919 Å. From these values, $\theta$ 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 method as was carried out for the ‘‘symmetric top’’ benzene–water dimer. In this case,

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

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

$$a(\text{Ar}_3) \times m(\text{Ar}_3) = a(\text{H}_2X) \times m(\text{H}_2X).$$

Of course, $a(\text{Ar}_3) + a(\text{H}_2X)$ gives $R$, the c.m.–c.m. distance between the two units. It is determined to be 2.928 and 3.454 Å for the $H_2O$ and $H_2S$ complexes, respectively. These val-
TABLE V. Geometry of the Ar₃–HX tetramers determined from the rotational constants (distances in Å and the angle in degs).

<table>
<thead>
<tr>
<th>Complex</th>
<th>R(Ar–Ar)</th>
<th>R(Ar–HX)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar₃⁺</td>
<td>3.811</td>
<td>⋯</td>
<td>⋯</td>
</tr>
<tr>
<td>Ar₃–Ne⁺</td>
<td>3.826</td>
<td>3.610</td>
<td>⋯</td>
</tr>
<tr>
<td>Ar₃–HF⁺</td>
<td>3.835</td>
<td>3.519</td>
<td>41</td>
</tr>
<tr>
<td>Ar₃–HCl⁺</td>
<td>3.851</td>
<td>3.978</td>
<td>37</td>
</tr>
<tr>
<td>Ar₃–HCN⁺</td>
<td>3.85¹</td>
<td>3.47</td>
<td>45</td>
</tr>
<tr>
<td>Ar₃–H₂O⁺</td>
<td>3.848</td>
<td>3.675</td>
<td>−74</td>
</tr>
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<td>3.822</td>
<td>3.687</td>
<td>⋯</td>
</tr>
<tr>
<td>Ar–H₂O⁰</td>
<td>⋯</td>
<td>3.691</td>
<td>−81</td>
</tr>
<tr>
<td>Ar–H₂S⁰</td>
<td>4.013</td>
<td>⋯</td>
<td>⋯</td>
</tr>
<tr>
<td>Ar₃–H₂S⁰</td>
<td>3.865</td>
<td>4.112</td>
<td>−13</td>
</tr>
</tbody>
</table>

aThe distance between Ar and the c.m. of the bonding partner to Ar₃.

bThe angle between the C₃ 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 H₂X, 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 Ar₃–HCl value.

ues could be used to estimate r, the Ar–Ar distance and Ar–c.m.(H₂X) distances using parallel axis theorem to define $I_b$ of the tetramer as given below,

$$I_b(Ar_3-H_2X) = I_b(Ar_3) + I_b(H_2X) + \mu_Hr^2. \quad (6)$$

Here, $I_b(H_2X)$, is the moment of inertia of H₂X about the b axis of the tetramer. The symmetric top nature of the tetramer encourages us to use an average value for $I(H_2X)$, i.e., $(I_a + I_c)/2$. It should be emphasized that the light tops H₂X 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 Ar₃. In Eq. (6), except for $I_b(Ar_3)$, all other terms are known and it is solved to get $I_b(Ar_3) = 2 \times m_3 \times (r/2)^2$. The Ar–Ar distance, r, is calculated to be 3.848 and 3.865 Å for H₂O and H₂S complexes, respectively. From these values, the Ar–c.m.(H₂X) distance is calculated as 3.675 and 4.112 Å.

Table V compares the structural parameters of some Ar₃–HX, where n = 1, 2 or 3 for HX=H₂F, HCl, HCN, H₂O, and H₂S and Ar₃ and Ar₃–Ne.²⁰ The Ar–Ar distance is fairly constant in all the Ar₃–HX, varying from 3.826 Å in Ar₃–Ne to 3.865 Å in Ar₃–H₂S. This can be compared to the theoretical estimate of 3.811 Å in the free Ar₃.²⁸ 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, H₂O and even Ne, the distance observed is 3.6(1) Å. For the second row hydrides, HCl and H₂S, it is about 4.0(1) Å. The Ar–H₂O and Ar–Ne distances are very close differing only in the second decimal. Table II includes the rotational constants for several Ar₃–HX and Ar₃–Ne tetramers. For Ar₃–D₂O and Ar₃–Ne (D₂O 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 H₂O it is much larger at around 74° implying that the Ar₃ and H₂O planes may be nearly parallel. For H₂S, 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) scheme 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 H₂S.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 H₂O above the plane of the Ar₃, 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.(H₂O) distances were 3.405 and 3.496 Å. Both these distances were significantly smaller than...
FIG. 3. Potential energy curves for Ar$_3$–H$_2$O as a function of $\phi$. The lower and upper curves are for $\phi=0$ and 180°, respectively. The difference between the two curves at any given $\theta$ gives the barrier to rotation about $\phi$. ($\theta$ and $\phi$ are defined in Fig. 1.)

The distances estimated from the rotational constants, as was found earlier in MMC calculations on Ar$_4$–H$_2$O system.\textsuperscript{17} Obviously it is one of the three equivalent minima and any one of 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 pointing in between the other two. For Ar$_3$–H$_2$S, very similar minimum and transition structures were found and the energy difference was again very small at 8 cm$^{-1}$.

For Ar$_3$–H$_2$O, the equilibrium value of $\theta$ 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 $\theta$. Calculations were done with $\theta$ fixed in 5° increments from 0 to 180°. All the other parameters were optimized except for $\phi$. Figure 3 shows the total energy of Ar$_3$–H$_2$O as a function of $\theta$. The transition structure discussed above turns out to be the optimum structure for $\theta=0°$. The lower curve is the energy calculated for $\phi=0°$ when both the hydrogens are pointing toward two argons. The upper curve is for $\phi=180°$ when both hydrogens are pointing away from the two argons, corresponding to the highest energy structure for a given $\theta$. The difference between the two curves gives the barrier for rotation about $\phi$ for a given value of $\theta$. It varies from 0 to 30 cm$^{-1}$ for various values of $\theta$. Figure 3 suggests that the H$_2$O is likely to exhibit some kind of a swinging motion with both $\theta$ and $\phi$ 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$_2$X. 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 implementation\textsuperscript{30} follows Anderson’s diffusion quantum Monte Carlo (DQMC) approach\textsuperscript{31} 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 $\tau$. A short time step of 4.0 a.u. (time) [1.0 a.u. (time) or 1.0 $\hbar/2(\pi E_b) = 2.418 88 \times 10^{-17}$ s] was used in the calculations on Ar$_x$–H$_2$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 19000 time steps of decreasing size and an overall duration of $1.1 \times 10^6$ 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 densities\textsuperscript{32} and rotational constants were calculated as an average by descendant weighting of

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

$^a$The energies are in cm$^{-1}$ and the rotational constants are in MHz.

$^b$Zero point energy in cm$^{-1}$.

$^c$Results for H$_2$S/D$_2$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 Ar₃–H₂X species are relatively small in that the available energy for vibrational excision is much more than the energy to overcome the barriers. Results for Ar₃H₂O/D₂O 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 Ar–H₂S dimer RBDQMC calculations could reproduce the experimental rotational constants to within 1%. The larger error in Ar₃–H₂S 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 Ar₃–H₂O and Ar₃–H₂S 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 ⁴₀Ar 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 H₂O and H₂S complexes, respectively. The Ar–c.m.(H₂X) distance was determined to be 3.675 and 4.112 Å. The average angle between the \( C₂ \) axis of H₂X and the symmetry axis of the tetramer is estimated to be 74° and 13° for the H₂O and H₂S 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 H₂X above the plane of the Ar₃ with both the protons pointing towards one Ar each. The barrier to “pseudorotation” of H₂X above the Ar₃ plane is estimated to be very small at 66(8) cm⁻¹ for H₂O(H₂S). However, the pseudorotation of H₂X 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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