

Rotational Spectra, Structure, and Dynamics of $\text{Ar}_m\text{-(H}_2\text{O)}_n$ Clusters: $\text{Ar}_2\text{-H}_2\text{O}$, $\text{Ar}_3\text{-H}_2\text{O}$, $\text{Ar-(H}_2\text{O)}_2$, and $\text{Ar-(H}_2\text{O)}_3$

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The Ar/H₂O system has been studied extensively as a prototypical model for hydrophobic interactions.¹⁻⁶ Such interactions⁶⁻¹⁰ may play a dominant role in diverse areas like protein conformation, micelle and biological membrane formation, and solvation thermodynamics. Therefore, a number of experimental techniques have been used to characterize the Ar-H₂O dimer¹⁻⁴ and Ar solutions in water.^{5,6} The results have been paralleled by theoretical investigations of the Ar-H₂O dimer¹¹⁻¹⁴ and Ar solutions in water.⁶⁻⁹ However, except for two theoretical papers^{7,11} in part on Ar₂-H₂O, the gap between these extremes seems not yet to have been explored. We address this lack by reporting in our communication pure rotational spectra for the smaller clusters Ar₂-H₂O, Ar₃-H₂O, Ar-(H₂O)₂, and Ar-(H₂O)₃. Our preliminary results suggest that the basic structures of the five clusters studied so far are describable as the close packing of spheres. The apparent sphericity of the water is attributed to its high mobility in the clusters, for which three different dynamic states have been found.

The rotational spectra were observed with a Balle/Flygare, pulsed nozzle, Fourier transform microwave spectrometer which has been described in detail previously.^{15,16} Argon was used as the carrier gas with about 10% of it bubbled through H₂O kept at ambient conditions. The backing pressure was typically 0.75 atm, and the nozzle diameter was 1 mm. The rotational spectra of Ar₂-H₂O and Ar₃-H₂O were predicted by assuming their structures would be similar to those of the previously reported Ar_m-HF clusters,^{17,18} which proved to be a good assumption. Some other transitions with a stronger dipole proved to be from Ar-(H₂O)₂. The Ar-(H₂O)₃ rotational spectrum was found by serendipity during the search for an Ar₂-H₂O transition.

Two sets of asymmetric top transitions were found for Ar₂-H₂O. Those at generally higher frequencies are sharp singlets; those at lower frequencies showed small hyperfine splittings (hfs) or unresolved broadening. They are assigned respectively to the *para* (singlet) and *ortho* (triplet) states of H₂O, which correlate with the ground 0₀₀ and first excited 1₀₁ rotational states of free

water. This assignment is similar to the behavior reported previously for the pseudolinear Ar-H₂O dimers.^{3,4}

Analysis of the spectra shows that the Ar₂-H₂O has a T-shaped structure with C_{2v} symmetry. The *b*-axis of the trimer is its C₂ axis, connecting the Ar₂ center of mass (cm) to that of H₂O. For such a trimer with two interchangeable spin-zero nuclei (Ar) only J_{K₋K₊} rotational levels with K₋ + K₊ even are present.¹⁷ That is, the levels are even-even (ee) or odd-odd (oo). As a result, none of the predicted (eo) ↔ (oe) transitions could be found. So far, 34 transitions have been observed for the *para* state and 26 for the *ortho*. They were fitted using Kirchoff's program to be consistent with our early work on Ar₂-HF.¹⁷ The sextic distortion terms were required, and the residues are within 3 kHz. The *A*, *B*, and *C* rotational constants are 3457.247 (3383.264), 1731.824 (1734.697), and 1144.628 (1129.488) MHz for the *para* (*ortho*) state, respectively.

Determination of structural dimensions for the trimer is inhibited by its dynamics. The experimental *B* value of 1731.824 MHz (0.057 77 cm⁻¹) is nearly identical to that of free Ar₂ dimer¹⁹ (0.057 78 and 0.057 76 cm⁻¹), suggesting that the H₂O does not contribute to the moment of inertia about the *b*-axis. This is to be expected if H₂O undergoes virtually free internal rotation. However, the large positive inertial defects, 3.524 and 6.729 μÅ², for the *para* and *ortho* states show that the rotational constants of the trimer are strongly perturbed by its rovibrations.²⁰ With this in mind, we employ the rotational constants for the *para* state to estimate the dimensions of the trimer with the inertial equations:

$$I_a = \mu_c R^2 \quad (1)$$

$$I_b = I(\text{Ar}_2) = \frac{1}{2} m r^2 \quad (2)$$

$$I_c = \frac{1}{2} m r^2 + \mu_c R^2 \quad (3)$$

where μ_c is the reduced mass of the cluster treated as pseudodiatom, m is the mass of Ar, r is the Ar-Ar distance, and R is the cm-to-cm distance between Ar₂ and H₂O. Equation 2 leads to an r value of 3.8216 Å, which is virtually identical to that observed in the free dimer, 3.821 Å. Equations 1 and 3 lead to R values of 3.1536 and 3.1914 Å, respectively. These values correspond to Ar-cm(H₂O) distances of 3.687 and 3.720 Å, which closely bracket that found in the Ar-H₂O dimer, 3.691 Å.

The Ar₃-H₂O is an oblate symmetric top with three interchangeable spin-zero Ar nuclei, so only $K = 3n$ levels are populated,¹⁸ where $n = 0, 1, 2, \dots$. Table 1 lists the rotational and centrifugal distortion constants determined by fitting the $J = 0 \rightarrow 1$ to $J = 5 \rightarrow 6$ transitions of Ar₃-H₂O and some of its isotopomers. The fact that Ar₃-H₂O is a symmetric top even though H₂O is an asymmetric top clearly shows that the effective orientation of H₂O is symmetric about the C₃ axis. Therefore, neglecting any vibrational tilt of Ar₃, one can write the following inertial equation:

$$I_b = I_b(\text{Ar}_3) + I_s(\text{H}_2\text{O}) + \mu_c R^2 \quad (4)$$

In view of the symmetric top behavior of the tetramer, $I_s(\text{H}_2\text{O})$ is taken to be the I_b of a hypothetical C_{3v} H₂O where the two proton masses are distributed evenly about the C₃ axis.

Now, assuming R does not change on ¹⁸O substitution, one can write

$$\Delta I_b = I_b' - I_b = I_s' - I_s + (\mu_c' - \mu_c) R^2 \quad (5)$$

where the primes indicate values for the isotopomer. Using the I_b values of the H₂¹⁶O and H₂¹⁸O clusters, we calculated R to be 2.948 Å. With this value of R in eq 4, one can determine r to

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Table 1. Rotational and Centrifugal Distortion Constants for Several Isotopomers of the Prolate $\text{Ar}-(\text{H}_2\text{O})_3^a$ and Oblate $\text{Ar}_3-(\text{H}_2\text{O})^b$ Symmetric Tops

isotopomer	B (MHz)	D_J (kHz)	D_{JK} (kHz)
$\text{Ar}_3-\text{H}_2\text{O}^c$	1172.1323(1)	7.199(1)	-5.535(2)
Ar_3-HDO	1155.9515(3)	6.847(4)	-4.907(8)
$\text{Ar}_3-\text{D}_2\text{O}$	1139.3953(3)	6.378(4)	-3.997(8)
$\text{Ar}_3-\text{H}_2^{18}\text{O}$	1137.8760(1)	6.595(1)	-4.318(3)
$\text{Ar}-(\text{H}_2\text{O})_3^c$	1529.301(1)	9.36(3)	54.15(8)
$\text{Ar}-(\text{H}_2^{18}\text{O})_3$	1447.1295(9)	8.14(1)	47.52(6)
$\text{Ar}-(\text{D}_2\text{O})_3$	1437.9645(9)	7.77(1)	49.05(9)

^a In $\text{Ar}-(\text{H}_2\text{O})_3$ and $\text{Ar}-(\text{H}_2^{18}\text{O})_3$, each transition is split into a multiplet with splittings of the order of 40 kHz due to rearrangement of the cyclic water trimer. For $\text{Ar}-(\text{D}_2\text{O})_3$, the splittings were not resolved, though quadrupole hyperfine structure from D nuclei could be seen. ^b Transitions were observed only for K -values of zero and integral multiples of 3 due to the presence of three indistinguishable spin-zero, ^{40}Ar nuclei. ^c The standard deviation of the fit is 0.8 kHz for $\text{Ar}_3-\text{H}_2\text{O}$ and 10.6 kHz for $\text{Ar}-(\text{H}_2\text{O})_3$.

be 3.843 Å, which is very close to the 3.835 Å found in Ar_3-HF ,¹⁸ supporting this model. Also, from these values for r and R , we estimate the $\text{Ar}-\text{H}_2\text{O}$ distance to be 3.688 Å, which is almost the same as that obtained above for $\text{Ar}_2-\text{H}_2\text{O}$. One would expect an excited internal rotor state ($m = 1$) for $\text{Ar}_3-\text{H}_2\text{O}$, but our search for it has been unsuccessful so far.

The $\text{Ar}-(\text{H}_2\text{O})_2$ trimer is an asymmetric top with $A = 6253.063$ (2), $B = 2428.433$ (1), and $C = 1739.565$ (1) MHz. The $\text{H}_2\text{O}-\text{H}_2\text{O}$, cm-to-cm line is the b -axis, and the line connecting Ar to the cm ($\text{H}_2\text{O})_2$ is the a -axis. So far, 25 b -dipole and 18 a -dipole transitions have been assigned. The a -dipole transitions are split by ≤ 1 MHz into a doublet with strong and weak components. Only the stronger component could be fitted, along with the b -dipole lines, to within experimental uncertainty. At this point we believe the stronger components correspond to the E_1 state of $(\text{H}_2\text{O})_2$ and the weaker to the A_1 state.²¹ The experimental rotational constants can be fitted approximately to $\text{Ar}-\text{H}_2\text{O}$ and $\text{H}_2\text{O}-\text{H}_2\text{O}$ distances of 3.64 and 2.99 Å, respectively.

The $\text{Ar}-(\text{H}_2\text{O})_3$ tetramer is a prolate symmetric top. However, each K -component is a close multiplet. The approximate line centers were fitted to a standard symmetric top equation, the results of which are included in Table 1. The identity of the cluster is supported by several observations. Changes in gas composition confirmed that it contains both Ar and H_2O . More detailed information is obtained via recent work by the Saykally group on an intriguing cyclic water trimer exhibiting splittings attributed to structural rearrangement.²² Also, the experimental B values given in Table 1 for several isotopomers of $\text{Ar}-(\text{H}_2\text{O})_3$ are consistent with the proposed structure.

The rovibrational spectrum of the cyclic water trimer is that of a symmetric top. However, each of the transitions for the parent species is a symmetric quartet with spacings of ~ 289 MHz.²² In $(\text{D}_2\text{O})_3$, the spacing drops to 5 MHz. With our cluster, careful examination of the $J = 4 \rightarrow 5$, $K = 0$ and 1 transitions showed them to be a triplet and a quartet, respectively, having spacings of about 40 kHz. But the deuterated species $\text{Ar}-(\text{D}_2\text{O})_3$

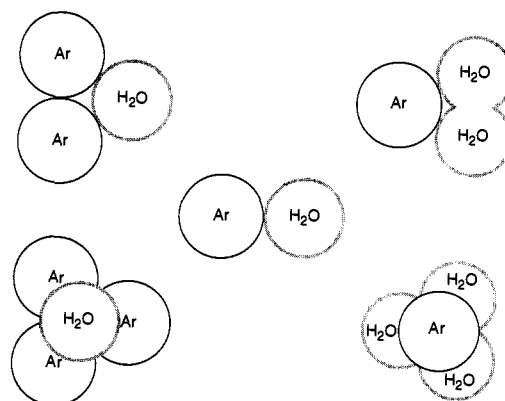


Figure 1. Geometrical structures determined for $\text{Ar}_m-(\text{H}_2\text{O})_n$ clusters. $\text{Ar}-\text{H}_2\text{O}$ was reported previously.¹⁻⁴ The effective $\text{Ar}-\text{Ar}$ distance in the clusters is 3.82–3.84 Å, the Ar to cm H_2O is 3.62–3.70 Å, and the cm H_2O to cm H_2O is 2.99 Å. In all these clusters the water occupies states of high mobility. For $\text{Ar}-\text{H}_2\text{O}$ and $\text{Ar}_2-\text{H}_2\text{O}$, the observed states correlate with the 0_{00} and 1_{01} rotational states of free H_2O . For $\text{Ar}_3-\text{H}_2\text{O}$, the H_2O is a nearly free internal rotor, while in $\text{Ar}-(\text{H}_2\text{O})_2$ and $\text{Ar}-(\text{H}_2\text{O})_3$, the protons interchange via complex tunneling related to those occurring in $(\text{H}_2\text{O})_2$ ²¹ and $(\text{H}_2\text{O})_3$.²² The rotational constants found for isotopomers of $\text{Ar}_2-\text{H}_2\text{O}$ and $\text{Ar}_3-\text{H}_2\text{O}$ indicate that at least one of their hydrogens lies between the Ar_m and the O.

gives no evidence of such splittings. At the lower J values, the hfs from the D nuclei could be seen, but at higher J values, when the hfs becomes less evident, the transitions appear as singlets. On the other hand, with both the H_2O and the H_2^{18}O species, the splitting was found to increase as a function of both J and K . These observations suggest that the dynamics of $(\text{H}_2\text{O})_3$ in the tetramer are very similar to those of free $(\text{H}_2\text{O})_3$ except that the Ar reduces the rearrangement rate by a factor of 10^3 , which seems reasonable.

An $\text{Ar}-(\text{H}_2\text{O})_3$ structure is also in agreement with the B values found for its various isotopic species. For example, if we assume the $(\text{H}_2\text{O})_3$ to be an equilateral triangle with 18 amu at each corner and an H_2O -to- H_2O edge of ~ 2.9 Å,²³ the B for $\text{Ar}-(\text{H}_2\text{O})_3$ gives an Ar-to-cm($\text{H}_2\text{O})_3$ distance of 3.33 Å. This translates to an Ar-to-cm(H_2O) distance of 3.73 Å, a value comparable to the 3.69 Å found above for $\text{Ar}_2-\text{H}_2\text{O}$ and $\text{Ar}_3-\text{H}_2\text{O}$. Moreover, the model, however crude, estimates the rotational constants for both $\text{Ar}-(\text{D}_2\text{O})_3$ and $\text{Ar}-(\text{H}_2^{18}\text{O})_3$ to be 1443 MHz, which shortly led to experimental values of 1438.0 and 1447.1 MHz, respectively. For comparison, if we assume the $\text{H}_2\text{O}-\text{H}_2\text{O}$ distance to be 2.99 Å, it leads to an $\text{Ar}-\text{H}_2\text{O}$ distance of 3.62 Å.

Schematic structures are given in Figure 1 for the $\text{Ar}-\text{H}_2\text{O}$ dimer and the four clusters studied in the present work. Further analyses of the rotational spectra for the four clusters are in progress. Preliminary results for $\text{Ar}_2-\text{H}_2^{17}\text{O}$ and $\text{Ar}_2-\text{D}_2\text{O}$ and for $\text{Ar}-(\text{H}_2^{18}\text{O})_2$ and $\text{Ar}-(\text{D}_2\text{O})_2$ give additional evidence about the dynamic state of H_2O in the trimers. More extensive accounts of our results for the Ar/ H_2O system will be reported elsewhere.

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