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Resonant ion-dip infrared spectroscopy of benzene–(methanol)$_m$ clusters with $m=1–6$

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Resonant ion-dip infrared spectroscopy has been employed to record cluster-size-specific spectra of $C_6H_6–(CH_3OH)_m$ with $m=1–6$ in the OH stretch fundamental region. The comparison of the spectra with the results of *ab initio* calculations on the pure methanol clusters enables the assignment of the hydrogen-bonding architecture in the clusters. In all cases, the methanol molecules aggregate together in a single subcluster. With $m=1$, a single infrared transition is observed, redshifted from that of a free methanol momomer by 42 cm^{-1} due to π hydrogen bonding between benzene and methanol. The $m=2$ spectrum features two strong transitions at 3506 and 3605 cm^{-1}. The lower frequency peak is redshifted from the free monomer value by 175 cm^{-1} and is assigned to the proton donor in the methanol dimer subcluster. The proton acceptor, which would be a free OH stretch in the absence of benzene, is redshifted by 76 cm^{-1} due to a strengthened π hydrogen bond. In benzene–$(CH_3OH)_3$, three sharp OH stretch transitions are observed at 3389, 3435, and 3589 cm^{-1}. The comparison of these absorptions with *ab initio* calculations and with experiments on the pure methanol trimer leads to a structure for benzene–$(CH_3OH)_3$ which incorporates a π hydrogen-bonded methanol trimer chain, confirming the earlier assignment based on its ultraviolet spectrum. The 3589 cm^{-1} transition, due to the π hydrogen bond of the terminal methanol, is redshifted from the free monomer by 93 cm^{-1}, a value approaching that of the donor methanol in methanol dimer (-107 cm^{-1}). The lower frequency transitions in the $m=3$ spectrum arise from the donor–acceptor and donor OH stretches in the methanol trimer chain. The spectral characteristics change when $m=4$. The OH stretch transitions are all located in a region around 3320 cm^{-1} and are significantly broadened compared to the smaller clusters. By comparison with *ab initio* calculations, the methanol tetramer structure in benzene–$(CH_3OH)_4$ is deduced to be a cyclic methanol tetramer. The spectra for $m=5$ and 6 are slightly redshifted but similar to $m=4$ and point toward cyclic structures as well. © *1997 American Institute of Physics.* [S0021-9606(97)02406-9]

I. INTRODUCTION

As the prototypical aromatic hydrocarbon, benzene possesses two dissimilar regions for interaction with polar solvents; an electron-rich hydrophilic out-of-plane region created by its π cloud and a hydrophobic in-plane region generated by its aryl hydrogens. An evident manifestation of benzene's different interactions with seemingly similar solvents is its immiscibility in water and complete miscibility in methanol. An important aspect of these intermolecular interactions is the different hydrogen-bonding properties of the protic solvents themselves. Whether in the liquid,[1] solid,[2] or in large gas-phase clusters,[3–6] water is known to prefer three-dimensional hydrogen-bonded networks. Methanol, in contrast, forms H-bonded chains as a solid,[7] and is thought to prefer such chains in the liquid[8] as well. At the same time, data on the pure gas phase methanol clusters[9–12] with $n=3–5$ suggest the formation of cyclic structures which maximize the number and strength of the methanol–methanol H-bonds. The interactions of these different H-bonding architectures with benzene, and the disruption caused by benzene in the network of H-bonds, undoubtedly play a significant role in the different solubilities of benzene in water and methanol.

The study of the gas-phase clusters of benzene with water and methanol can provide critical tests of the intermolecular potentials involved, which, it is hoped, will lead to a better molecular-scale understanding of the bulk solutions themselves. Much of the work that has been done on benzene–(water)$_n$ and benzene–(methanol)$_n$ clusters probes the perturbations imposed by the solvent molecules on the electronic spectrum of benzene.[13–15] Size selection of the clusters is typically accomplished in these studies using resonant two-photon ionization (R2PI) coupled with time-of-flight mass spectroscopy (TOFMS). Our group used a combination of rotational band contour analysis and vibronic level arguments to study benzene–$(H_2O)_n$ clusters[13] (denoted BW_n) with $n=1–8$ and benzene–$(CH_3OH)_m$ clusters[14] (denoted BM_m) with $m=1–5$. The vibronic level probes used in these studies took advantage of the high symmetry of benzene and the forbidden nature of the $S_1 \leftarrow S_0$ transition in isolated benzene. In the presence of solvent molecules, this symmetry is reduced, turning on new transitions (e.g., the origin) and splitting degeneracies (e.g., the $e_{2g}\nu_6$ vibration) in benzene's spectrum. Among the vibronic level probes of the cluster structure were the vibronic frequency shift, the extent of fragmentation induced by photoionization, the presence of van der Waals absorptions, the $0_0^0/6_0^1$ intensity ratio, and the magnitude of the 6_0^1 splitting. The vibronic spectros-

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copy provides evidence that the water or methanol molecules in these clusters form a W_n or M_n subcluster containing all the solvent molecules in a single H-bonded aggregate, but provides only circumstantial evidence for the H-bonded structure of the W_n or M_n subclusters themselves.

In the BM_m clusters of interest here, the R2PI spectra[14] [reproduced in Figs. 1(a)–(d)] suggest that the methanol molecules in BM_m when $m=1–3$ are H-bonded chains which retain the π hydrogen bond with benzene, while $m=4$ and 5 do not possess a π H bond and therefore were suggested to be cyclic. This was most notably evident in the vibronic frequency shifts of the transitions relative to free benzene (Fig. 1), which are increasingly blueshifted through $m=3$ due to the π H bond, but shift dramatically back to the red in $m=4$ and 5.

In the present paper we test these tentative structural conclusions much more directly by recording infrared spectra of the clusters in the OH stretch region. In hydrogen bonded molecules (Y···HX), the H–X stretching vibration is one of the more powerful and sensitive probes of the intermolecular hydrogen bond. The OH stretch is sensitive to the strength, type, and number of hydrogen bonds in which it participates because it vibrates directly against the hydrogen bond. When a hydrogen bond is present, the H–X stretch fundamental shifts its frequency to the red, increases in breadth, and typically increases in intensity.[16,17]

In the condensed phase,[18] the observed consequence of the extended H-bonded networks on the OH stretch absorption band is its enormous breadth, typically extending from 3700 to 3100 cm^{-1}. Liquid methanol in particular has a strong, broad, and essentially featureless OH stretch band peaked at 3337 cm^{-1} while solid methanol's OH stretch absorption shows substructure peaked at 3187 (s) and 3284 cm^{-1} (vs), with a shoulder at 3443 cm^{-1}.[18]

By studying the expansion-cooled, gas-phase clusters, one hopes to probe the OH stretch absorptions of conformation- and size-specific H-bonded aggregates with sufficient resolution to observe the individual OH stretch bands ''underneath'' the broad absorption present in the condensed phase. Recently, using a pulsed tunable IR source in combination with R2PI-time-of-flight mass spectrometer (TOFMS) our group[3–5,19] probed the OH stretch region of size-specific hydrogen-bonded BW_n clusters with $n=1–7$ using a technique first developed by Page, Shen, and Lee[20] which we call resonant ion-dip infrared spectroscopy (RIDIRS). In RIDIRS, the absorption of an infrared photon removes population from the ground state and is detected by a decrease in the mass-selected ion signal produced by a fixed UV laser tuned to a given vibronic transition of the cluster of interest. Figure 2(B) reproduces the RIDIR spectra of BW_n with $n=1–7$. These spectra will serve as a point of comparison with the present results on BM_m. In the work on BW_n, the interaction between benzene and the W_n subcluster is always found to be through a π H bond. The comparison of the spectra with *ab initio* calculations on BW_n and W_n clusters provide clear assignments for the H-bonding structure of the clusters. The BW_n clusters with $n=3–5$ are seen to have cyclic W_n subclusters, while the spectra of the $n=6$ and 7 clusters were assigned to π H-bonded W_n subclusters which were three-dimensional, H-bonded networks containing several ''double donor'' water molecules.[3–5,19]

Using the same technique, the emphasis of this study is the OH stretch region of BM_m ($m=1–6$) clusters. We will demonstrate that the predictions previously made through the $S_1 \leftarrow S_0$ spectroscopy of the clusters[13,14] are correct; namely, (i) that the BM_m clusters with $m=1–3$ form H-bonded chains which retain the π H bond to benzene, and (ii) that the larger BM_m clusters contain a cyclic M_m subcluster. The *ab initio* calculations of the structures, vibrational frequencies, and infrared intensities of the pure M_m clusters, which are presented in detail elsewhere,[21] (and hereafter referred to as paper I) play an important role in arriving at these conclusions. We shall also see that the presence of benzene and its perturbative effect on the M_m cluster are evident in the IR spectra of the clusters, and interpretable in terms of reasonable distortions of the M_m subcluster.

II. EXPERIMENT

RIDIR spectra in the OH stretch region are recorded using methods described previously.[3–5,19] Briefly, cold, gas-phase BM_m clusters are formed by expanding a mixture containing benzene and methanol in helium from a pulsed valve of 0.8 mm diam operating at 20 Hz. The concentration of these vapors is controlled by metering the flows of helium over the room temperature liquids using needle valves and mixing these flows with a balance of helium. Typical expansion conditions employ 0.1% benzene and 0.1%–0.5% methanol at a total pressure of 2 bar. The clusters are passed through a skimmer, located 4 cm downstream from the pulsed nozzle, and into the ion-source region of the time-of-flight mass spectrometer (TOFMS), where the cluster of interest is singled out for study using resonant two-photon ionization (R2PI) through its $S_1 \leftarrow S_0 6_0^1$, transition. The pulsed ultraviolet laser (0.1–0.5 mJ/pulse) used for the R2PI traverses twice through the ionization region of the TOFMS in a 1-mm-diam collimated beam. The ions of equal mass created from the two passes are born at slightly different potentials in the ion source and arrive at the microchannel plate ion detector as two ion packets separated by 100–200 ns. The arrival times of the ion mass of interest are monitored with a digital oscilloscope. The pulsed, tunable IR output of an optical parametric oscillator (OPO)[19] is spatially overlapped with one of the UV beams while temporally preceding the UV pulse by 80–400 ns. When an IR absorption occurs out of the same ground state level as that monitored in R2PI, a decrease in ion signal from the overlapped UV beam is observed. Normalization of the two ion signals allows the percent depletion in ion signal as a function of OPO wavelength to be attained. The dual-beam method reduces the noise arising from shot-to-shot UV laser power fluctuations.

Typical idler pulse energies of 1–3 mJ/pulse are used. The OPO power curve over the frequency range of interest is included above the RIDIR spectra of Fig. 2(A). The dip in idler power over the 3460–3510 cm^{-1} region is due to an impurity absorption in the $LiNbO_3$ crystal, which in the

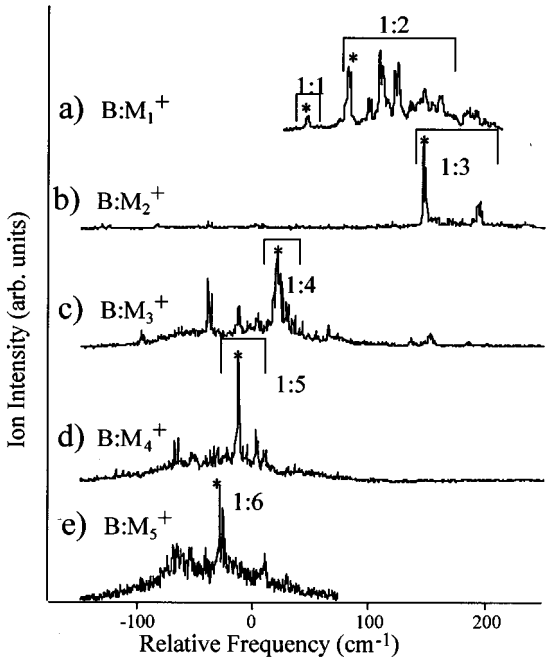

FIG. 1. One-color resonant two-photon ionization scans of BM_m clusters with $m=1$–6 in the 6_0^1 region of the $S_1 \leftarrow S_0$ transition of benzene. Efficient fragmentation occurs following photoionization by loss of one methanol so that the BM_m cluster is monitored in the $BM_{m-1}{}^+$ mass channel. See Ref. 14 for details of the assignments. 1:m designates the B_1M_m cluster. The bands marked with asterisks are those monitored in recording resonant ion-dip infrared spectra.

present crystal is more substantial than in the BW_n spectra [Fig. 2(B) top]. While the idler power is not zero in this region, it is small enough that absorptions in this region are significantly reduced in intensity. The RIDIR spectra are not corrected for the wavelength dependence of the OPO power.

The observed depletions are necessarily large, approaching 50% in some cases. In our previous work on BW_n clusters[3–5,19] [reproduced in Fig. 2(B)], even larger depletions were observed. In all the spectra of Fig. 2, vibrational predissociation or hydrogen-bond breaking in the cluster may be occurring following OH($v=1$) excitation, allowing depletions greater than 50% to occur. Given the large depletions observed, saturation effects will distort the relative intensities in the spectra by artificially raising the intensity of weak transitions relative to strong ones.

III. RESULTS

A. R2PI spectra

As mentioned earlier, Figs. 1(a)–1(d) reproduce the one-color R2PI spectra reported in our previous work[14] on BM_m clusters. The assignments for the cluster sizes responsible for the observed transitions are given in Fig. 1. The BM_m clusters undergo efficient fragmentation following photoionization by loss of a single methanol molecule. Support for these assignments has been given elsewhere.[14] The transitions marked with an asterisk in Fig. 1 are used to selectively monitor the indicated BM_m cluster in the RIDIR spectra. The additional transitions in the BM_3^+ mass channel have recently been assigned to conformational isomers of B_2M_3 clusters.[22]

The R2PI spectrum of BM_6, shown in Fig. 1(e), has not been reported previously. The spectrum is dominated by a doublet at -27 cm^{-1} which we assign to BM_6. There are undoubtedly contributions to the broad background in the spectrum from larger clusters. The spectrum of BM_6 has an unmistakable resemblance to the spectrum of the ''stem'' benzene in the benzene dimer.[23] The -27 cm^{-1} frequency shift continues the trend set in BM_4 and BM_5 toward increasing redshift, which here approaches the value of -41 cm^{-1} for the benzene dimer stem molecule. Like BM_5, little van der Waals's structure is evident in the spectrum of BM_6. The 6_0^1 splitting in BM_6 is 3.2 cm^{-1}, indicating that the six-fold symmetry of benzene has been broken to lower than three-fold symmetry by the M_6 subcluster.

B. RIDIR spectra

Overview RIDIR spectra of the BM_m ($m=1$–6) clusters in the OH stretch region are shown in Fig. 2(A), spectra (a) and (f). The frequencies of the transitions are listed in the first column of Table I. Assignments of the features in Fig. 2(A) are given in the last column of Table I and will be considered later. The RIDIR spectra for each cluster size in Fig. 2(A) were obtained by monitoring the ion signal that resulted from the R2PI laser being fixed on the peak maximum of the 6_0^1 transition of the given cluster [indicated by an asterisk in Fig. 2(A)] while scanning the IR OPO frequency.

The general development of the RIDIR spectra with cluster size reflects the sensitivity of the methanol molecule to its hydrogen-bonding environment. The key spectral features of the smaller clusters ($m=1$–3) are as follows. First, a transition around 3600 cm^{-1} appears in each of the spectra, which is redshifted by about 20 cm^{-1} with the addition of each successive methanol molecule. Second, the lowest-frequency transitions shift about 125 cm^{-1} further to the red with the addition of each methanol molecule, to a lowest frequency of 3389 cm^{-1} in BM_3. Third, the transitions are quite narrow, ranging from 2.8 to 7.7 cm^{-1} full width at half-maximum (FWHM).

These features of the smaller clusters' spectra are in sharp contrast with the $m=4$–6 data. First, in these larger clusters, the transition around 3600 cm^{-1} is notably absent. Second, the frequency shift of the transitions which are observed change far less with increasing cluster size than their smaller counterparts. With the addition of the fifth methanol, the maximum absorption shifts just 60 cm^{-1} from the $m=4$ cluster center frequency, while the addition of the sixth methanol molecule shifts the center frequency by only about 20 cm^{-1} further. Third, the widths of the majority of transitions are approximately 30 cm^{-1}, almost an order of magnitude greater than the widths in the smaller clusters. Finally, the transitions span an O–H spectral region from 3360 to 3150 cm^{-1}. This encompasses the peak maxima observed in the O–H stretch region in liquid and solid methanol.

TABLE I. Experimental and calculated OH stretch frequencies (cm^{-1}), frequency shifts (cm^{-1}), and assignments for C_6H_6–$(CH_3OH)_m$ and $(CH_3OH)_m$ clusters.

	Expt.[a] C_6H_6–$(CH_3OH)_m$		Calc.[b] C_6H_6–$(CH_3OH)_m$	Expt. $(CH_3OH)_m$ Gas phase[c]		N_2 matrix[d]	Calc.[b] $(CH_3OH)_m$	
	ν	$\Delta\nu$	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	Assignment
$m=1$	3639	−42	−33					πH bond
				3681.5		3640	0	Free O–H
$m=2$	3506(s)	−175	−189(s)	3574.4(s)	−107	3504	−150(s)	M–M H bond
	3605(s)	−76	−57(s)					πH bond
				3684.1(w)	+3	3654	−4(w)	Free O–H
	3640(w)	−41						Combination band
$m=3$							−297(w)	
				3462(s)	−219	3440–3450	−241(s)	Cyclic
							−228(s)	
								Chain
	3389(s)	−292				3389.2	−259(s)	second M–M H bond
	3435(s)	−246				3433.3	−208(s)	first M–M H bond
	3589(s)	−92						πH bond
						3661.94	+13(s)	Free O–H
$m>3$				3290	−391			Higher polymers
$m=4$	3204(w)	−477					−462(w)	
	3290(s)	−391				3284	−371(s)	Cyclic
	3321(s)	−360					−371(s)	
	3360(w)	−321					−334(w)	
$m>4$						3220		Higher polymers
						3242		
						3260		
$m=5$	3171(w)	−510					−504(w)	
	3243(s)	−438					−425(s)	
	3286(w)	−395					−414(s)	Cyclic
	3314(w)	−367					−358(w)	
							−358(w)	
$m=6$	3177	−504						
	3224	−457						Cyclic
	3280	−401						
	3315	−366						

[a]Results from this work.
[b]Harmonic frequencies at the DFT Becke3LYP/6-31+G* level of theory. Frequency shifts are reported with respect to methanol momomer's OH stretch.
[c]Reference 11.
[d]Reference 23.

C. Density functional theory calculations

In addition to the extensive calculations from paper I on the pure M_m clusters,[21] we have carried out calculations of the structures, binding energies, vibrational frequencies, and infrared intensities of BM_1 and BM_2 at the same level of theory as in that work [density functional theory (DFT) Becke3LYP/6-31+G*]. Corresponding calculations on larger BM_m clusters were not carried out due to the increasing complexity and length of the calculations. Figures 3(a) and 3(b) show pictorially the fully optimized structures for the clusters. The prediction of the calculation is that, as in BW_1 and BW_2, the BM_1 and BM_2 clusters are both π H bonded to benzene, with the M_2 subcluster in BM_2 largely retaining the structure of the free methanol dimer when in the presence of benzene.

A Becke3LYP/6-31+G* binding energy of $D_e=-2.4$ kcal/mol was calculated for the BM_1 complex. In this optimized structure, methanol is π H bonded to benzene with an oxygen-to-benzene plane distance of 3.41 Å. The calculated frequency shift of the methanol OH stretch in BM_1 is −33 cm^{-1} (Table I). As a comparison of the relative strength of the π H bond present in the BM_1 complex, the methanol dimer possesses a calculated binding energy of $D_e=6.3$ kcal/mol and a calculated OH stretch frequency shift of −150

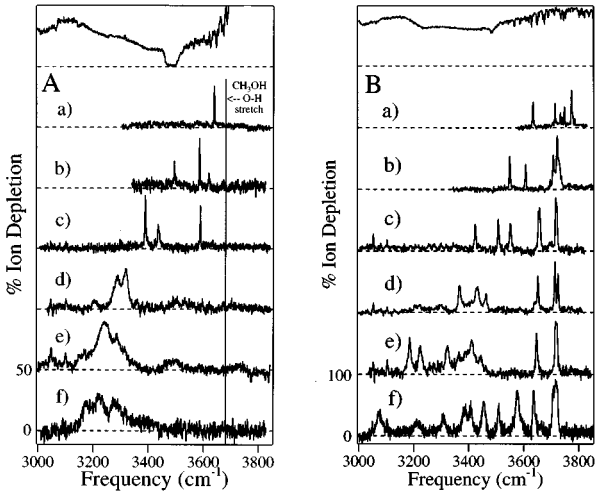

FIG. 2. (A) Overview RIDIR spectra of BM_m with (a) $m=1$ to (f) 6, respectively. The vertical line indicates the frequency of the OH stretch in methanol monomer (3681 cm^{-1}). (B) Analogous RIDIR spectra of BW_n with (a) $n=1$ to (f) 6, respectively, for comparison. The top most trace on each figure is the OPO power curve for the $LiNbO_3$ crystal used for the study. The spectra have not been corrected for OPO power.

cm^{-1} at the same level of theory (paper I). The BM_1 calculation predicts that the methanol molecule is pulled off the sixfold axis of benzene, presumably in order to gain additional interaction of the methyl group with the π cloud. The degree of nonrigidity of this complex has not been tested by calculation, but one might expect that the methanol molecule experiences only a small barrier to internal rotation about benzene's sixfold axis.

Several results from the BM_2 calculation suggest a cooperative strengthening of the H bonds in BM_2 relative to those in the dimeric subclusters BM_1 and M_2. First, in BM_2 the O–O distance decreases by -0.024 Å from its value in the free methanol dimer (2.862 Å). Second, the calculated π H-bond distance in BM_2 is 0.019 Å shorter than in BM_1.

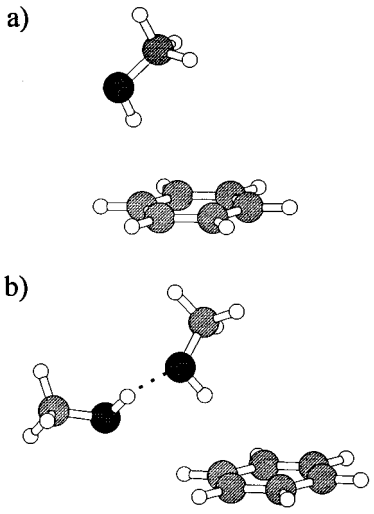

FIG. 3. Minimum energy structures calculated for (a) BM and (b) BM_2 using the DFT Becke3LYP/6−31+G* level of theory.

Third, the total binding energy of BM_2 is -14.6 kcal/mol, over 6 kcal/mol greater than the sum of the calculated BM_1 (-2.2 kcal/mol) and M_2 (-6.28 kcal/mol) binding energies at the same level of theory. Finally, the calculated OH stretch frequency shifts of the donor and π H-bonded methanol molecules from their monomer values are -190 and -58 cm^{-1}, respectively, values which are significantly greater than those calculated for the corresponding vibrations in M_2 (-150 cm^{-1}) and BM_1 (-33 cm^{-1}), respectively.

IV. DISCUSSION

In analyzing the RIDIR spectra of the BM_m clusters, IR data on the M_m clusters provide excellent points of comparison. Table I list the observed O–H stretch absorptions in BM_m and compares these absorptions to gas-phase data,[11] matrix data,[24] the *ab initio* calculations on pure methanol clusters from paper I, and the analogous calculations on the two smallest BM_m clusters. The comparison of the present data on BM_m [Fig. 2(A)] with corresponding data[3–5,19] on BW_n will also be made in order to assess the similarities and differences which exist.

A. C_6H_6–(CH_3OH)

The RIDIR spectrum of BM_1 [Fig. 2(A), spectrum (a)] is composed of a single absorption in the O–H stretch region at 3639 cm^{-1}. This transition is 42.5 cm^{-1} redshifted from the free methanol OH stretch (3681.5 cm^{-1}) and is assigned to a π H-bonded OH stretch. This is consistent with the *ab initio* structure calculated for BM_1. In fact, the calculated redshift of the OH stretch (-33 cm^{-1}) is in good agreement with that observed experimentally. No combination bands are observed.

There is little apparent similarity between the RIDIR spectra of BM_1 and BW_1 [Fig. 2(B), spectrum (a)]. If the BW complex were rigid, its OH stretch RIDIR spectrum would consist of two transitions due to its symmetric and antisymmetric stretch. Such a simple spectrum is in fact observed in B_2W_1 (Ref. 22) and fluorobenzene–W_1.[25] However, in the case of BW_1, at least seven resolved transitions are observed.[19] The four most intense transitions are assigned to OH stretch/internal rotation combination bands created by the nearly free internal rotation of the water about benzene's sixfold axis. The weaker transitions are assigned to OH stretch/in-plane torsion combination bands. Based on these assignments, center frequencies for the symmetric and asymmetric stretches of water in BW_1 are computed to be 23 and 25 cm^{-1} redshifted, respectively, from their frequencies in the water monomer.

Methanol, with its single OH functional group and ''bulky'' methyl group, forms a complex with benzene in which the OH orientation is significantly more constrained than in BW_1, thereby producing an uncongested spectrum that is characterized by its single π H-bonded OH absorption. The somewhat greater frequency shift (-43 cm^{-1}) in BM_1 than in BW_1 ($-23/-25$) may be ascribed to a strengthened π H bond associated with the increased polarizability of CH_3OH and a more highly directed π H bond involving a

single OH group. The lack of combination bands due to the internal rotation of methanol, which are so prevalent in the benzene–H_2O spectrum [Fig. 2(B), spectrum (a)] may be largely a consequence of the much smaller internal rotation constant for methanol by comparison to H_2O.

B. C_6H_6–$(CH_3OH)_2$

Figure 4(c) presents a close-up of the RIDIR spectrum of BM_2, with its three transitions at 3506, 3605, and 3640 cm^{-1}. The small intensity of the lowest-frequency transition is an artifact of the low OPO power in the 3460–3510 cm^{-1} region mentioned previously. Upon correction for this reduced power, the 3506 cm^{-1} band is several times as intense as the 3605 cm^{-1} band. The donor and acceptor OH stretch absorptions of gas phase methanol dimer have been identified[11] at 3574.4 and 3684.1 cm^{-1}, respectively (Table I). In a nitrogen matrix,[23,26,27] the same absorptions occur around 3504 and 3654 cm^{-1}. In Figs. 4(a) and 4(b), the calculated infrared spectra of the methanol dimer and of BM_2 are shown for comparison with the experimental spectrum of BM_2. Based on these comparisons, we assign the band at 3506 cm^{-1} to the donor OH stretch and that at 3605 cm^{-1} to the π H-bonded OH stretch of a distorted methanol dimer in BM_2, as shown in Fig. 3(b).

The donor transition (3506 cm^{-1}) is redshifted by 79 cm^{-1} from its value in the free methanol dimer, while the shift of the π H-bond transition (-76 cm^{-1}) is nearly twice its value in BM_1 (-42 cm^{-1}). As anticipated by the *ab initio* calculations, the magnitude of these shifts suggests significant cooperative strengthening of the π H bond and methanol–methanol H bond in the BM_2 cluster relative to those in BM_1 and M_2, respectively. In the previous R2PI study of BM_m,[14] it was suggested that the increase in the strength of the π hydrogen bond is responsible for the further blueshift in the vibronic transitions of BM_2 relative to BM_1 in the UV spectrum of Fig. 1(a).

The weak absorption at 3640 cm^{-1} cannot be an OH stretch fundamental, but must instead be a combination band of one of the OH stretch bands with an intermolecular vibration of the BM_2 cluster. If this intermolecular mode is built on the π H-bonded OH, its frequency is about 35 cm^{-1}. The intense intermolecular structure in the R2PI spectrum of BM_2 [Fig. 1(a)] includes strong bands at 28 and 41 cm^{-1}, either of which could have a corresponding frequency in S_0 at 35 cm^{-1}. Furthermore, it is physically reasonable that the 35 cm^{-1} combination band is built off the π H-bonded OH stretch which is responsible for perturbing the benzene molecule in the R2PI spectrum.

Based on the RIDIR spectra, the structures of BM_2 and BW_2 are quite similar, incorporating a methanol or water dimer in which the acceptor molecule is π H bonded to benzene. The donor O–H stretch transitions of BM_2 and BW_2 are at 3506 and 3550 cm^{-1}, respectively, corresponding to frequency shifts of -175 and -156 cm^{-1} from their respective monomer's free OH stretch. The somewhat larger frequency shift in BM_2 is probably reflecting the slightly stronger H bond in M_2 than in W_2. No ready comparison can be made between the π H-bonded OH stretch modes of BM_2 and BW_2, because the acceptor water in BW_2 probably interacts with benzene's π cloud through both its hydrogens.[13]

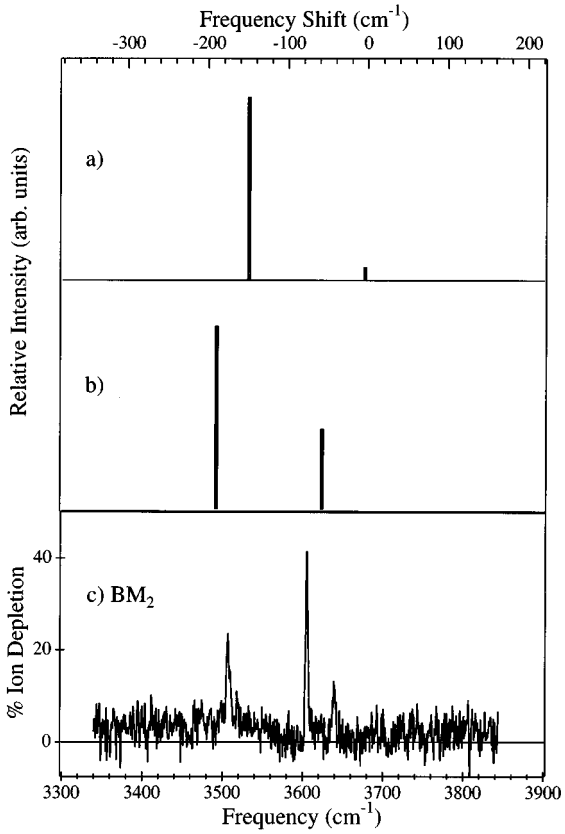

FIG. 4. (a) and (b) Calculated OH stretch harmonic frequency shifts and infrared intensities for the free methanol dimer (a) and BM_2 (b). (c) RIDIR spectrum of BM_2 for comparison.

C. C_6H_6–$(CH_3OH)_3$

Based on the *ab initio* calculations of the methanol trimer from paper I, it is apparent that the methanol trimer has several conformational structures which could bind to benzene, including cyclic [(3)], chain [$\underline{3}$], and branched [$\underline{2}+1$] H-bonded structures. The notation for the M_m structures is that introduced in paper I, in which cyclic clusters are designated by parentheses (m), chain structures by an underlined $\underline{m}$, and branched-cyclic and branched-chain structures with a branch of n methanols by $(m)+n$ and $\underline{m}+n$, respectively. As shown in paper I, in the free methanol trimer the lowest energy structure predicted by calculation is that observed experimentally;[9–11,23] namely, the cyclic trimer. For this structure, Huisken *et al.*[11] have observed a single OH stretch band at 3462 cm^{-1}. However, in a matrix,[23] the cyclic trimer breaks a H bond under infrared irradiation to form a chain methanol trimer with absorptions at 3661.94, 3433.3, and 3389.2 cm^{-1}.

The two lower-frequency transitions observed in BM_3 (3389 and 3435 cm^{-1}) match the matrix-isolated open chain trimer's absorptions to within 2 cm^{-1}. The highest frequency OH stretch fundamental at 3589 cm^{-1} in BM_3 is shifted by

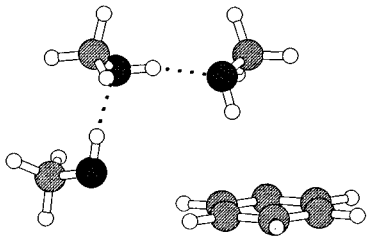

FIG. 5. A schematic picture of the BM_3 ''hydrogen-bonding'' structure which is determined from the RIDIR spectroscopy. The structure includes a methanol trimer chain (3) with two methanol–methanol H bonds and a π H bond with benzene.

$-73\ cm^{-1}$ from the end-of-chain methanol's OH stretch frequency in the matrix-isolated chain trimer, a shift which is easily accounted for if the methanol trimer chain attaches to the π cloud of benzene through the only free OH available in the chain, as pictured schematically in Fig. 5. This is the same structure deduced from the R2PI spectroscopy for BM_3 previously,[14] but now RIDIR spectroscopy provides more direct evidence to support that deduction.

As shown in Fig. 6, the DFT calculations from paper I on the cyclic and open chain methanol trimers confirm the distinct spectral signatures of cyclic and chain M_3 and the better match of the latter structure with the experimental spectrum of BM_3. The calculated transitions shown in Figs. 6(a) and 6(b) are shown as frequency shifts from the methanol monomer OH stretch ($3681.5\ cm^{-1}$). Both the redshift in the highest-frequency OH stretch transition in M_3 compared to BM_3 and its greatly increased intensity are due to formation of the π H bond in the latter cluster. Note that the intensity of the π H-bonded OH stretch even approaches that of the OH groups in the M_3 chain.

The experimental spectrum of BM_3 also differs from the calculated spectrum for $\underline{3}$ in its reversal of the relative intensities of the two lower-frequency OH stretch transitions. The calculated normal modes for $\underline{3}$ from paper I indicate a local mode OH composition which is 80%/20% localized on the terminal/interior methanol for the lowest frequency transition ($-259\ cm^{-1}$) and 20%/80% for the $-203\ cm^{-1}$ transition. Since we do not have calculations for BM_3 (due to their size), we can only suggest that the degree of delocalization of these modes may be altered in the presence of benzene, leading to the observed change in intensity.

It is interesting to compare the spectra and structures of BM_3 and BW_3 in Fig. 2(A), spectrum (c) and Fig. 2(B), spectrum (c), respectively. In BW_3, RIDIR spectroscopy[3,4,20] has shown that the water trimer is cyclic, while in BM_3 the methanol trimer takes on a H-bonded chain structure. In the absence of benzene, both W_3 and M_3 have a cyclic lowest-energy structure. These cyclic structures have highly nonlinear H bonds which are thereby weakened;[19(b),21] however, the ring strain is more than compensated by gaining a third H bond in the cyclic structure by comparison to the two linear H bonds in the chain trimer. In the presence of benzene, the water trimer retains its cyclic structure because it can π H bond to benzene via one of its free OH groups. This weak π H bond shifts one of the free OH stretch frequencies by about $60\ cm^{-1}$ [Fig. 2(B), spectrum (c)]. In addition, the benzene molecule asymmetrizes the cyclic water trimer structure enough that (i) the degeneracy of the two single donor OH vibrations which carry IR intensity in W_3 is split, and (ii) intensity is induced in the lowest-frequency single donor OH stretch which is forbidden in W_3.

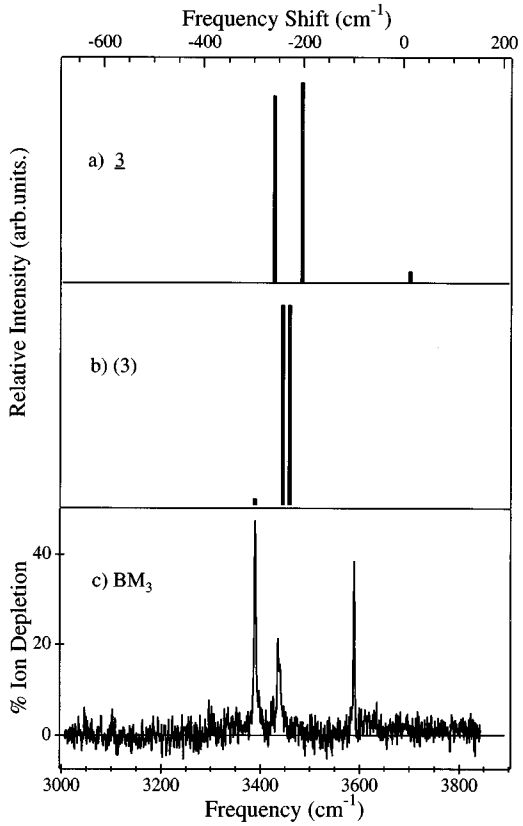

FIG. 6. (a) and (b) Calculated OH stretch harmonic frequency shifts and infrared intensities for the chain (a) and cyclic forms (b) of the free methanol trimer. (c) RIDIR spectrum of BM_3 for comparison.

In contrast, in BM_3, the presence of benzene reverses the stabilities of the cyclic and chain methanol trimers. The cyclic methanol trimer, which has no free OH's available for π H bonding, is destabilized by its weak interaction with benzene. Instead, the chain M_3 forms two strong methanol–methanol H bonds (paper I) and a strengthened π H bond, thereby producing a greater total binding energy for this structure in the presence of benzene. The BM_3 cluster thus is a particularly clear case in which the presence of the benzene solute changes the lowest-energy H-bonding configuration of its surrounding solvent (methanol trimer).

D. C_6H_6–$(CH_3OH)_4$

It is at BM_4 that the dramatic change is seen in both the R2PI and RIDIR spectra, pointing to a significant structural rearrangement. The RIDIR spectrum is dominated by a pair of bands at 3290 and $3321\ cm^{-1}$, with two barely visible satellite bands at 3204 and $3360\ cm^{-1}$. Notably absent is any absorption in the 3500–$3600\ cm^{-1}$ region, which could be

ascribed to a π H-bonded OH stretch transition. The sharp, weak transitions at 3048 and 3101 cm^{-1} are due to the Fermi-resonance split C–H stretch bands of benzene. As in the BW_n clusters, the C–H stretch bands are unperturbed by the presence of the solvent molecules.

The prediction of the R2PI spectroscopy[14] is that BM_4 binds benzene to a cyclic methanol tetramer. In order to test the RIDIR results against this prediction, the calculated OH stretch infrared frequency shifts and intensities of the methanol tetramer chain 4 [Fig. 7(a)], (3)+1 structure as representative of a branched cycle [Fig. 7(b)], and the tetramer cycle (4) [Fig. 7(c)] are compared with experiment on BM_4. The qualitative match-up of the experimental spectrum for BM_4 with the calculation for the cyclic M_4 cluster is excellent. Furthermore, recent gas-phase[11] data on M_4 have identified a single OH stretch band at 3290 cm^{-1} (3284 cm^{-1} in a nitrogen matrix[23]) which has been tentatively assigned to the cyclic methanol tetramer. The close correspondence of this transition frequency with the intense pair of bands in BM_4 provides strong evidence for a cyclic M_4 subcluster in BM_4.

Furthermore, the presence of benzene is expected to distort the OH stretch infrared spectrum from that of cyclic M_4 in precisely the way observed. As discussed in more detail in paper I, the highly symmetric cyclic clusters have OH stretch vibrations which are delocalized around the ring. As is apparent from Fig. 7(c), the infrared spectrum of cyclic M_4 has a degenerate pair of vibrations (with two ''nodes'' in the phases of the OH oscillators) which carry all the infrared intensity. The OH stretch vibrations above and below this in frequency are forbidden for symmetry reasons, having four and zero nodes, respectively. However, in the presence of benzene, the cyclic structure is distorted away from its high symmetry, thereby partially localizing the OH stretch vibrations. This in turn breaks the degeneracy of the donor OH stretch vibrations and induces intensity in the otherwise forbidden bands above and below the main pair of bands.

This symmetry-breaking effect of benzene has been analyzed recently[20] in some detail in accounting for the RIDIR spectrum of the BW_3 cluster [Fig. 2(B), spectrum (c)]. In that case the benzene–W_3 interaction is via a π H bond formed with one of the dangling hydrogens on the cyclic W_3 cluster. The effect on the intensities of the bands is quite dramatic in BW_3. In contrast, if the methanol tetramer in BM_4 is cyclic, all OH groups in the M_4 subcluster will be involved in H bonding with other methanol molecules. As a result, the interaction of the tetramer cycle with benzene is relegated to benzene–methyl interaction(s) which are weaker than the π H bonds present in BW_n (or in the chain structures of BM_m with $m=1$–3). As a result, the symmetry-breaking effect of benzene is lessened. In keeping with this, one observes a 31 cm^{-1} splitting of the degeneracy of the main bands, and only weakly induced intensity in the satellite bands at 3204 and 3360 cm^{-1}. The positions of these weak satellite bands are very near the calculated frequencies for the forbidden bands in M_4 [Fig. 7(c)].

The present data firmly assign the H-bonded architecture in BM_4 as cyclic, just as it is in BW_4. The *ab initio* results from paper I indicate that the energy difference between cyclic and chain structures of M_4 is sizable enough (>8 kcal/mol) that the strong π H bond afforded by the chain structure cannot make up the energy difference. In BM_4, then, no solvent restructuring occurs as it did in BM_3.

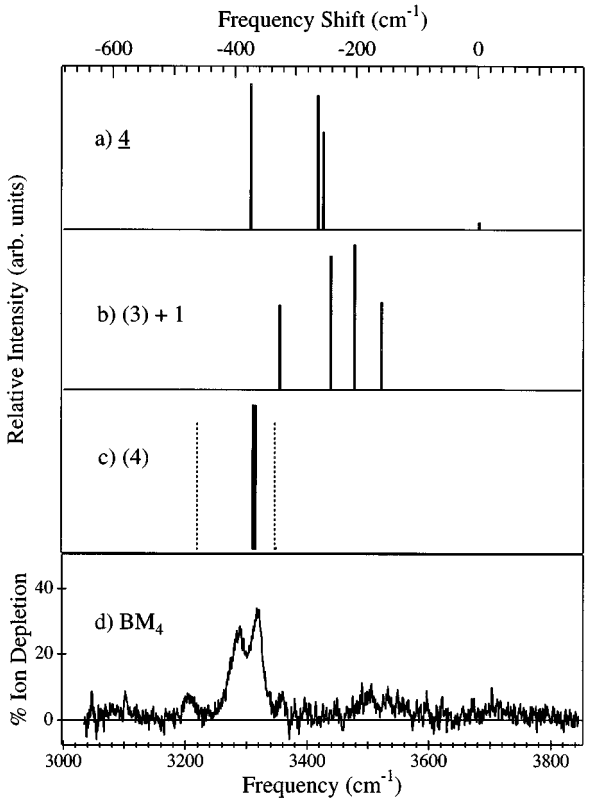

FIG. 7. (a), (b), and (c) *Ab initio* calculated OH stretch harmonic frequency shifts and infrared intensities for the (a) chain, (b) $(3)+1_1$ branched-cyclic, and (c) cyclic forms of the free methanol tetramer. In (c), the bold bar indicates the doubly degenerate OH stretch, while the dotted lines locate the positions of the forbidden ''satellite'' OH stretch fundamentals. (d) RIDIR spectrum of BM_4 for comparison.

Although the cyclic structure of M_4 in BM_4 is well-established, what is not well-characterized by the RIDIR spectrum is the orientation or degree of rigidity of the M_4 cycle with respect to the benzene ring. In BW_4, the π H-bonded OH stretch is clearly observed in the spectrum, ensuring that the cyclic water tetramer interacts with benzene primarily via an out-of-plane interaction. However, in BM_4, where no dangling OH groups are available for π H bonding, the orientation is less well-defined. Now, armed with the firm structural conclusion for the M_4 subcluster from the RIDIR data, it is worthwhile recalling the R2PI data[14] on BM_4 which more directly probes the interaction of benzene with the M_4 cycle. The electronic frequency shift of the vibronic transitions of the cluster relative to free benzene probes the type of interaction which dominates. A blueshift is consistently associated with a π H-bonding interaction with benzene, while a redshift is found when purely dispersive interactions dominate.[28] Consistent with this, the vibronic transitions of the BM_m clusters with $m=1$–3 are 44, 80, and 147 blueshifted from the corresponding transitions in free benzene, respectively. This reflects the increased strength of

the π H bond in these clusters. In BM_4, the vibronic transitions [Fig. 1(c)] shift dramatically back toward the red to a value only 19 cm^{-1} above that of free benzene. This is consistent with the loss of π H-bonding interaction in forming cyclic M_4 in BM_4.

The R2PI spectrum of BM_4 is also notable for its closely spaced, intense set of intermolecular transitions which each vibronic transition of benzene supports. In Fig. 1(c), the entire clump of transitions subtended by the bracket is due to BM_4, as has been confirmed by IR–UV hole-burning.[24] The presence of many low-frequency intermolecular bands suggests that the M_4 subcluster can librate against benzene with little cost in energy. In a previous paper[14] on the R2PI spectroscopy of BM_m, OPLS calculations[29] were used to optimize structures for the BM_m clusters. These predicted that the M_4 subunit interacts with benzene primarily via one methyl group on a single side of benzene, but with M_4 beginning to wrap around the side of benzene. In Fig. 8(a) an alternate structure is shown in which the *ab initio* calculated structure for M_4 acts as a cavity which accepts benzene in an edge-on approach. An interesting feature of this suggested structure is that two of the methyl groups on M_4 interact with opposite sides of the benzene ring, albeit rather weakly due to the small size of the tetramer cavity. Future experiments will need to be designed to test whether this pleasing picture is in fact that taken on by the BM_4 cluster.

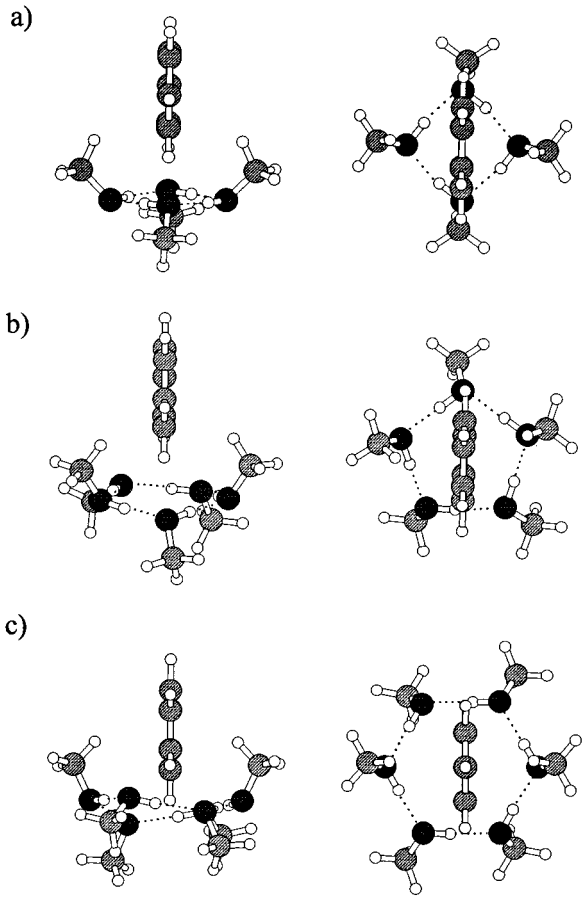

FIG. 8. Schematic pictures of the cyclic ''hydrogen-bonding'' architectures of (a) BM_4, (b) BM_5, and (c) BM_6. In no case is the orientation of the M_m cycle with respect to benzene known from experiment. The proposed structure for BM_6 incorporates a boat-shaped M_6 cycle whose nonplanarity induces intensity in otherwise forbidden transitions, qualitatively in keeping with experiment. This boat structure has a cavity which accepts benzene ''edge-on'' in such a way that the ''bow'' and ''stern'' methyl groups interact with opposite sides of the π cloud of benzene.

E. $C_6H_6-(CH_3OH)_5$

The RIDIR spectrum of BM_5 reproduced in Fig. 9(b) provides the first look at the OH stretch region of the methanol pentamer, here perturbed by the presence of benzene. No data on the OH spectrum of the gas-phase methanol pentamer is available for comparison; however, Coussan *et al.*[23] attribute the features at 3260, 3242, and 3220 cm^{-1} in a nitrogen matrix to M_m polymers with $m>4$.

As with BM_4, the spectrum of BM_5 is dominated by broadened band(s) shifted well to the red of the free OH region. The main band is centered at 3243 cm^{-1}, roughly 60 cm^{-1} further shifted than the intense transitions in BM_4, and precisely in the same range as the M_m polymers observed by Coussan *et al.*[23] (3220–3260 cm^{-1}). A shoulder at 3286 cm^{-1} is clearly evident in the spectrum of BM_5, while hints of a further substructure can be seen at 3171 and 3314 cm^{-1}. No π H-bonded OH transition is observed, though a weak, broad feature does appear near 3500 cm^{-1}, which we attribute to a combination band built on the 3243 cm^{-1} fundamental. As before, the narrow features at 3048 and 3108 cm^{-1} result from the CH stretch transitions of benzene in the BM_5 cluster.

Figure 9 compares the experimental OH stretch frequencies to those calculated for the cyclic methanol pentamer (5) and the (4)+1 branched cycle from paper I. The other pentamer structures from paper I bear little resemblance to the experimental spectrum and thus have not been included here. Of the calculated spectra, the cyclic pentamer is the best match with experiment; however, the (4)+1 branched cycle also shows some correspondence with experiment. Arguing against this latter structure is the considerably more intense sidebands predicted for (4)+1 than observed experimentally. Given the closer match with (5) and the significantly stronger binding energy calculated for (5) than for (4)+1 (paper I), we tentatively assign the H-bonded architecture of the M_5 cluster in BM_5 as cyclic.

In making this assignment, we correlate the main band at 3243 cm^{-1} with the near-degenerate pair of transitions in cyclic M_5 which carry the majority of the OH stretch intensity. The shoulder at 3284 cm^{-1} and (possibly) at 3314 cm^{-1} match well with the calculated peaks at 3311 and 3324 cm^{-1}, respectively. In cyclic M_5, these bands gain some intensity both from the asymmetry associated with the odd number of methyl groups in the pentamer ring and from the slight puckering of the ring. Finally, the shoulder at 3171 cm^{-1} is tentatively assigned to the calculated peak at 3178 cm^{-1}. In BM_5, this transition and the shoulders on the blue edge of the main band may gain additional intensity over that predicted in Fig. 9(a) due to the asymmetry provided by complexation to benzene. Such asymmetry causes partial local-

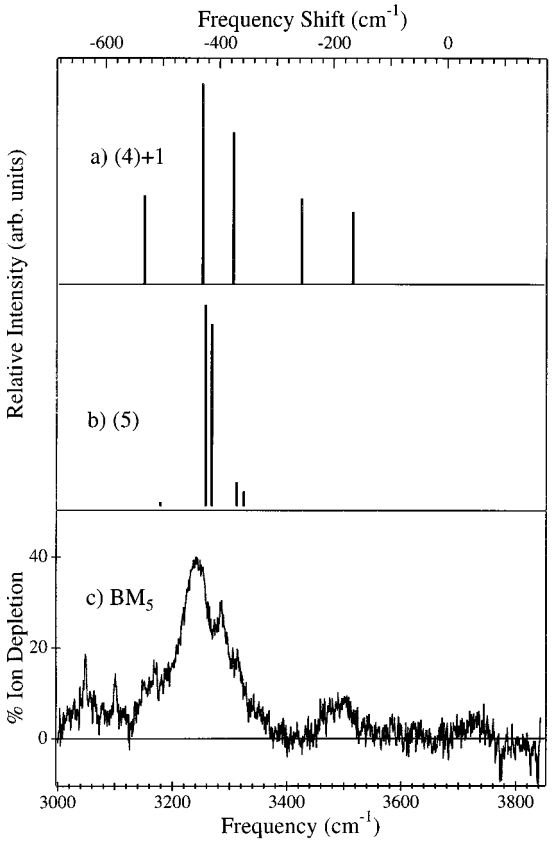

FIG. 9. *Ab initio* OH stretch harmonic frequency shifts and infrared intensities for the (a) (4)+1 branched cyclic and (b) cyclic methanol pentamer. (c) RIDIR spectrum of BM_5 for comparison.

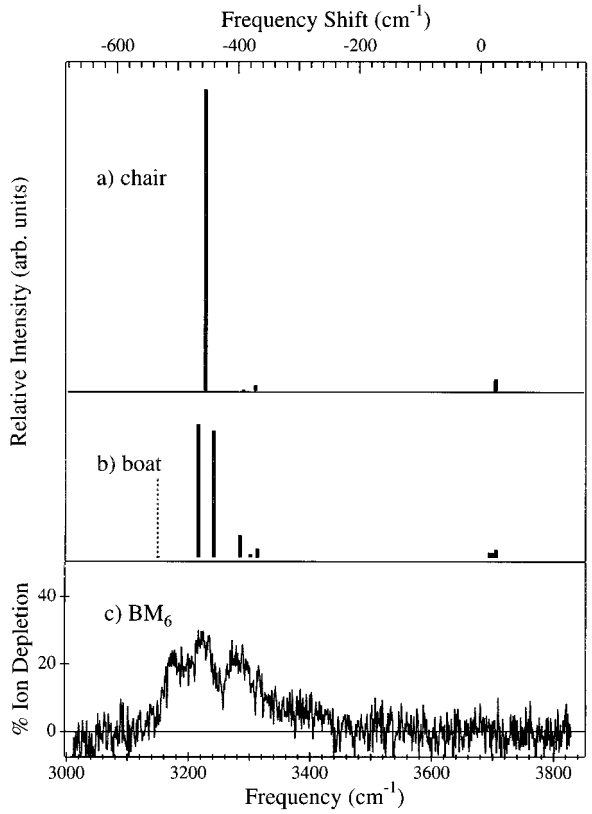

FIG. 10. *Ab initio* OH stretch harmonic frequency shifts and infrared intensities for the (a) chair cyclic, and (b) boat cyclic forms of the free water pentamer. The calculated frequencies have been shifted by -81 cm^{-1} to bring the calculated frequency for the methanol monomer OH stretch into agreement with the experimental (anharmonic) fundamental frequency. (c) RIDIR spectrum of BM_6. In making the comparison with the W_6 structures, attention is focused on the H-bonded OH stretches of W_6, since these have a direct analog in the OH stretch modes of M_6.

ization in the OH stretch vibrations, thereby altering the intensities of the transitions.

Once again, the orientation of the cyclic M_5 subcluster relative to benzene is not well-established. The R2PI spectrum[14] of BM_5, which one expects to be sensitive to the orientation of benzene in the cluster, shows an $S_1 \leftarrow S_0$ frequency shift of -19 cm^{-1} relative to free benzene. This is an additional redshift of 33 cm^{-1} relative to that in BM_4. In our earlier work, OPLS calculations[14] predicted that the M_5 cycle would be positioned on the side of the benzene ring. Figure 8(c) presents a slightly modified version of this structure in which the *ab initio* structure from paper I is used for the cyclic M_5 subcluster rather than the OPLS structure. Note that the expanded size of the pocket in M_5 relative to M_4 may allow stronger methyl–π interactions which could shift the electronic transition frequency to the red from that in BM_4, as observed.

F. C_6H_6–$(CH_3OH)_6$

The RIDIR spectrum of BM_6 is shown in close-up form in Fig. 10(c). The spectrum provides a first look at the OH stretch region of the methanol hexamer (here perturbed by benzene), since no experimental data on the these vibrations of M_6 are available. As with BM_4 and BM_5, the lack of a π H-bonded peak is strong evidence against a chain or branched-chain structure (paper I). Furthermore, a branched cycle would of necessity be a smaller cycle and/or contain a small branch which would have its OH stretch transitions at significantly higher frequencies than those observed ($\sim$3500 cm^{-1}). The remaining structural type is that expected to be most strongly bound; namely, the cyclic methanol hexamer. Once again we make a tentative assignment of BM_6 as containing a cyclic methanol hexamer.

If this assignment is correct, it must also be capable of explaining the substructure present in the RIDIR spectrum, which consists of at least three, and possibly four overlapping bands at 3177, 3224, 3280, and (possibly) 3315 cm^{-1}. The overall band center in BM_6 is hardly shifted from that in BM_5, suggesting a saturation in the strength of the H bonds with increasing ring size. This is what is predicted by the OPLS calculations of M_6 by Buck *et al.*,[30] where the average H-bond energy in the cyclic pentamer and hexamer are -7.95 and -8.12 kcal/mol, respectively.

As in the $m=5$ case, no size-specific experimental data in the OH spectral region of the methanol hexamer exist for comparison to BM_6. Buck *et al.*[10] have observed two absorptions for M_6 in the CO stretch region at 1041.2 and 1052.5 cm^{-1}. This is a break in the trend set by the cyclic methanol trimer, tetramer, and pentamer in which only one absorption

TABLE II. Calculated harmonic frequencies[a] and intensities for the chair and distorted boat structures of the water hexamer.

Mode No.	Frequency	Intensity	Symmetry
	Chair		
37	3245.6	0.0	*A*
38	3328.4	2965.8	*E*
39	3328.4	2965.8	*E*
40	3391.2	0.5	*E*
41	3391.2	0.5	*E*
42	3410.9	91.4	*A*
43	3806.9	172.4	*A*
44	3807.0	12.3	*E*
45	3807.0	12.3	*E*
46	3807.9	108.5	*E*
47	3807.9	108.5	*E*
48	3808.5	4.5	*A*
	Boat		
37	3256.4	4.6	*A*
38	3322.3	2617.8	*B*
39	3347.6	2499.6	*B*
40	3390.8	425.0	*A*
41	3408.2	51.5	*A*
42	3419.4	157.3	*B*
43	3803.7	88.7	*B*
44	3803.8	63.2	*A*
45	3808.1	26.4	*B*
46	3808.5	87.7	*A*
47	3813.8	147.4	*B*
48	3813.9	0.6	*A*

[a]These frequencies have not been shifted relative to the free methanol monomer.

was observed. Monte Carlo and molecular dynamics calculations performed by Buck *et al.*[30] find two nearly degenerate isomers, one with S_6 (chair) and the other with C_2 (boat) symmetry, having binding energies of -48.75 and -48.6 kcal/mol, respectively. The two absorptions in the CO stretch region have been ascribed to nonequivalent methanol environments in a single distorted cyclic M_6 structure.

Due to the size of the M_6 cluster, Becke3LYP/6-31+G* level calculations were not performed on M_6. However, calculations of the infrared frequencies and intensities of the chair and boat conformers of the water hexamer (with six less heavy atoms than M_6) have been carried out at the same level of theory in the expectation that the H-bonded OH transitions in W_6 will faithfully mimic the qualitative trends in the OH stretch modes of the corresponding conformers of M_6. Table II summarizes the vibrational data on the chair and boat forms of W_6. As expected based on the results on the smaller cyclic clusters, essentially all the intensity in the H-bonded OH stretch modes of the chair form is carried by a degenerate pair of transitions at 3328.4 cm^{-1}. Figure 10(a) shows the calculated spectrum of the W_6 chair when plotted versus frequency shift from the water monomer free OH.[19] By comparison, the experimental spectrum has no single transition dominating the spectrum, but three or four bands which have comparable intensities.

The match-up with the boat form [Fig. 10(b)] is more encouraging. In forming the boat structure [Fig. 8(c)], the planarity of the OH···O ring is substantially broken. As a result, even in the absence of benzene, the degeneracy of the central pair is broken, and the forbidden nature of the sidebands is removed. Nevertheless, while the positions of the bands are qualitatively in keeping with the experimental spectrum of BM_6, the intensities of the sidebands are still too weak. It is reasonable to assume that the sidebands could gain further intensity from the added symmetry-breaking induced by benzene.

Note that the calculated boat conformation is not the lowest-energy boat structure,[30] but one which has the free hydrogens on both ''bow and stern'' molecules in axial positions. This conformation corresponds with our intuition as to the best binding arrangement of a cyclic M_6 cluster to benzene, as shown in Fig. 8(c). In this conformation of M_6, the two axial hydrogens of W_6 are replaced by methyl groups which can interact with opposite sides of the benzene ring. The cavity so formed nicely accepts the benzene molecule edge-on, and in fact was the initial basis for thinking that similar conformations could play a role in the BM_4 and BM_5 clusters as well [Figs. 8(a) and 8(b)]. The total binding energy of the W_6 chair and this conformation of the W_6 boat are calculated to be -55.66 and -54.16 kcal/mol, respectively.

The suggestion put forward here is thus that, in the coexpansion of benzene and methanol, the lowest energy BM_6 structure contains a cyclic M_6 subcluster which is distorted into a boat conformation in order to form a better template for maximal interaction with benzene. This distortion maximizes the interaction between benzene and M_6 at the expense of the rearrangement energy from chair to boat conformations of M_6 ($\sim$1.5 kcal/mol), much as occurred in favoring chain over cyclic forms of M_3 in BM_3. In summary, the suggested structure for BM_6 meets an initial test provided by the W_6 calculations, but will require further experimental and theoretical work before a firm assignment is in hand.

Finally, the very different infrared spectra of BM_6 and BW_6 [Figs. 1(A), spectrum (f) and Fig. 1(B), spectrum (f), respectively] and the contrasting structures tentatively assigned to them highlight the unique interactions of water and methanol solvents with benzene. Water hexamer has a number of low energy structures including both cyclic and three-dimensional (3D) cage structures.[20,31] While the cyclic W_6 cluster contains six strong H bonds, the 3D cages form additional H bonds in which some of the water molecules donate both hydrogens to neighboring water molecules. The work of Kim, Jordan, and Zwier[5] compared the structures, binding energies, and OH stretch infrared spectra of the cyclic and two of the lowest energy cagelike W_6 structures with the objective of establishing the water solvent's structure in BW_6. The comparison clearly established the presence of double-donor water molecules in BW_6, a result which is consistent only with a 3D cage structure for W_6 in BW_6. The experimental spectrum best matches the theoretical spectrum of a cage structure containing two double-donating and four single-donating water molecules. Saykally and co-workers[6] have recently made the first experimental detection of precisely this form of W_6 in the far infrared. One can surmise on this basis that benzene does not seem to greatly effect the

structure of W_6, largely because dangling hydrogens on the 3D cage are still available for π H bonding with benzene.

In the methanol hexamer, the single OH group on each methanol removes the possibility of double donation and produces an energy cost for forming chain or branched-chain structures which have dangling hydrogens available for π H bonding to benzene. The result is a significant energetic preference for cyclic or branched cyclic structures in the larger M_m clusters, as demonstrated by the calculations on methanol trimer, tetramer, and pentamer in paper I. Thus, in the cyclic methanol hexamer, there is little inducement to break the cycle in complexing with benzene. Yet, the significant flexibility of these larger cyclic clusters can allow distortions which maximize the dispersive interactions with benzene at little cost in H-bonding energy in the M_6 cluster.

Thus, in BW_6, a stiff W_6 3D cage attaches to benzene via a π H bond involving one of the dangling hydrogens in the structure. This π H bond effectively holds the compact W_6 structure on one face of the benzene ring. In BM_6, the flexible M_6 cycle interacts weakly with benzene, but can nevertheless deform to accommodate a best interaction with benzene with little cost in energy. We propose a deformation in which the M_6 cycle wraps around the side of the benzene ring [Fig. 8(c)] and interacts with similar strength with both sides of benzene, not unlike the beginnings of a first solvent shell.

G. The breadths of the OH stretch transitions

The OH stretch transitions in Fig. 2 are those of a single configuration of a finite-sized H-bonded cluster at a few degrees kelvin. The observed breadths serve as a limiting case for comparison with the breadths of the OH stretch spectra in H-bonded liquids and solids.[1,2,7,8]

In the cold, gas-phase BW_n and BM_m clusters, the breadths of the transitions show significant dependence on cluster size and type of OH stretch mode. The OH stretch transitions are instrumentally broad in the H-bonded chain structures of BM_1–BM_3. However, the rearrangement of the M_4 substructure in BM_4 to a cyclic structure is accompanied by an increase in the breadths of the transitions to about 30 cm^{-1} FWHM. Even greater widths are apparent in BM_5 and BM_6. The *ab initio* calculations of paper I[21] highlight the cooperative strengthening of the H bonds in cyclic M_m clusters and the delocalization of the OH stretch modes over the OH bonds in the cycle. Both these features would suggest strong coupling of the OH stretch modes to the intermolecular modes associated with the H bonds. Yet, such coupling does not typically produce combination bands in the spectrum, but rather broadens the individual transitions, indicating coupling to a high density of background states. One suspects that the primary coupling of the OH stretch modes may be to the bath of states associated with ring-opened structures involving the breaking of a hydrogen bond (as in a DF trimer[32]) or to dissociative states involving breakup of the cluster (as in a HF trimer[33]). However, a detailed understanding of the magnitudes and sources of the broadening in these clusters is still needed. Nevertheless, the results on BW_n and BM_m clusters set a quantitative standard against which dynamical models of mode–mode coupling in H-bonded networks can be tested.

V. CONCLUSION

The OH stretch vibrations of size-specific benzene –$(methanol)_m$ ($m=1$–6) clusters has been investigated by means of resonant ion-dip infrared spectroscopy. The frequencies and band widths of the observed OH stretch fundamentals are strongly dependent on the structure of the cluster. By comparing the experimental frequencies to both experimental and calculated frequencies of the free methanol clusters, the H-bonding structure in the M_m subcluster can be firmly assigned.

In BM_1–BM_3, the structures probed by the present study incorporate one, two, and three methanol molecules in a H-bonded chain whose terminal methanol is π H bonded to benzene. The cooperative strengthening of the π H bond with increasing chain length is evident in the increasing redshift of the π H-bonded OH stretch frequency. By BM_3, the redshift (-92 cm^{-1}) is nearly as large as the frequency shift of the donor methanol in the free methanol dimer (-108 cm^{-1}).[11] Since the lowest-energy structure for the free methanol trimer is cyclic, the apparent dominance of the chain structure in BM_3 is evidence of a significant structural rearrangement induced by the presence of benzene. In the language of bulk solution, one could say that the benzene molecule has changed the lowest-energy structure taken on by its surrounding solvent.

In BM_4, the M_4 subcluster is cyclic, the same structure calculated to be lowest in energy in the absence of benzene. In this case, the effect of benzene is much more subtle because the interaction with benzene with a cyclic M_m cluster is quite weak. The OH stretch spectroscopy reflects the perturbations imposed by benzene in a splitting of the degenerate vibrations which carry all the intensity in M_4, and a weak inducement of intensity in two otherwise IR-forbidden transitions.

Finally, in BM_5 and BM_6, the RIDIR spectra show only broadened features centered around 3200–3250 cm^{-1}, corresponding to frequency shifts of 450–500 cm^{-1} from the OH stretch fundamental in methanol monomer. The lack of transitions to the blue and the general correspondence with the *ab initio* calculated frequencies of cyclic M_5 and W_6 suggest cyclic M_m structures for both BM_5 and BM_6. In BM_6, the intensity spread and substructure of the OH stretch absorptions are consistent with a distortion of the cyclic M_6 subcluster which breaks degeneracies and turns on transitions which are forbidden in the lowest-energy S_6 symmetry chair structure. We propose the distortion to form a boat structure somewhat analogous to the higher-temperature C_2 structure put forward for M_6 by Buck *et al.*[10,30] in the pure M_6 clusters. In BM_6, however, we raise the possibility that the ''bow and stern'' methyl groups are in axial positions. When one brings the benzene molecule up to this structure, the boat forms a cavity for edge-on approach of benzene which can accommodate interactions between the axial methyl groups

and the π cloud on either side of the benzene ring.

The one-for-one comparison of the results on BM_m with the previous RIDIR spectra[3–5,19] on BW_m present a series of interesting contrasts all of which arise from the presence of two H-bonding OH groups in water and one in methanol. The spectrum of BM_1 is a single OH stretch transition, while BW_1 has an exceedingly complex set of seven or eight transitions[19] reflecting the large-amplitude torsion and internal rotation of the water molecule in the complex. These motions of H_2O swap the OH groups involved in the π H bond, and are thus quenched or reduced in BM_1. BW_2 and BM_2 have similar structures, but in BW_3, the water trimer is cyclic while the methanol trimer in BM_3 has a chain M_3 structure. Again, the presence of dangling hydrogens in the W_3 cycle enables BW_3 to retain the three highly nonlinear H bonds in W_3 without sacrificing a favorable π H bond with benzene. In contrast, cyclic M_3 ties up all its OH groups in H bonding between methanol molecules, significantly weakening the interaction with benzene's π cloud and favoring formation of the chain structure which retains a cooperatively strengthened π H bond to benzene.

The $m=4$ and 5 structures of both BW_m and BM_m are cyclic, but the spectra of the BM_m are only slightly perturbed from their M_m counterparts due to the weak interactions with benzene when all OH groups are tied up in methanol–methanol H bonds.

Finally, the structure of the water hexamer in BW_6 is a three-dimensional cage structure while the methanol hexamer in BM_6 is tentatively assigned as cyclic. The 3D cage is only possible by employing both OH groups in some of the water molecules in H bonds; furthermore, another of the dangling OH groups is involved in π H bonding with benzene. The cyclic M_6 structure uses all OH groups in the cycle. At the same time, the size of the hexamer cycle is sufficient to allow significant conformational flexibility in the cycle with little cost in energy. The tentatively proposed structure for BM_6, which incorporates a boat-shaped cycle to which benzene binds ''edge-on,'' is reminiscent of the beginnings of a first solvent shell around the benzene solute. In summary, in these small gas-phase benzene/solvent clusters, the tendency of water to self-associate with little deference for benzene and of methanol to rearrange or distort in order to accommodate an increased interaction with benzene at least hints at the molecular-level basis for benzene's immiscibility in water and infinite solubility in methanol.

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