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OH stretch IR spectra of $(H_2O)_3$ and benzene-$(H_2O)_3$

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Abstract. The OH stretch IR spectrum of $(H_2O)_3$ is significantly altered upon complexation of the cluster with a benzene molecule. Theoretical calculations show that the differences in the OH stretch spectra of $(H_2O)_3$ and benzene-$(H_2O)_3$ are primarily due to mode localization induced by the benzene molecule.

Key words: Clusters – Hydrogen bonding – Vibrational frequencies

1 Introduction

Recent years have witnessed a sharp upsurge in research on small water clusters. This has been driven by experimental advances, permitting characterization of the clusters in the microwave [1–4], near IR [5, 6], and far IR [7–10] regions, as well as by computational advances, enabling accurate ab initio calculations [11–22] of the structures, stabilities, and vibrational spectra of the clusters.

Mixed clusters containing water and organic molecules are also receiving increased attention. Benzene-$(H_2O)_n$ (hereafter referred to as BW_n) clusters, in particular, have been the subject of a number of experimental [23–32] and theoretical studies [33–36]. Near IR spectra have been published for clusters as large as BW_7 [30–32]. The hydrogen bonding topologies of the W_n cluster sub-units in the BW_n clusters closely mimic those of the pure W_n clusters of the same size. Since the OH stretch infrared spectra are sensitive to the number, type, and strength of the hydrogen bonds present, they serve as sensitive spectral signatures for various fundamental H-bonding topologies. The BW_n clusters themselves provide examples of H-bonded cycles, cubes, and three-dimensional networks.

One important question which arises in the study of these fundamental H-bonding topologies is the sensitivity of their spectral signatures to their local environment. In particular, one wonders whether the presence of a solute molecule will perturb them, and if so, in what way. Given the tremendous interest in W_n clusters and the availability of data on the BW_n clusters, the comparison of ab initio results on the two systems can provide just such insight into the perturbing effects of benzene on W_n clusters. Furthermore, such studies of the mixed clusters provide insight into how interactions at a molecular level influence macroscopic behavior such as miscibility. Finally, the availability of spectroscopic and high-quality ab initio data on the pure and mixed clusters will prove valuable in the development of new, improved model potentials for carrying out Monte Carlo and molecular dynamics simulations.

In every case studied so far, comparison of the OH stretch IR data for the BW_n and W_n clusters indicates that the lowest energy structure for the W_n cluster is retained in the presence of benzene [30–32]. This is consistent with the observation that the interaction between water molecules is greater than that between benzene and water molecules (the estimated D_o values of the W_2 and BW_1 dimers are 3.6 and 2.2 kcal/mol, respectively [37, 38]). Nonetheless, the presence of the benzene molecule can induce significant changes in the OH stretch spectra of the water clusters [30–32, 35]. Intuitively, we expect that the impact of the benzene molecule on the OH stretch spectra will be greater for highly symmetrical than for non-symmetrical water clusters. This follows from the observation that in the high symmetry clusters, the OH stretch normal modes are highly delocalized over all water molecules in the cluster, while addition of the benzene will causes partial mode localization. In contrast, for the non-symmetrical clusters, the OH stretch vibrations are already localized, and the interaction with the benzene should cause relatively small perturbations on the spectra. This is borne out experimentally [30–32] as well as by calculations [35].

The simplest water cluster for which complexation with benzene could potentially cause significant mode localization is the dimer [30, 31, 34]. The dimer possesses

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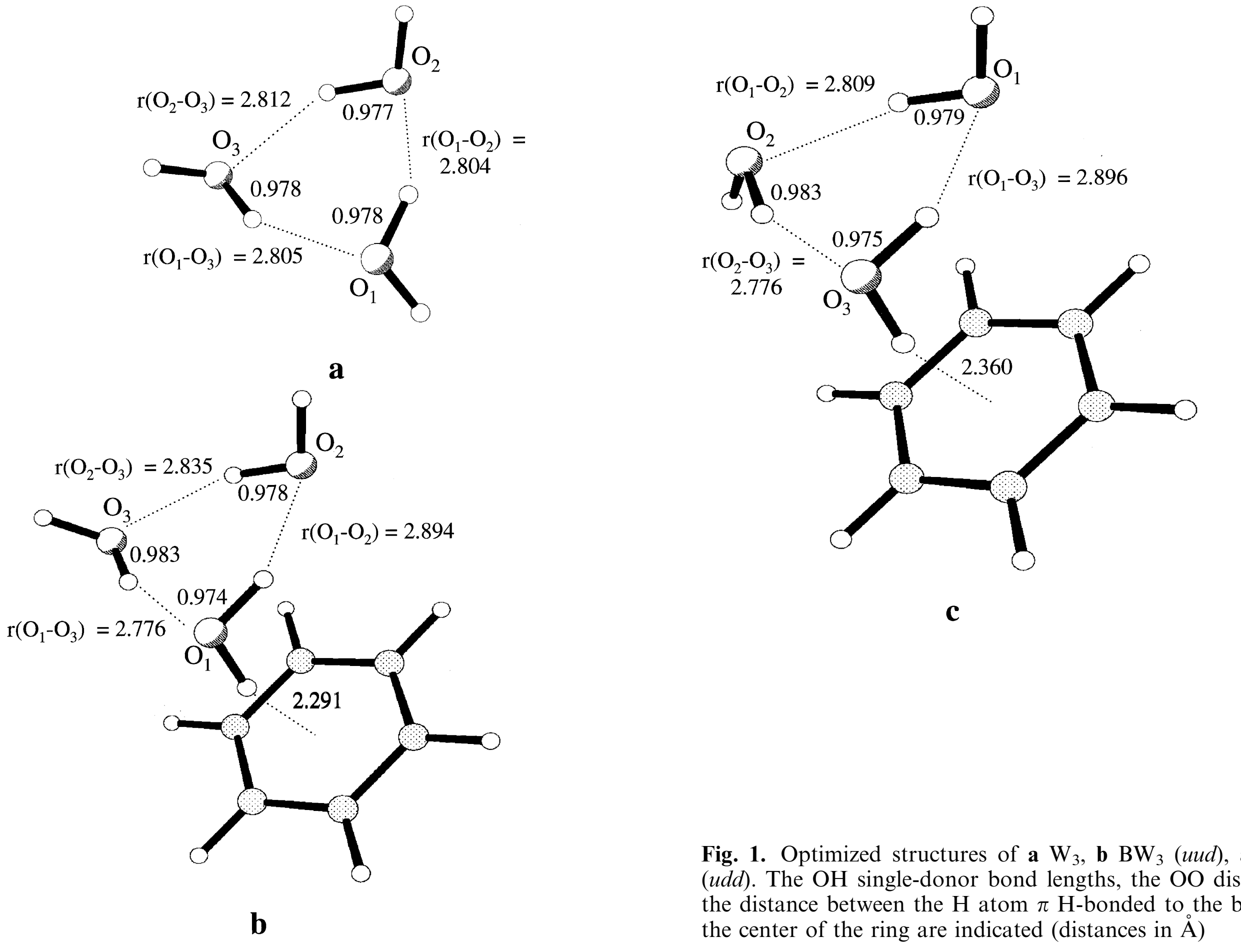

Fig. 1. Optimized structures of **a** W_3, **b** BW_3 (*uud*), and **c** BW_3 (*udd*). The OH single-donor bond lengths, the OO distances, and the distance between the H atom π H-bonded to the benzene and the center of the ring are indicated (distances in Å)

C_s symmetry, and as a result, the two OH groups of the acceptor monomer are symmetrically equivalent. In the global minimum structure of BW_2 the W_2 molecule π H-bonds to the benzene ring through one of the H atoms of the acceptor group, and this breaks the symmetry. In the absence of tunneling between different permutational isomers, the two OH stretch modes on the acceptor monomer would then be localized. However, the barriers for tunneling are sufficiently low [36] for it to be likely that under experimental conditions [30, 31] these modes remain delocalized. The dimer with symmetrically equivalent OH groups on one monomer is a special case; more common are clusters in which two or more water monomers are symmetrically equivalent or nearly so. Members of this class of clusters include the cyclic water trimer, tetramer, and pentamer, and the cubic forms of the octamer.

In the present investigation, W_3 is chosen as representative of water clusters for which the complexation with a benzene molecule causes a large perturbation of the vibrational spectrum. W_3 has a cyclic global minimum structure, with each monomer acting as a single H-donor as shown in Fig. 1. Two of the free OH groups are on one side of the OOO plane, and the third is on the other side [9–12, 21, 22, 39–41]; as a result, the global minimum structure is of C_1 symmetry. Nonetheless, the cluster (even in a single potential minimum) may be viewed as having approximate threefold symmetry, as evidenced by the fact that the three OO distances are nearly equal, as are the three single-donor OH bond lengths [11, 12, 39]. Moreover, the barriers for flipping the H atoms of the free OH groups and for torsional exchange of the free and single-donor OH groups of the monomers are low, making possible rapid interconversion of the equivalent global minima [12, 21, 22, 39, 40]. The molecular symmetry group appropriate for the tunneling spectra is isomorphic with the C_{3h} point group [9].

In Ref. [35], we reported theoretical structures and normal-mode OH stretch spectra of W_n and BW_n, $n = 1$–3, clusters. The present study extends this earlier work by examining more closely the localization of the OH stretching modes in BW_3, by presenting the calculated spectrum of two different forms of BW_3, and by reporting also the calculated vibrational spectra in regions other than the OH stretch regions. Visualization of the normal modes is particularly useful for understanding the changes induced by the benzene, and animations of the normal modes are accessible via the Internet archive.

2 Structural information

All theoretical results reported here were obtained from MP2 calculations employing the 6–31+G[2d,p] basis set. The details of the calculations are presented in Ref.

[35]. Figure 1 depicts the structures, including the OO and OH distances, of W_3 and of two isomers of BW_3, labeled as BW_3 (*uud*) and BW_3 (*udd*). The "*u*" and "*d*" denote, respectively, whether a particular free OH group is pointing up or down with respect to the OOO plane, where the direction of *u* and *d* is set by benzene being placed below the W_3 cycle [41]. For the free W_3 species the (*uud*) and (*udd*) species are two of the 96 energetically equivalent minima in the relevant subgroup of the full permutation inversion group [39–41]. However, in both BW_3 isomers, the W_3 entity is π H-bonded to the benzene ring through one of the free OH groups, thereby breaking the degeneracy between BW_3 (*uud*) and BW_3 (*udd*). The BW_3 (*uud*) isomer is the global minimum on the BW_3 potential energy surface, whereas the BW_3 (*udd*) isomer is calculated to lie 217 cm^{-1} higher in energy. It follows from this that the tunneling dynamics for BW_3 will be very different from that of the bare W_3 cluster. In fact, the most important tunneling motion in BW_3 most likely involves motion of the W_3 relative to the benzene rather than motion of the H atoms of the W_3 portion of the cluster.

As expected, the interaction with the benzene ring destroys the approximate threefold symmetry present in the bare W_3 cluster. For example, the three OO distances in the BW_3 (*uud*) cluster are 2.776, 2.835, and 2.894 Å, whereas those in the bare W_3 cluster fall in the narrow range of 2.804 to 2.812 Å. Complete structural information is available electronically via the Internet archive.

3 Vibrational spectra

Figure 2 compares the OH stretch spectra of W_3 and the (*uud*) isomer of BW_3. The figure includes both the MP2 [35] and experimental results [30, 31]. The spectral transitions are reported relative to the mean of the two OH stretch frequencies (calculated or experimental as appropriate) of water monomer. The complete calculated spectra for W_3, BW_3 (*uud*) and BW_3 (*udd*) are available via the Internet archive.

A detailed analysis of the OH stretch spectra of W_3 and BW_3 has been reported in Ref. [35], and only the most important details are repeated here. The IR spectrum of W_3 is characterized by two pronounced transitions in the OH stretch region (with shifts of +14 and −173 cm^{-1}). Based on the calculations, it is seen that one of these is due to the three free OH stretch modes, which are nearly degenerate in the MP2 calculations (shifts +14 to +20 cm^{-1}). The second intense transition is due to two nearly degenerate single-donor OH stretch modes (calculated shifts: −237, −249 cm^{-1}). The third single-donor OH stretch mode, which involves an in-phase oscillation of the three OH groups, is even further shifted than the other two single-donor modes. It carries near zero intensity (as a result of the approximate threefold symmetry of the cluster) and is not observed in the experimental studies.

The OH stretch spectrum (both calculated and measured) of BW_3 is markedly different from that of W_3. The experimental spectrum shows five intense lines, the assignment of which is straightforward. The band due to the three free OH stretch transitions of W_3 is split into two bands near +10 and −49 cm^{-1} in BW_3. The latter "split-off" transition is associated with the OH group π H-bonded to the benzene ring. The presence of the benzene also causes the three single-donor OH stretch transitions to spread out and to acquire nearly equal intensities.

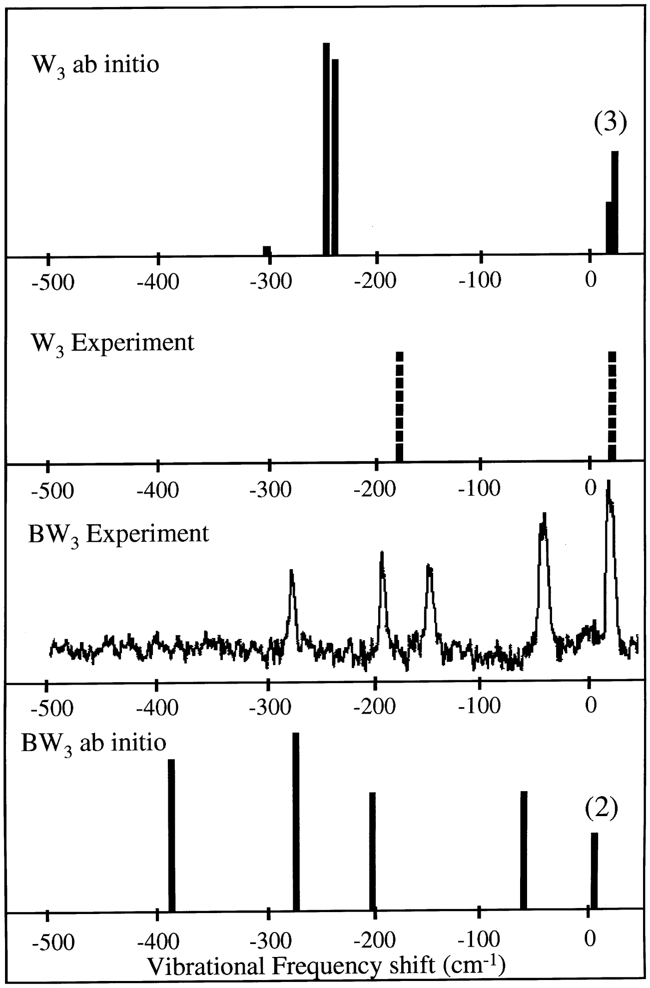

Fig. 2. Calculated (MP2 level) and experimental vibrational frequency shifts for the OH stretch region of W_3 and BW_3 (*uud*). The shifts are with respect to the average of the OH stretch frequencies of the water monomer, from theory (3900 cm^{-1}) or experiment (3706 cm^{-1}), as appropriate. Experimental results are from Ref. [1] for W_1, Ref. [6] for W_3, and Ref. [32] for BW_3

The MP2 calculations closely reproduce the changes in the OH stretch spectra in going from W_3 to BW_3. The one shortcoming of the MP2 calculations is that they predict larger shifts (in the negative direction) in the single-donor OH stretch frequencies than are observed experimentally. This is due to the underestimation of the OO distances at this level of theory; this deficiency can be remedied by the inclusion of higher-order correlation effects [35].

The (*uud*) and (*udd*) forms of BW_3 have similar OH stretch spectra. The most important difference is in the free OH stretch region of the spectrum. In the (*uud*) isomer two of the free OH stretch modes remain nearly degenerate, whereas in the (*udd*) isomer the splittings among the three free OH stretch lines are sufficiently large to allow the observation of three distinct bands in the experimental spectrum (if this isomer were present in sufficiently high amount under the experimental conditions). This difference between the (*uud*) and (*udd*) isomers is a consequence of the fact that there are two free OH groups pointing toward the benzene ring in the latter isomer but only one, that π-hydrogen bonded to the benzene, pointed toward the ring in the former isomer.

The MP2 calculations predict that the free OH stretch modes are localized in both W_3 and BW_3. In the case of the bare W_3 cluster, this is a consequence of the very weak coupling between the three free OH groups and the fact that the MP2 calculations neglect tunneling between the equivalent potential energy minima. The free OH stretch modes of W_3 would be found to be delocalized if averaging over the low-frequency tunneling motions were included. In contrast, the localization of the free OH modes of BW_3 would "survive" averaging over the low-frequency motions. The greatest effect of the interaction with the benzene molecule is on the OH stretch mode associated with the OH group π H-bonded to the benzene ring. This mode is shifted to lower frequency and experiences a large increase in intensity. The large intensity change derives from variation of either the polarization of the electron distribution of the benzene or the extent of charge transfer between the water cluster and the benzene molecule accompanying motion along this OH stretch coordinate [35].

The MP2 calculations predict the single-donor OH stretch modes to be delocalized in the bare W_3 molecule, but to be highly localized in the (*uud*) and (*udd*) BW_3 isomers. In the mixed clusters over 80% of the weight of each mode is associated with a single OH group. MPEG animations of the six OH stretch modes of W_3 and of the global minimum structure of BW_3 are available electronically via the Internet archive.

The splitting pattern for the three single-donor OH stretch modes of the bare W_3 can be understood by consideration of the simplified Hückel-like Hamiltonian matrix

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}, \tag{1}$$

where the diagonal (α) entries refer to the frequencies of the OH stretch modes localized on each of the three monomers, and the off-diagonal (β) entries describe the coupling between the localized OH stretch modes. The three diagonal entries were set equal as were the various off-diagonal entries to account for the effective threefold symmetry of the cluster. Comparison of the eigenvalues ($\alpha - \beta$, $\alpha - \beta$, $\alpha + 2\beta$) of this Hamiltonian with the calculated spectra gives a value of 23 cm^{-1} for the coupling. This is about half as large as the coupling (50 cm^{-1}) between the two localized OH stretch modes of the water monomer.

The overall splitting among the three single-donor OH stretch modes of BW_3 (*uud*) is 192 cm^{-1}, approximately 2.8 times greater than that in W_3. Most of the splitting between the single-donor OH stretch modes of BW_3 is the result of the geometrical changes induced by the benzene rather than the coupling between the localized OH stretch modes. In particular, the interaction with the benzene causes large spreads in the single-donor OH and OO distances (Fig. 1), which in turn causes the frequencies of the three single-donor OH stretch local modes to differ appreciably. In order to verify this interpretation, the vibrational frequencies were calculated for each of the three distorted W_2 species that can be generated from the optimized structure for BW_3. These calculations give single-donor OH stretch frequencies of 3706, 3651, and 3561 cm^{-1}, with an overall splitting of 145 cm^{-1}, in fairly good agreement with that calculated (and measured) for the BW_3 cluster.

4 Discussion

The results presented in this study demonstrate that the interaction of the W_3 cluster with a benzene molecule causes significant changes in the OH stretch IR spectrum of W_3. In the single-donor OH stretch regions these changes include an increased splitting between the three transitions and a redistribution of the intensities (with all three lines acquiring nearly equal intensity). The changes in this portion of the spectrum are the result of localization of the normal modes, which, in turn, is due to the structural changes in the W_3 cluster induced by the interaction with the benzene molecule. In the free OH region of the spectrum, the most significant change in going from W_3 to BW_3 is the shift to lower frequency and the large increase in intensity in the mode associated with the OH group π H-bonded to the benzene ring.

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