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A molecular level study of the aqueous microsolvation of acetylene

Demeter Tzeli [a], Aristides Mavridis [a,1], Sotiris S. Xantheas [b,*]

[a] *Department of Chemistry, Laboratory of Physical Chemistry, National and Kapodistrian University of Athens, P.O. Box 64 004, 157 10 Zografou, Athens, Greece*

[b] *Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, 906 Battelle Boulevard, P.O. Box 999, MS K8-91, Richland, WA 99352, USA*

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Abstract

We present an analysis of the structural, energetic and spectral features associated with the different hydrogen bonded networks found in the first few acetylene–water clusters AW_n ($n = 1$–4) from first principles calculations. Contrary to the predictions of an empirical interaction potential, acetylene is incorporated into a hydrogen bonded ring when it clusters with two or three water molecules. This structural pattern changes for $n = 4$ with the formation of a water tetramer interacting with acetylene. This structural transition from $n = 3$ to 4 is spectroscopically manifested by a qualitative change in the appearance of the infrared spectra of the corresponding global minima. © 2001 Published by Elsevier Science B.V.

1. Introduction

The ability of the water molecule to interact with a variety of molecular systems and the paramount importance of these interactions to both chemistry and biology is well established. Numerous experimental and theoretical investigations related to these systems have been reported [1]. For instance, considerable computational work has been reported for water clusters $(H_2O)_n$, $n = 2$–6 [2–7] and the interaction of water with molecules such as benzene [8,9] and phenol [10–12]. Yet only limited experimental and theoretical work has been reported on the hydrophobic system acetylene–water (AW_n, $n > 1$) [13–15] despite its prototypical character and acetylene's relatively high, with respect to other hydrocarbons, solubility in water [16]. The pertinent question therefore lies in the mechanism of the acetylene microhydration as to whether it breaks-up the water hydrogen-bonded network or forms clusters of water molecules that are attached to the hydrocarbon as in the case of benzene [17,18]. Probing the structures of the first few acetylene–water clusters from first principles calculations provide the necessary information for their characterization by experimental (i.e. spectroscopic) methods as well as for the benchmarking and parametrization of empirical models that can be used to model the solvation of acetylene in water.

Choi et al. [13] have previously studied the ion/molecule reactions occurring within the acetylene–water heterocluster ions, $(C_2H_2)_n \cdot (H_2O)_m^+$ using

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[*] Corresponding author.
E-mail address: sotiris.xantheas@pnl.gov (S.S. Xantheas).
[1] Also corresponding author.

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an electron impact time of flight (TOF) mass spectrometer. Dykstra [14] applied the molecular mechanics for clusters (MMC) potential model for the C_2H_2–$(H_2O)_2$ (AW_2) system and obtained an interaction energy of $\Delta E_e = -12.65$ kcal/mol ($\Delta E_0 = -8.17$ kcal/mol including zero-point energy corrections), a value that is rather large when compared with our findings (vide infra). Voorhis and Dykstra [15] have furthermore examined the AW_3, AW_4, A_2W_2 and A_3W systems via the MMC model. For the AW_3 cluster they reported five minima (with an interaction energy of −22.32 (−15.12) kcal/mol for the global minimum), concluding that C_2H_2 cannot participate in a four-member ring with three water molecules; no numerical results were presented for the AW_4 cluster. Concerning the AW_3 cluster our findings are qualitatively different: we have located 10 low-lying minima, the computed interaction energies are weaker and several of these form four-member rings with water.

The present work builds on our previous C_2H_2–H_2O (AW) dimer study [19], where two minima were found on the PES (cf. Fig. 1). In the global minimum, the water molecule acts as an acceptor to the acetylenic hydrogen (AW-Y) whereas there exists a shallow local minimum in which the water molecule bonds as a donor to the triple bond (AW-T) like, for instance, the benzene–water dimer [8,9]. However, the local minimum is washed out (i.e. there is no barrier to the global minimum) when zero-point energy (ZPE) corrections are taken into account, a fact that is consistent with the experimental observation of only one minimum resembling the AW-Y arrangement experimentally [20,21]. Here we extend our previous study to clusters of acetylene with several water molecules. The goal of our study is to provide the first ab initio results on clusters of acetylene with more than one water molecules and – in the absence of experimental information – their infrared (IR) vibrational spectra that can be used as guidelines in order to assign future experimental data. The theoretical approach is outlined in Section 2. The results for the structures and energetics of the global and low-lying local minima of the AW_n, $n = 2$–4 clusters are presented in Section 3 and final conclusions are drawn in Section 4.

2. Theoretical approach

The optimal geometries of the AW_n, $n = 2$–4 clusters are obtained at the MP2 level of theory with the family of correlation-consistent aug-cc-pVDZ ($n = 2$–4) and aug-cc-pVTZ ($n = 2$) basis sets [22,23]. At this level of theory all structures were fully optimized and harmonic frequencies were determined for the AW_n, $n = 2, 3$ clusters with both basis sets. For the $n = 4$ cluster, ZPE corrections were calculated at the MP2/aug-cc-pVDZ level of theory for the global and two other local minima only. A total of 4, 10 and 30 minima were found for the AW_n, $n = 2$–4 clusters, respectively, in an attempt to explore the relative stabilities of several networks and perform a thorough sampling of the configuration space. Here we present the results for the global and several low-lying minima for each cluster. Recognizing the importance of basis set superposition error (BSSE) [24] in van der Waals systems [25,26] we have incorporated these corrections in the calculation of the cluster binding energies following a scheme that includes terms arising from the intramolecular deformation of the monomers in the cluster geometry [27]. Insights into the magnitude of the various interactions and their contribution the energetic stabilization of the different networks can be obtained from the analysis of the interaction energy into 2- through n-body terms [5]. This decomposition requires the evaluation of the energy of $\binom{n}{1}$ monomers, $\binom{n}{2}$ dimers, $\binom{n}{3}$ trimers, up to the $\binom{n}{n}$ cluster, where $\binom{n}{i}$ stands for the corresponding binomial coefficient. All calculations were performed with the GAUSSIAN 94 [28] suite of programs.

3. Results and discussion

3.1. Structures and energetics

The minimum energy configurations of the AW_n, $n = 1$–4 clusters together with selected geometrical parameters (distances in Å, angles in degrees) are shown in Fig. 1. Their interaction

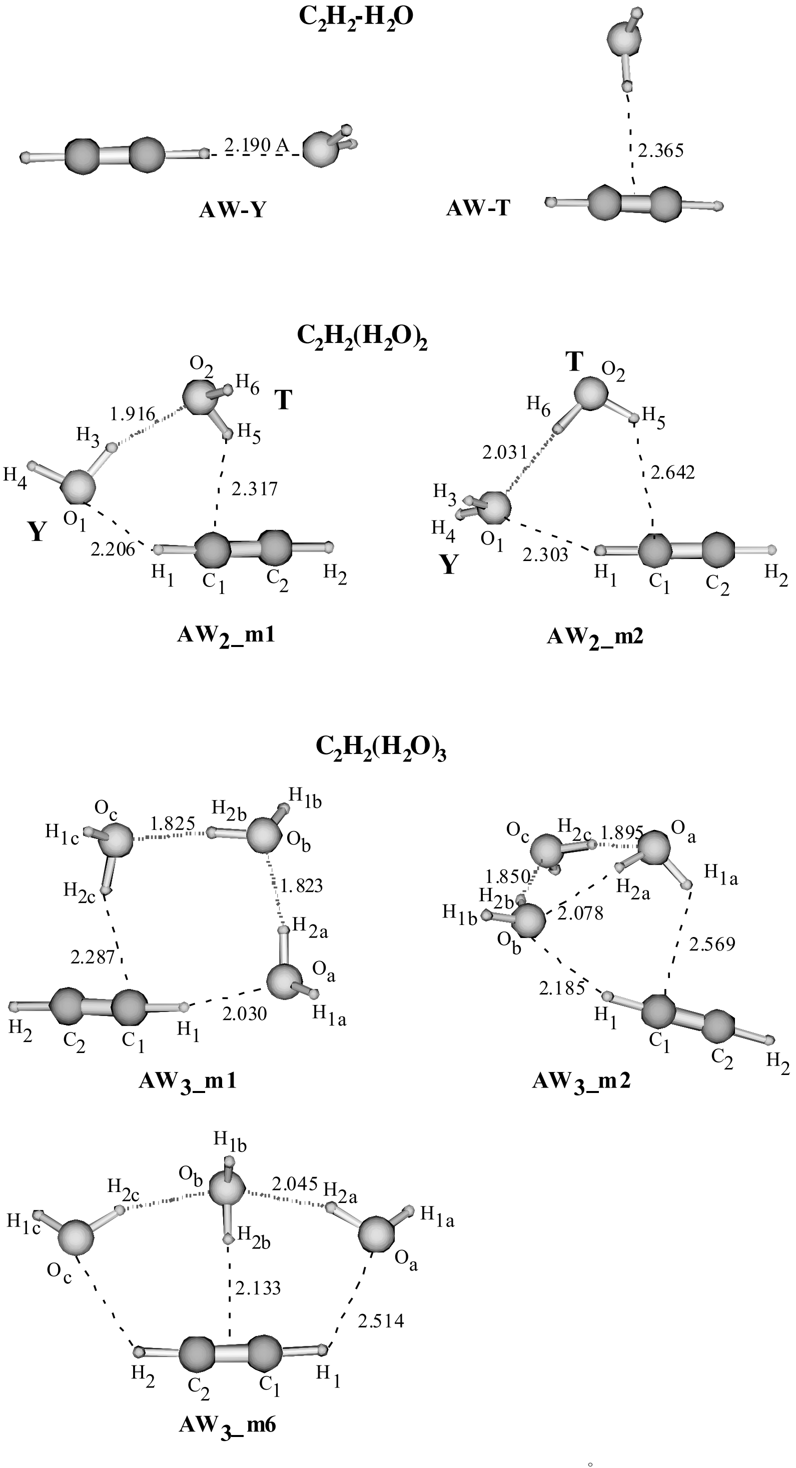

Fig. 1. Geometrical parameters of selected AW$_n$, $n = 1$–4 minima. Bond distances in Å. The global minimum is always denoted by (m1).

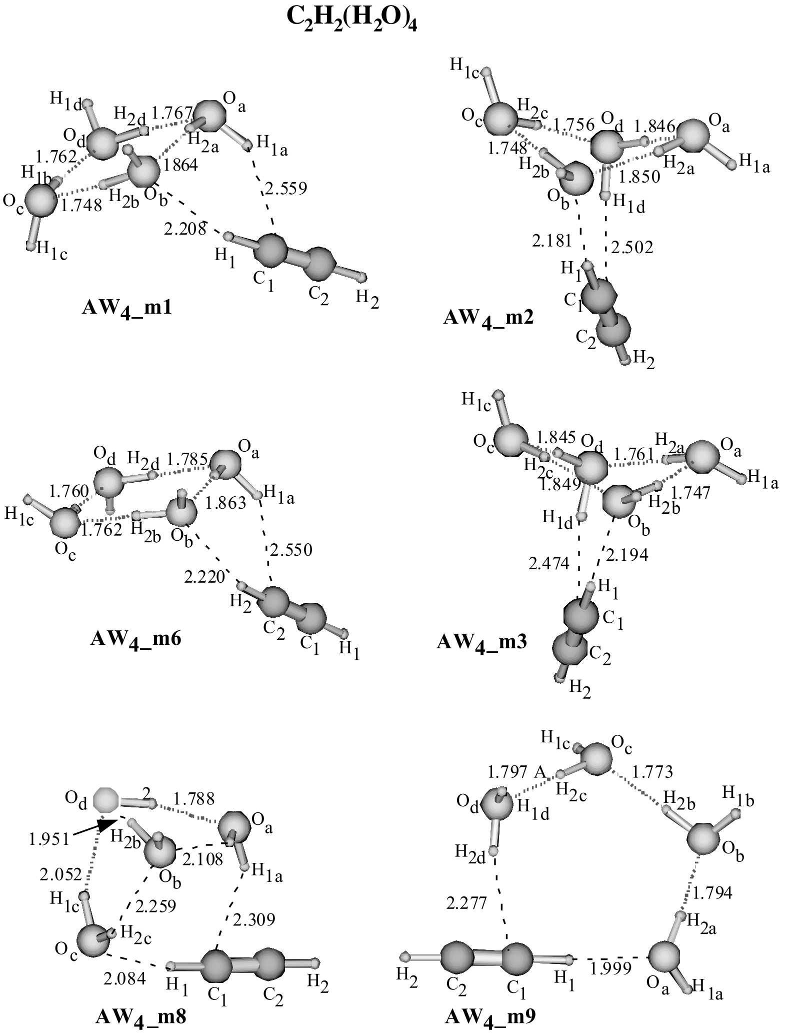
$C_2H_2(H_2O)_4$

Fig. 1. (continued)

energies (ΔE_e) corrected for BSSE [ΔE_e(fCP)] and ZPE [ΔE_0(fCP)] are listed in Table 1. In this notation the indication 'fCP' denotes the BSSE-corrected energies that were obtained using the function counterpoise method [24]. The energy decomposition is listed in Table 2. The numbering scheme of the various local minima corresponds to their relative position in an energy scale with respect to the global minimum, which is denoted by (m1) for each cluster size. The uncorrected ΔE_e's were used to construct the absolute energy scale with the realization that corrections for BSSE might change the order between some local minima as is the case, for example, for the (m8) and (m9) local minima of AW_4. In this notation (m6), for example, denotes the sixth local minimum above the global one in absolute energy order. We have chosen to use the uncorrected rather than the BSSE-corrected interaction energies for the ordering of the isomers, since, as was found during previous studies of hydrogen bonded clusters [29–31], the uncorrected numbers are closer to the complete basis set (CBS) limit than the BSSE-corrected ones with the family of augmented correlation-consistent bases and *especially* for the smaller aug-cc-pVDZ set. Nevertheless, the effect

Table 1
Interaction energies (ΔE_e) including BSSE [ΔE_e(fCP)] and zero point energy corrections [ΔE_0(fCP)] in kcal/mol for selected minima of the AW_n, $n = 1$–4 clusters

Species	Level of theory	ΔE_e	ΔE_e(fCP)	ΔE_0(fCP)
AW-Y	MP2/aug-cc-pVDZ[a]	−3.61	−2.62	−2.58
	MP2/aug-cc-pVTZ[a]	−3.17	−2.72	−2.21
	MP2/aug-cc-pVQZ[a]	−2.97	−2.80	−1.85
	MP4/aug-cc-pVDZ[a]	−3.68	−2.62	−1.59
	MP4/aug-cc-pVTZ[a]	−3.22	−2.77	−1.82
	MP4/aug-cc-pVQZ[a]	−2.98	−2.83	−1.88
AW_2(m1)	MP2/aug-cc-pVDZ	−12.02	−9.60	−5.76
AW_2(m1)	MP2/aug-cc-pVTZ	−11.57	−10.36	−6.70
AW_2(m2)	MP2/aug-cc-pVDZ	−8.92	−6.88	−3.71
AW_2(m2)	MP2/aug-cc-pVTZ	−8.31	−7.35	−4.37
AW_3(m1)	MP2/aug-cc-pVDZ	−21.96	−17.80	−11.46
AW_3(m2)		−21.49	−17.54	−11.09
AW_3(m6)		−17.30	−13.81	−8.47
AW_4(m1)	MP2/aug-cc-pVDZ	−33.89	−28.01	−18.67
AW_4(m2)		−33.68	−27.47	–
AW_4(m3)		−33.57	−27.35	–
AW_4(m6)		−33.08	−27.25	–
AW_4(m8)		−30.81	−25.01	−15.89
AW_4(m9)		−30.64	−25.14	−16.57

[a] Ref. [19].

Table 2
Decomposition of the interaction energy for the global minima of the $AW_n, n = 1$–4 clusters

n		ΔE_e	Deformation	2-body	3-body	4-body	5-body
2	m1	−9.60	0.18	−8.60	−1.18		
	m2	−6.88	0.03	−7.25	+0.34		
3	m1	−17.80	0.43	−14.60	−3.36	−0.27	
	m2	−17.54	0.44	−15.08	−2.91	0.01	
	m6	−13.81	0.34	−13.07	−1.14	0.06	
4	m1	−28.01	1.03	−21.90	−6.65	−0.51	0.01
	m2	−27.47	1.03	−22.00	−6.14	−0.38	0.03
	m3	−27.35	1.05	−21.94	−6.14	−0.36	0.03
	m8	−25.01	0.72	−21.81	−3.88	−0.03	0.00
	m9	−25.14	0.68	−19.56	−5.57	−0.65	−0.04

All energies (kcal/mol) are BSSE-corrected and obtained with the aug-cc-pVDZ set.

of BSSE changes the relative order of only two of the higher lying isomers in AW_4 (m8 and m9), a fact that does not affect any of the conclusions of our study.

The results for the different size cluster minima are as follows:

AW_2: we have located four minima that all lie within 5 kcal/mol in energy. The lowest two are shown in Fig. 1. In the global minimum (m1) the four heavy atoms lie practically on a plane (dihedral angle is 1.61°), while a low-lying local minimum (m2) has C_s symmetry. The other two higher lying local minima are configurations with two non-interacting water molecules either as both acceptors from the C–H bond or as both donors to the triple bond. These are higher in energy since the hydrogen bonding network in these structures is not fully connected (the water molecules are on either side of acetylene) and therefore there is a smaller number of hydrogen bonds than in the lowest lying (m1) and (m2) minima. The interaction energies ΔE_e, ΔE_e(fCP) and ΔE_0(fCP) are −12.02, −9.60, −5.76 kcal/mol for (m1) and −8.92, −6.88 and −3.71 kcal/mol for (m2) at the MP2/aug-cc-pVDZ level, respectively. The corresponding results with the aug-cc-pVTZ set are ca. 0.4–0.6 kcal/mol less. The energy difference between (m1) and (m2) can be equally attributed to differences in the 2- (1.35 kcal/mol) and 3-body (1.52 kcal/mol) terms (cf. Table 2). As regards the components of the 2-body term, the water–water interaction in both isomers is practically identical and lies within <0.1 kcal/mol from the corresponding value of −4.43 kcal/mol in the water dimer at this level of theory (MP2/aug-cc-pVDZ, BSSE-corrected) [27]. Therefore the difference in the 2-body term is mainly due to the sum of the two acetylene–water interactions, which is different in the two networks (−4.27 kcal/mol for (m1) vs. −2.86 kcal/mol for (m2)). The difference in the 3-body term (cf. Table 2) arises from the fact that the homodromic [2] (m1) network has a larger cooperative (3-body) term (−1.18 kcal/mol) than the (m2) structure (+0.34 kcal/mol) in accordance with previous results for water cluster networks similar to the ones encountered here [32].

AW$_3$: Out of the 10 investigated minima, Fig. 1 shows the global (m1) and the local (m2) and (m6) minima. The global (m1) minimum resembles a homodromic network formed by the participation of the C–H bond. The (m2) local minimum is a cyclic water trimer interacting with acetylene. The next three minima (m3)–(m5) are different conformers of these two main arrangements. The (m6) local minimum has C_s symmetry resembling an 'open' water trimer [33] interacting with acetylene. The interaction energies of (m1) and (m2) differ by less than 0.5 kcal/mol (cf. Table 1). The total 2-body term for (m2) is larger than that of (m1), but the homodromic (m1) network exhibits the largest cooperative (3- and 4-body) effect. The difference of 0.75 kcal/mol in the sum of the total 3- and 4-body energies between the two minima is crucial in stabilizing (m1) with respect to (m2) although the latter has a total 2-body energy that is larger by 0.5 kcal/mol with respect to the former (the deformation energies being equal). As regards (m6), it was found that it has the largest (95%) contribution from the 2-body interaction among the three networks.

Our results are in contrast with the ones by van Voorhis and Dykstra [15] using the MMC approach which reported a global minimum resembling (m2) with $\Delta E = -22.32$ kcal/mol ($\Delta E_0 = -15.12$ kcal/mol), and concluded that acetylene cannot participate in a four-member ring. Our results suggest quite the contrary, namely that the global minimum (m1) of AW$_3$ is a four-member ring cyclic structure formed by the insertion of the acetylene C–H bond into the water homodromic network. The discrepancy probably lies in the poor description of the magnitude of non-additive terms (which are crucial in stabilizing the (m1) minimum) with the MMC approach.

AW$_4$: Out of 30 minima found for the AW$_4$ cluster, the main families of minima denoted as global (m1) and local (m2), (m3), (m6), (m8), and (m9) are shown in Fig. 1. In the (m1), (m2), (m3), and (m6) minima a cyclic quasi-planar water tetramer interacting with A is formed; in the (m1) and (m6) two adjacent water molecules, and in (m2) and (m3) two 'diagonal' water molecules interact with A through two van der Waals 'bonds'. The water arrangement in isomers (m1) and (m6) resembles, in essence, the global (S_4) and low-lying (C_i) water tetramer (W_4) ring minima [4]. These are, however, distorted from the corresponding S_4 and C_i symmetries due to the interaction with A. The (m8) minimum can be considered as a perturbed 'cage' water tetramer and (m9) is a homodromic network like a cyclic pentamer in which A participates via the C–H bond. The first seven minima, (m1)–(m7), lie within ~1 kcal/mol, while all 30 minima span an energy range of about 14 kcal/mol. The network of the (m1) global minimum

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[2] From the Greek word 'ομοδρομος' meaning 'going the same way'. This term is used to denote a specific class of networks in which the heavy atoms form a quasi-planar ring and the H atoms participating in the hydrogen bond are arranged along the same direction (i.e. clockwise) around the ring.

of the AW_4 cluster (water tetramer bound to A) is qualitatively different from the one found for the AW_3 cluster (homodromic cyclic network that incorporates A).

The many-body analysis of Table 2 suggests the reason behind the stabilization of (m1) with respect to (m9) is the formation of a smaller ring of water in the former when compared to the latter that consequently enhances the individual and 2- and 3-body water interactions. The energy difference between these two minima can be accounted for from the differences in the sums of the total 2- and 3-body interactions. This is consistent with the trend previously observed for the water hexamer ring and cage isomers [32] and it has its origin in the fact that the individual 2-body (mostly the diagonal) terms weaken as the ring gets larger. For all these networks we note the predominance of the 2- and 3-body interactions. For the global minimum (m1) the components of the many-energy terms due to water only, dominate as the 2-, 3-, and 4-body W_n interactions. The sum of the four water-only (W-W-W) 3-body terms (21.8%) practically comprises the total of all 3-body terms (23.7% of total interaction energy), suggesting that there is little contribution from the (A-W-W) terms to the total 3-body energy of the cluster.

3.2. Vibrational spectra

As noted earlier, experimental IR spectra have been currently measured only for the $n = 1$ (AW) cluster. The harmonic vibrational spectra of the global minima (m1) of the AW_n, $n = 1$–4 clusters, obtained at the MP2/aug-cc-pVDZ level of theory, are shown in Fig. 2.

For $n = 1$ the most intense band at 3390 cm^{-1} corresponds to the antisymmetric C–H vibration (denoted by '$*$' in Fig. 2). This band is red-shifted by 27 cm^{-1} in the $n = 2$ cluster. The most intense band in the $n = 2$ cluster is the water dimer donor hydrogen bonded OH stretch (denoted by '+' in Fig. 2) at 3647 cm^{-1}, red-shifted by 56 cm^{-1} from the corresponding band in the gas phase water dimer. The rest of the water OH stretching bands, such as the dimer acceptor symmetric band at 3734 cm^{-1} and the two anti-symmetric ones at 3891 cm^{-1} (dimer acceptor) and 3899 cm^{-1} (dimer donor), gain intensity through their interaction with A.

For $n = 3$ the C–H antisymmetric vibration at 3297 cm^{-1} is now red-shifted by 93 cm^{-1} with respect to the one in the $n = 1$ cluster. The two intense bands at 3532 and 3581 cm^{-1} correspond to the in-phase and out-of-phase motions of the hydrogen bonded atoms H_{2a} and H_{2b} in structure AW_3_m1 of Fig. 1. The band at 3694 cm^{-1} is

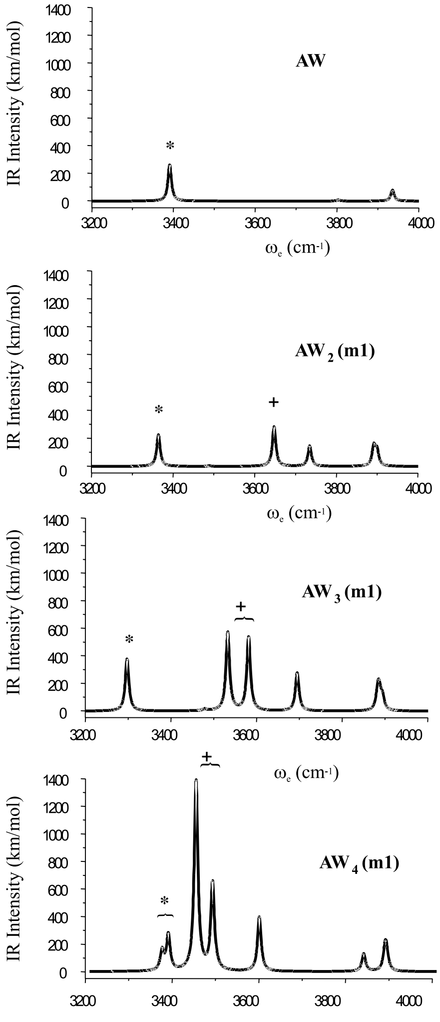

Fig. 2. Calculated harmonic IR spectra for the global minima of the AW_n clusters ($n = 1$–4) at the MP2/aug-cc-pVDZ level of theory. The CH vibrations are denoted by '$*$' whereas the ones for the hydrogen bonded OH stretches by '+'.

mostly the vibration of the OH stretch of the water that is donating a hydrogen atom to the triple bond of A (atom H_{2c} in structure AW_3_m1 of Fig. 1). Finally the antisymmetric OH stretches of the three water molecules are at 3883, 3886 and 3894 cm^{-1}, respectively. The appearance of several IR active bands at 3446 and 3483 cm^{-1} in the OH stretching region for $n = 4$ (as opposed to a single band at 3486 cm^{-1} for the ring tetramer of S_4 symmetry) is a consequence of the symmetry breaking of the water tetramer ring moiety due to its interaction with A. The fact that the red shift of the OH stretches increases with cluster size for $n = 2$–4, eventually results in their coupling with the C–H stretch for $n = 4$. The spectroscopic signature of this effect is a doublet at 3367 and 3381 cm^{-1} for $n = 4$. These vibrations are almost in the same position as for the $n = 2$ cluster, reversing their monotonic progression towards lower frequencies with respect to the AW dimer, viz. 27 cm^{-1} ($n = 2$), 93 cm^{-1} ($n = 3$) and 23 cm^{-1} ($n = 4$). In contrast, the vibrations of the hydrogen bonded OH stretches (denoted by '+' in Fig. 2) are progressively red-shifted with increasing cluster size. The calculated harmonic spectra are certainly not expected to predict the absolute position of the various bands, however their *shifts* relative to the isolated fragments as well as their progression with cluster size can serve as useful guides in searching for the IR active bands of the various cluster experimentally. This approach has been successfully followed before for hydrogen bonded clusters [31,34]. For a quantitative prediction of the anharmonicity of these bands and a direct comparison with the experimentally measured spectra, large portions of the PESs of the clusters need to be sampled and approaches like vibrational SCF and its extensions need to be employed [35]. However, the size of the clusters that are examined in this study is currently prohibitive in using these methods in order to estimate accurate anharmonic corrections.

4. Conclusions

We have studied the microhydration mechanism of acetylene from first principles. Although initially ($n = 2, 3$) the formation of cyclic homodromic rings that incorporate the C–H bond of A in the network prevails, eventually ($n = 4$) the formation of complexes of small cyclic clusters interacting with A is energetically more favorable. This is in contrast to the results of previous studies performed with more approximate methods that concluded that acetylene does not participate in a four-member ring with three water molecules. The disagreement is most likely attributed to the inadequate description of the magnitude of the non-additive components of the interaction energies with the previous methods. The structural transition from homodromic to van der Waals structures is associated with a qualitative change in the appearance of the IR spectra. These spectral features and qualitative changes in the IR spectra with cluster size present a guide for the experimental probe of the different structural networks found in the global minima of the acetylene–water clusters AW_n and in particular the structural transition between different hydrogen bonding networks found from $n = 3$ to 4.

Acknowledgements

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