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Water Docking Bias in [4]Helicene

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Abstract

We report on the one- and two-water clusters of [4]helicene, the smallest polycyclic aromatic hydrocarbon with a helical sense, captured in the gas phase using high-resolution rotational spectroscopy. The structures of the complexes are unambiguously revealed using microwave spectra of isotopically-enriched species. In the one-water cluster, the apparent splitting pattern is consistent with a tunnelling motion that encompasses an exchange of strongly- and weakly-bonded water hydrogens. This motion is “locked” in the two-water cluster. The pertaining intermolecular contacts, symmetry, and aromaticity effects are unveiled for the micro-solvated chiral topologies. These observations entail the first glance at the structures and internal dynamics of water binding-motifs comprising a chiral polycyclic aromatic hydrocarbon.

The interstellar medium's carbon resources are thought to be loaded with a plethora of polycyclic aromatic hydrocarbons (PAHs), given the prominent and abundant mid-IR emission bands attributed to them.[1, 2] Among dense clouds, however, and because of suppressed IR emission, these carbon-based aromatic molecules are believed to also exist as part of cold grains, forming interstellar ices. Cosmic water ices containing PAHs rise thus as likely catalytic sites for chemical reactions driven by ultraviolet radiation. These complex molecular systems have started to be explored over the last decade by employing advanced laboratory astrophysics experiments aiming to reveal the photochemistry of PAH-containing ices.[3, 4]

Prototypical clusters of small PAHs with a few water molecules provide simplified models to determine the initial steps of ice grain formation and infer chemical reactivity from the local environment.[3–5] Studies performed on non-centrosymmetric substrates are, however, yet poorly explored. Chiral PAHs such as helicenes are good model systems to investigate the initial steps of ice grain evolution taking place in a medium intrinsically lacking a center of symmetry. These scenarios are rich probes for symmetry-breaking events leading to handedness biasing in space and homochirality.[6] In addition, given the proposed relationship between adiabatic ionisation potentials of PAH oligomers and aromaticity[7], helicenes and their aromatically-twisted topologies emerge as good case studies within an astrochemical framework.

Here we report on the structure, steric effects and internal dynamics of water aggregated with a chiral aromatic substrate, mimicked here as [4]helicene, the smallest PAH with a helical sense.[8] By combining chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy[9] and the cold conditions of a supersonic jet, we obtained the rotational spectrum of [4]helicene complexed with one and two water molecules, capturing the first steps in the solvation of a chiral PAH. Rotational spectroscopy demonstrates here once again an undeniable ability to provide a definite assignment of complex molecular geometries.[10–18] Because of the direct correspondence between unique moments of inertia and molecular structure, geometries and cluster topologies can be differentiated from their rotational spectrum and directly compared with theoretical structure predictions. Furthermore, isotopic substitution allows to precisely solve the atomic make-up of a molecular complex from the local changes in the atomic mass of the cluster, resolving conformational ambiguities on the theoretical potential energy surface.

Lacking a sizeable permanent dipole moment, [4]helicene is by itself undetectable using microwave spectroscopy. However, the very first addition of one water molecule onto the surface of [4]helicene generates a permanent dipole moment. In Fig. 1 we show theoretical predictions for the three energetically more stable molecular complexes of [4]helicene with one water molecule. In all complexes, the permanent dipole moment is > 2 Debye. Unlike other observations of water aggregated with achiral PAHs of comparable size,[19] the asymmetry of the aromatic template generates distinct, inequivalent binding motifs. In the complexes [4]h-AB and [4]h-BC, the water engages on a dual aromatic embedding via two $\text{OH} \cdots \pi$ interactions with rings (A and B) and (B and C) of [4]helicene, respectively.

Figure 1: Molecular geometries of the [4]helicene-H₂O complex calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory using Gaussian09.[20] In the global minimum geometry, [4]h-CD, the water molecule docks onto the substrate via two OH $\cdots\pi$ interactions to rings C and D, and a secondary CH $\cdots$ O contact via the inner hydrogen of ring A. The species [4]h-AB and [4]h-BC (which are slightly higher in energy with +0.45 kJ/mol and +0.56 kJ/mol, respectively, considering zero-point corrected energies) are shown where water aggregation to the template occurs via two contacts to rings (A and B) and (B and C), respectively. Bond lengths between the water hydrogens and the relevant ring centroids are depicted.

In the [4]h-CD topology, the water molecule is anchored onto the [4]helicene via three contact points: two OH $\cdots\pi$ interactions to rings D and C, and one CH $\cdots$ O interaction where the inner hydrogen from ring A participates and locks the position of the water. The zero-point corrected energies of [4]h-AB and [4]h-BC are predicted to be only +0.45 kJ/mol and +0.56 kJ/mol higher in energy with respect to [4]h-CD. This is no longer the case if one considers the Gibbs energies: [4]h-AB is more stable than [4]h-CD by 0.82 kJ/mol. Similar differences in the predicted relative energies for the three complexes prevail using other levels of theory (see table S4 of the supporting information).

Two spectral portions of the microwave spectrum of [4]helicene with water (H₂¹⁶O:H₂¹⁸O, 1:1) are shown in Fig. 2. The experimental spectrum, shown as the upper trace (in black), has been recorded using the Hamburg COMPACT[21, 22] spectrometer. Experimental details are given in the supporting information. The coloured spectral lines represent a simulation obtained from the fitted spectroscopic parameters given in Table 1. Rotational transitions $J_{K_a K_c} \leftarrow J'_{K'_a K'_c}$ are denoted as J , K_a and K_c , with J being the rotational angular momentum quantum number and K_a and K_c being the projections of J onto the principal axes at the prolate and oblate symmetric top limits, respectively. Panels C and D show quartet progressions of [bccb] transitions for the [4]H:H₂¹⁸O and [4]H:H₂¹⁶O isotopologs, respectively. The observed splitting of each K -doublet into a quartet can be ascribed to the tunnelling motion encompassing interchange of water hydrogens (1) and (2) (Fig. 2). For further reading on water tunnelling dynamics the reader is referred to previous work and references therein.[23–26] A total of 609 rotational transitions were assigned for [4]H:H₂¹⁶O and [4]H:H₂¹⁸O isotopologs. The primary rotational constants (A, B, C) and quartic centrifugal distortion constants were determined through a recurrent fit using the

Figure 2: [4]helicene–H₂O topology: panel A and panel B show two views of an overlay between the calculated structure of the [4]h–CD complex (B3LYP-D3(BJ)/def2-TZVP) and the experimentally determined position of the water oxygen retrieved via the r_s method. The principal axis frame is shown with relative intensities of the dipole moment components to scale. Splitting of rotational transitions in the [4]H:H₂O complex: panels C and D show rotational patterns assigned to the [4]H:H₂¹⁸O and [4]H:H₂¹⁶O isotopologs, respectively. The split transitions arise from the tunnelling states of the water moiety, commonly represented as 0[−] and 0⁺. See main text for further information.

A-reduced semirigid rotor Hamiltonian as implemented in PGOPHER.[27] Rotational frequencies and quantum numbers of all assigned transitions are given in the supporting information.

In Table 1 we compare the experimentally obtained results with quantum chemistry calculations. The 0[−] and 0⁺ states for both isotopologs are unambiguously resolved despite the small difference in rotational constants. The splitting is on the order of a few tens of kHz. Moreover, the predicted rotational constants for the [4]h–CD complex are in very good agreement with the experimental parameters: dispersion corrected functionals seem to capture accurately the topology of the complex.[28] Calculations at other levels of theory, including the rotational constants for the other complexes, are given in the supporting information. A definitive position for the water oxygen atom within the principal axis frame is determined using the Kraitchman equations [29–31] including the rotational parameters for both isotopologs (r_s method). Again, the agreement with theoretical predictions is very good, as can be visually assessed in Fig. 2 (panels A and B). A comparison of experimental and predicted coordinates for the water oxygen is given in the supporting information. With a validated model for the global minimum geometry, 4[h]–CD, and in agreement with the zero-point energy predictions, we will now further analyse its structural details with a focus on the hierarchy of the steric and electronic intermolecular interactions at play.

Table 1: Rotational constants, dipole moments, and centrifugal distortion constants for [4]H:H₂O and [4]H:(H₂O)₂. The errors for the measured values are standard errors. N is the number of lines included in the fit, and σ is the standard deviation of the fit. Values between brackets were kept fixed during the fit. The experimental frequency accuracy is 25 kHz. ¹ [4]h-CD complex at the B3LYP-D3(BJ)/def2-TZVP level of theory. ² predicted/scaled constants for ([4]h-CD) [4]H:H₂¹⁸O using the CORSCL program.[32] ³ y=observed; n=not observed;

	[4]H:H ₂ ¹⁶ O			[4]H:H ₂ ¹⁸ O			[4]H:(H ₂ ¹⁶ O) ₂	
	0 ⁻	0 ⁺	theory ¹	0 ⁻	0 ⁺	theory ²	expt.	theory ¹
A/MHz	610.01581(13)	610.06705(30)	616.98	595.796279(80)	595.847894(99)	595.12	457.28296(26)	479.67
B/MHz	318.301928(94)	318.29312(15)	324.29	315.191437(62)	315.181188(93)	315.38	303.03780(13)	302.79
C/MHz	236.969422(79)	236.97448(12)	238.41	235.237870(44)	235.243434(48)	235.30	205.20434(12)	209.95
D _J /kHz	0.01552(43)	0.01542(71)	-	[0.01552(43)]	[0.01542(71)]	-	0.00669(24)	-
D _{JK} /kHz	0.0662(18)	0.0735(36)	-	[0.0662(18)]	[0.0735(36)]	-	0.0349(33)	-
D _K /kHz	0.0474(16)	0.0446(33)	-	[0.0474(16)]	[0.0446(33)]	-	0.0345(64)	-
d _J /kHz	0.00285(20)	0.00256(32)	-	[0.00285(20)]	[0.00256(32)]	-	-	-
d _K /kHz	-0.0295(31)	-0.0173(57)	-	[-0.0295(31)]	[-0.0173(57)]	-	-	-
μ_a /D	y ³	n	0.2	n	n	-	n	0.0
μ_b /D	y	y	1.8	y	y	-	y	1.4
μ_c /D	y	y	1.3	y	y	-	y	0.6
N	202	150	-	157	100	-	140	-
σ /kHz	5.1	6.6	-	6.3	5.3	-	6.5	-

To guide our interpretation of the intermolecular binding contacts, we performed a non-covalent interaction (NCI) analysis using NCIPLOT[33]. This methodology has been shown to assist in the interpretation of molecular assemblies and to quantify the type of intermolecular interactions present in a large variety of complex topologies.[34, 35] In Fig. 3 we show the results of the NCI study for the [4]h-CD complex. *Intramolecular* interactions are dominated by steric hindrance, located in the fjord region, i.e., the inner part of the helix, with a twist angle of 29° (angle between the planes defined by rings A and D). The *intermolecular* contacts arise primarily via two OH · π interactions with markedly different strengths, featuring a dual-aromatic embedding of the water hydrogen atoms onto the helicene substrate (relevant interaction points are depicted in Fig. 1 and Fig. 3). We note that, because of its relative orientation, the weaker OH · π contact (3.605 Å to ring C centroid) is prone to being initially disregarded as an intermolecular interaction and considered a free water hydrogen. The NCI analysis provides evidence otherwise, and an actual aromatic embedding is predicted between the water and both rings C and D (see Fig. 3).

Finally, an interaction is established via a CH··O bond between the water oxygen lone pair and the inner hydrogen of ring A. This interaction seems to tip the scale and provide that additional stability that results in the small preference for this topology rather than the [4]h-AB and [4]h-BC complexes. This intuitive explanation is consistent with the results from symmetry adapted perturbation theory (SAPT)[36] calculations, given in table S5 of the supporting information. We find that whilst in the [4]h-AB and [4]h-BC complexes electrostatic and dispersion contributions are similar, in the [4]h-CD cluster electrostatic energy has a noticeable dominance over dispersion. Furthermore, the existence of a secondary CH··O weak hydrogen bond hampers the large amplitude motion of the water molecule along its C₂ axis as observed in its almost free internal rotation on corannulene, the bowl-shaped PAH.[37] The asymmetry of the helical substrate thus results in a binding configuration where the water acts as

Figure 3: Non-covalent interaction analysis, HOMA and NICS(0) values for the [4]h-CD complex. The isovalue for the NCI plot is 0.5. The red dots at the center of each ring indicate strong repulsion forces. α is the angle between the planes defined by rings A and D. The NICS(0) values were calculated at the same level of theory (B3LYP/6-311++G**) for each ring centroid. The HOMA values were determined for each ring independently. Calculated bond lengths between the water hydrogens and the relevant ring centroids are depicted.

a hydrogen donor to rings C and D on the bottom-end of the helix, and as an acceptor to the top-end of the helix (ring A). Consequently, the symmetry of the system drops the C_2 point group to become C_1 upon hydration.

To tentatively quantify the water-induced effects on the aromaticity of [4]helicene we utilised the harmonic oscillator model of aromaticity (HOMA)[38]. This simple model delivers a normalised sum of squared deviations of bond lengths with respect to a fully aromatic system, such as benzene, and is defined as: $HOMA = 1 - \frac{257.7}{n} \sum_i^n (d_{opt} - d_i)^2$, where n is the number of C=C bonds, d_{opt} is the aromatic-optimised bond length and d_i is the predicted bond length (Å). In addition, we also compare the HOMA values with the nucleus-independent chemical shift (NICS)[39] values, that deliver the absolute magnetic shielding at the center of each ring. Relevant values are depicted in Fig. 3. Whilst the HOMA index provides rather inconclusive values, the NICS values suggest that the water molecule alters the aromaticity of the bound ring "D" with respect to its *antipodal* equivalent ring "A", resulting in electronic asymmetry along the helical plane. Moreover, a time-dependent DFT calculation on the [4]h-CD cluster anticipates a shift of the first electronic excitation by ~ 13 nm (0.22 eV) to the red, when compared with the unbound [4]helicene.

To ascertain if the biased docking observed in the one-water complex progresses over larger order clusters, we extended our spectral search to track rotational signatures of the two-water complex. Interestingly, all the remaining lines in our spectrum can in fact be assigned to a species heavier than

Figure 4: Overlay of calculated (B3LYP-D3(BJ)/def2-TZVP) and r_s structure for [4]H:(H₂O)₂. NCI analysis (isovalue 0.25), HOMA and NICS(0) values for the complex depicting additional OH $\cdots$ O interactions between water molecules. Similarly to [4]H:(H₂O), dual OH $\cdots$ π interactions with rings C and D are present. Steric hindrance at the fjord region is characterised by the angle α between the planes defined by rings A and D, $\sim 1^\circ$ smaller approaching planarity when compared with [4]H:(H₂O). The NICS(0) values were calculated at the same level of theory for each ring centroid. The HOMA values were determined for each ring independently. Bond lengths between the water hydrogens and the relevant ring centroids are depicted. Other relevant intermolecular contacts are also shown.

that of the one-water complex. In Table 1 we show the fitted and calculated rotational parameters for the complex of [4]helicene with the water dimer. The assignment is readily conclusive based on the quantum chemistry calculations. Nonetheless, using both singly-substituted ¹⁸O isotopologs (see the ESI) we were able to experimentally lock the positions of the water oxygens and further confirm our assignment of the observed molecular geometry of [4]H:(H₂O)₂. Remarkably, we find that the previous bias (docking to rings C and D) observed for the one-water cluster prevails for the two-water aggregate. In Fig. 4 we show the overlay of the experimental oxygen atom positions (r_s method) and the calculated geometry, as well as the NCI analysis for the cluster. The second water molecule acts as a bridge between the first water and the inner hydrogen of ring A, thereby maintaining the CD docking onto the aromatic substrate. The HOMA and NICS indices reflect again a break of symmetry in aromaticity along the helical plane and inspire further studies to build a model for ice grain evolution including more water molecules aggregated onto a chiral PAH substrate.

In summary, we uncovered the structure and prevailing intermolecular interactions, symmetry properties, aromaticity and tunnelling dynamics of the one- and two-water complexes with [4]helicene, the smallest chiral PAH. Using high resolution rotational spectroscopy of isotopically-enriched species we determined the structures of the complexes and studied its intermolecular contacts aided by theoretical methods. The observed splitting pattern in the rotational spectrum of the one-water complex is in line with an interchange of strong- and weakly-bonded water hydrogens to the aromatic substrate. Quantum chemistry computations and an NCI analysis paired with SAPT calculations provide us with a solid hierarchy of the intermolecular interactions at play for all observed species. These results lay the ground work for the pursue of higher-order clusters of water with chiral aromatic templates aiming at revealing the principles of asymmetrical ice grain evolution in an astrochemical framework.

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