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Far-IR and UV spectral signatures of controlled complexation and microhydration of the polycyclic aromatic hydrocarbon acenaphthene

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In this work we report on the experimental and theoretical investigations of the progressional complexation of the polycyclic aromatic hydrocarbon (PAH) acenaphthene (Ace) with itself and with water. In the interstellar medium, PAH complexes are an important link between molecular gas and solid state configurations of carbon, and in the form of grains they are postulated to serve as chemical catalysts. However, no direct detection of PAHs or their (microhydrated) complexes in interstellar space has been achieved as of yet. Therefore, we provide UV and far-infrared ion dip spectra of homogeneous PAH multimers and their hydrated clusters. The far-IR region of the IR spectrum is especially interesting since it contains the most spectral features that arise due to complexation or microhydration. We present microhydrated PAH complexes up to the third order, where we show that the water clusters are locked with little perturbation on the different PAH platforms. Density functional theory (DFT) calculations involving hydrogen bond interactions still seem challenging for predicting the far-IR frequency range, although applying anharmonic corrections lead to slight improvements.

1 Introduction

Weakly bound complexes of polycyclic aromatic hydrocarbons (PAHs) bridge the gap between molecular gas and solid-state dust configurations of carbon^{1,2}. In astrochemistry, PAH complexes are promising candidates as carriers of the unidentified infrared emission bands at wavelengths of 3–20 μm where they might explain the observed but not yet understood broad plateaus^{3–5}. Besides the infrared emission, the diffuse interstellar bands (DIBs) are also proposed to (partly) originate from PAHs. However, because of a lack of laboratory data, neither the infrared emission nor the DIBs origin has been confirmed.

Similar to the PAH complexes, heterogenous PAH-molecule complexes are believed to play an important role in the chemistry of the interstellar medium, in particular in cold molecular clouds⁵. Weakly bound complexes involving water molecules are especially interesting because of the ubiquity of

water in the universe. In addition, PAHs have been proposed to exist within interstellar ices, where they influence the structure of water and its reactivity^{6–8}. Besides the astrochemical interest, condensation of water molecules on aerosol particles is at the heart of cloud formation and, therefore, of importance in planetary atmospheres. Combustion based emission of carbonaceous particles, such as PAHs, may also contribute to atmospheric chemistry and the climate by forming complexes with water molecules^{9,10}. However, the molecular mechanisms of the formation of such PAH-water complexes are still not understood at the molecular level¹², but several experimental and theoretical studies are being undertaken to help elucidate this.

Gas phase high-resolution spectroscopy provides a direct connection between laboratory and astronomical or atmospheric studies^{11,12}. In combination with quantum chemical calculations, these experiments supply information on molecular structures and transition frequencies for example in Ref. 13 using far-IR and in Ref. 14 with microwave spectroscopy. For molecules of astronomical interest, the obtained transition frequencies can be used to elucidate astronomical IR spectra^{5,15} or support new searches for molecular species^{16–19}. Within high-resolution spectroscopy, the molecular beam technique is a well-established tool to produce the necessary isolated and cold molecular clusters in the gas phase with rovibrational temperatures typically of a few Kelvin^{20,21}, thereby simulating the astrophysical environment.

Some gas phase spectroscopic studies have been performed in the UV-VIS and mid-IR range for either benzene-water clusters or pure PAH clusters (e.g. in Ref. 22–27 for neutrals and

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Ref. 28,29 for cations) but so far, no far-IR studies of microhydrated PAHs have been performed to our knowledge. In addition, several quantum chemical simulations have been carried out on PAH clusters (e.g. in Ref. 30–34) that give insight into the preferred geometry of clusters of PAHs. Besides these, the most related work is a parallel study in the broadband microwave range that has been performed on the PAH studied in this paper: acenaphthene-water (Ace-W)¹⁴, which revealed the first steps of PAH-water complex formation. In that study, structures of the Ace-W_m (m=1–4) complexes were determined using isotopic substitution and in particular, the cyclic water trimer ((H₂O)₃) structure was observed for the first time, complexed to a molecule. Comparison with the structures of the free water clusters and SAPT calculations provided clear indications that the water clusters are loosely bound to the PAH surface. Internal water dynamics were observed in the water clusters, similar to the corannulene-water³⁵ complex previously studied. It will be interesting and most insightful to further explore these Ace-water complexes with IR spectroscopy^{36,37}. Especially of interest is the far-IR frequency range, where the clusters and other weakly bound complexes involving PAHs can directly contribute to the unidentified infrared emission bands. Moreover, the James Webb infrared space telescope will be equipped with far-IR detection capabilities, making far-IR laboratory studies timely. In the present work, we investigate the complexes of clustered-PAH acenaphthene (Ace) molecules and Ace-water complexes (Ace-W) using IR-UV ion dip spectroscopy to obtain spectroscopic signatures in the 100–1800 cm^{−1} region. This spectral region, that includes the far-IR, allows us to probe low energy vibrational modes³⁸. The far-IR region, besides being of astrochemical interest, helps to verify calculated structures and vibrational modes. Additionally, we will be able to investigate the extent of perturbation that complex formation or microhydration has on the vibrational frequencies of PAH monomers.

2 Methods

Experimental

The experiments were performed at the FELIX laboratory in the Netherlands where the IR spectra were measured via IR-UV ion dip spectroscopy using a pulsed supersonic jet expansion extensively discussed in Ref. 39. Acenaphthene (99%) was purchased from Sigma Aldrich and inserted into a molecular beam source consisting of a resistively heated sample compartment and a series 9 pulsed valve from General Valve. The source was operated at 85 °C and 20 Hz with water vapor enriched argon as carrier gas. A backing pressure of around 2.5 bar was used. The saturation of the molecular beam with water was prohibited by means of regulating the gas flow through an external water container and simultaneously monitoring the mass spectrum. The gas is expanded into vacuum, skimmed and delivered internally cold to the interaction region. In the interaction zone, the molecular beam interacted with a UV laser beam of about 1 mJ/pulse provided by a Nd:YAG-laser pumped UV dye laser (DCM in ethanol) tuned between 31100–32300 cm^{−1}.

¹. The molecular species were ionized via resonance-enhanced multi-photon ionization (REMPI)⁴⁰. Subsequently, the ions were mass-separated and detected with a time-of-flight mass spectrometer. In order to acquire an IR spectrum, the UV laser beam was tuned to an electronic transition of the molecular species of interest and preceded by the tunable IR laser beam provided by the free electron laser FELIX, performing IR-UV ion dip spectroscopy²⁰. The IR pulses delivered by FELIX are 8–10 μs long with energies ranging from 10–60 mJ and a bandwidth of about 1% of the energy. Whenever the IR laser was tuned to a vibrational transition, the population of the ground state was depleted resulting in a decreased ion signal. The IR beam was set alternating on and off to simultaneously obtain a background signal, directly correcting for fluctuations in the ion signal. In order to convert to absorbance, the logarithm of the on-off signal ratio was taken. A minimum of 90 averages per wavelength was recorded. An IR spectrum is obtained by scanning the IR laser with steps of about 1–1.5 cm^{−1} over the complete wavelength range (100–1800 cm^{−1}) and monitoring the ion signal. Every spectrum has been corrected for laser power and number of photons present in the laser beam.

Theoretical

Using the quantum chemical program package TURBOMOLE⁴¹, the Ace monomer and its complexes with other Ace molecules or water molecules have been optimized at the PBEh-3c⁴² and SCS-MP2⁴³(1.1;2/3)⁴⁴/def2-QZVP⁴⁵ levels of theory. The resolution-of-identity (RI) approximation for the Coulomb integrals was applied using matching default auxiliary basis sets⁴⁶. The quantum chemical calculations using the B3LYP functional with dispersion correction D3⁴⁷ and SVWN^{48,49}/DZ⁵⁰ are performed using the program package Gaussian09⁵¹. The conformation found for the Ace₂-W₁ in the joint parallel microwave study serves as starting point geometry for optimization of the Ace₂ structure. The Ace-W_m (m=1–3) conformations from the same study were used as starting point geometry for optimization of the Ace-W_m (m=1–3) complexes. Note that optimization may result in the (slight) modification of a molecular structure. From these optimized structures, IR frequencies were calculated. Calculated spectra of other (non-parallel) Ace₂ conformers overlap in the 100–1800 cm^{−1} infrared range. For Ace₃, both parallel and perpendicular geometries were used as a starting point geometry. The simulated infrared spectra are convoluted with a gaussian profile that matches approximately the FELIX bandwidth.

To go beyond scaling, individual anharmonic corrections for each normal mode were computed using vibrational perturbation theory (VPT)^{52,53} as implemented in Gaussian09⁵¹. The SVWN^{48,49} local density approximation (LDA) functional was used together with Dunning's double-zeta (DZ) basis set⁵⁰, downloaded from the EMSL basis set exchange database⁵⁴. The anharmonic correction was obtained by adding the difference between the anharmonic and the harmonic frequencies at the SVWN/DZ level of theory to the harmonic PBEh-3c result. The SVWN/DZ level has been used previously with good success for

Figure 1: Calibrated TOF mass spectra of (a) acenaphthene (Ace) complexes with water and (b) solely Ace. Microhydration of the PAH(-clusters) with up to 3 water molecules is readily achieved. Acenaphthene complexes up to the heptamer are detected. Trace (a) is recorded using a UV wavelength of 31250.0 cm^{-1} , trace (b) using 31474.1 cm^{-1} . The Ace monomer signal in trace (b) is saturated.

the anharmonic correction of computed rotational constants of medium sized organic molecules⁵⁵. For this purpose, the normal modes computed with the two methods were related to each other in a one-to-one fashion by evaluating the matrix of their overlaps, which was calculated after having oriented the molecules in the principal axis system. The latter was done with help of the molden visualisation software⁵⁶. The harmonic intensities were not modified.

3 Results and discussion

UV spectra of Ace and Ace-water complexes

The time-of-flight mass spectra of the $\text{Ace}_n\text{-W}_m$ ($n=1-4$, $m=1-4$) and Ace_n ($n=1-7$) clusters are presented in Fig. 1a and Fig. 1b respectively. Ace clusters up to the heptamer were detected. Clusters of the Ace monomer complexed with up to three water molecules were readily formed, together with a significant amount of higher order clusters. Following the identification of clusters in our beam by mass spectrometry, UV one color Resonance Enhanced Multi Photon Ionization (REMPI) spectra of the desired complexes were obtained (Fig. 2).

The Ace monomer origin was found to be at 31474.1 cm^{-1} , close to the previously reported value⁵⁷. Complexation of Ace with a second or third Ace monomer to form Ace_2 or Ace_3 results in a redshift of the origin to 31329.5 and 31289.0 cm^{-1} , respectively. Comparing the UV spectrum of Ace_2 in Fig. 2b with Ace in Fig. 2a reveals an increase in vibronic transitions for Ace_2 . The narrow linewidths in the Ace_2 spectrum indicate a molecular excitation^{58,59}; the two monomer units in Ace_2 have a slightly different electronic environment and therefore two slightly different UV spectra of the monomer units comprise the UV spectrum of Ace_2 . Astronomically the splitting of the bands is interesting in the framework of the DIBs, where clusters of PAHs have only been rarely considered as possible carriers⁶⁰. This spectrum in particular is interesting since it contains very

narrow bands, whereas dimers of other small PAHs show significantly more broadening^{24,61}. The broad features in the UV excitation spectrum of Ace_3 in Fig. 2c are typical for excitonic excitations⁵⁹ in oligomers, and distinct lines are not observed anymore. A similar red shift upon complexation has been observed previously in PAH clusters of anthracene and was also ascribed to an excitonic nature of the excited state²⁴.

With respect to the observed line splitting and broadening upon complexation we speculate that some variations in the line positions or linewidths of the DIBs could be due to the formation of clusters. However, it must be noted that the broadening of the spectral features can also be a result of less efficient cooling of the larger clusters. Dissociation of higher order clusters that end up in the smaller sized cluster mass detection channels and thereby introduce dynamics may also contribute in broadening.

Similarly, as for the higher order Ace_n complexes, broader absorption features are observed in the UV REMPI spectra of the Ace-W_m ($m=1-4$) complexes (Fig. 2e-h). However, in contrast to the Ace_n complexes, higher order Ace-W_n ($n>2$) clusters exhibit a blue shift of the electronic origin. The three main features in the Ace spectrum (overlaid in grey in Fig. 2e-h) are still recognizable in the Ace-W_n complexes unlike in the Ace_n spectra in Fig. 2a-d where the UV spectra change drastically upon complex formation.

Infrared spectra of pure Ace complexes

Following the determination of the resonant two photon ionization wavelengths, IR action spectra in the 100-1800 cm^{-1} range were obtained for the Ace_n ($n=1-3$) complexes and are displayed in Fig. 3a-c. The various UV frequencies used in the IR-UV ion dip experiments are listed in Table SI.1. Multiple UV frequencies were selected in order to determine if different conformers possibly existed in the molecular beam. They would be expected to have a different IR spectrum. However, this was not the case for any of the clusters, and the spectra were assigned to single conformations. In addition, IR-UV hole burning experiments, where the IR laser was fixed on a unique transition, also did not indicate the presence of more than one conformer.

By selecting the UV probe wavelengths carefully, we managed to minimize infrared ion gain effects⁶² in the spectra of Ace and Ace_2 , see Fig. SI.1. Infrared ion gain can be a result of intramolecular vibrational energy redistribution that causes a broadening and redshift in the UV absorption (as shown in Ref. 62), or it occurs due to an increase of UV dissociation of higher order clusters after IR absorption. As the gain signals distort the IR spectra and possibly mask or disturb weaker IR absorption peaks, they are undesired. The Ace_3 spectrum (Fig. 3c) shows some gain features at 251 cm^{-1} where it indeed prevented us from acquiring a 'clean' IR absorption spectrum via the intended IR-UV ion dip scheme.

Depicted in blue in Fig. 3a-c are theoretically calculated spectra (DFT), performed using the PBEh-3c level of theory. The corresponding optimized molecular structures are shown on the right hand side in Fig. 3a-c. The stacked structure found for

Figure 2: 1+1 REMPI spectra of (a-d) Ace_n ($n=1-4$) complexes and (e-h) Ace-W_m ($m=1-4$) complexes. The origin of Ace is found to be at 31474 cm^{-1} . The Ace spectrum (a) is added in gray in the (e-h) Ace-W_m ($m=1-4$) spectra for comparison.

the $\text{Ace}_2\text{-W}_1$ in the joint parallel microwave study is used as a starting point for Ace_2 . The stacked Ace_3 conformation led to an optimized geometry with lower energy than structures containing perpendicular (T-shaped) Ace molecules. This result matches previous computational studies which found that for relatively small PAH complexes the stacked configuration is most stable³⁰.

The PBEh-3c calculations and the experimental spectra are in good agreement with respect to peak positions: a standard deviation of 6.2, 4.9 and 4.6 cm^{-1} is determined for Ace, Ace_2 and Ace_3 , respectively. The good agreement allows for the assignment of the measured peaks in the spectra even in the far-IR, where generally more elaborate computational techniques have to be applied¹³. Solely global normal modes are found below 700 cm^{-1} , including the bending, stretching and folding modes of the carbon rings. The more local C-C and C-H vibrations are present above 1000 cm^{-1} . The relatively stronger lines at 780 and 1602 cm^{-1} correspond to the CH and CH_2 out of plane motion and the concerted C-C stretch vibration, respectively. It must, however, be noted that the transition observed in all Ace_n complexes at 1759 cm^{-1} is absent in the calculations. We believe that this transition is a combination mode similar to the transitions in PAHs above 1700 cm^{-1} as calculated in Ref. 63.

At first sight, the IR signatures of the monomer do not change upon complexation. In other words, the addition of another Ace molecule does not alter most IR vibrations of the Ace it complexed to. It appears that the stacking interaction does not shift many of the normal modes in the mid-IR range. Most spectroscopic features of complexation seem to manifest themselves in the spectrum below about 300 cm^{-1} , in the far-IR region. The global bending mode is observed at 214 and 231 cm^{-1} respectively for Ace and Ace_2 . This normal mode is concerted for Ace_2 and it results in a single peak. However, the same bending mode in Ace_3 is split into at least two frequencies, both of which were observed experimentally as predicted in our calculations. The mode is now decoupled due to the increased size of the complex. We speculate that in the astronomically observed infrared emission bands, in the limit of larger complexes, the slightly shifted decoupled global bending modes cumulatively result in a broad feature in the far-IR before significant broadening will be observed in the higher infrared region^{26,64}. A second spectroscopic feature of PAH clustering is observed in the region just below 1300 cm^{-1} . Upon complexation a band appears at 1294 cm^{-1} , which is not present in the theoretical spectrum. The appearance of this peak is in agreement with a previous investigation of astronomical spectral maps using singular value decomposition, which resulted in the assignment of an IR peak at this frequency to

Figure 3: (a-c) Mid- to far-infrared gas phase action spectra of jet cooled Ace_n ($n=1-3$) complexes in black. Displayed in blue are the corresponding calculated spectra on the PBEh-3c level of theory (uncorrected, but scaled with 0.95). The corresponding calculated structures of Ace_n ($n=1-3$) complexes on the PBEh-3c level of theory are displayed on the right.

very small grains (VSGs)³⁴. Our finding is additional evidence for their proposal that the VSGs might be composed of PAHs. At last, the relative intensity of the transitions at 780, 1363 and 1602 cm^{-1} seems to change significantly. The transition at 780 cm^{-1} grows in relative intensity upon further PAH complexation.

Infrared spectra of Ace water complexes

Adding a controlled amount of water vapor to the backing gas allowed us to complex the Ace_n ($n=1-3$) complexes with one or more water molecules, see Fig. 1. The experimental IR spectra of the Ace-W_m ($m=1-3$) complexes are presented in Fig. 4a-c (plotted in black) along with theoretical spectra at various levels of theory in color. The experimental IR spectra show multiple isolated peaks together with some broad bands. The broad IR signatures might indicate the presence of dynamic hydrogen bond interactions. This could be expected since in the microwave study¹⁴, internal dynamics and tunneling were also observed for the Ace-W_1 complex. The assigned structures that were found in our microwave study in Ref. 14 have been used as starting point geometries for the calculations presented here. In both experiments, the molecular beam technique was used to measure the microwave spectra or the infrared spectra (although it must be mentioned that argon was used as carrier gas in this study instead of neon). The structures that were optimized at the PBEh-3c level of theory are presented on the right side in Fig. 4. Since the structures of the Ace-water complexes were experimentally determined in the microwave study, we can use these Ace-W_m ($m=1-3$) clusters to evaluate the preciseness of our computational methods to describe IR signatures and present intermolecular interactions, which are extremely hard to predict⁶⁵. Note that the optimization of the clusters has led to modification of the molecular structure. The

$(\text{H}_2\text{O})_2$ in the Ace-W_2 complex is moved with respect to the Ace platform and the orientation of the hydrogen atoms of $(\text{H}_2\text{O})_3$ in the Ace-W_3 complex is more towards the Ace platform after optimization. As described in the methods section, the PBEh-3c calculations are corrected for anharmonicity and most emphasis will be on the performance of this method. However, the widely used B3LYP and SCS-MP2 as well as the uncorrected PBEh-3c infrared spectra are also shown for comparison. The infrared range below 800 cm^{-1} is selected, since we expect to see most spectral changes here upon complexation with water molecules based on the DFT calculations.

PBEh-3c (with and without anharmonic correction). Both the experimental as well as the theoretical IR spectrum of the Ace-W_1 complex (Fig. 4a) show the most intense transition at 777 cm^{-1} . This peak and the smaller peaks on both sides of this strong transition are assigned to the CH and CH_2 out of plane motion, and are well represented by the PBEh-3c calculations. The anharmonic correction induces a small red shift resulting in an improved agreement with the experimental signatures. The remaining transitions are observed deep into the far-IR and have significantly weaker intensities. The main difference between the uncorrected PBEh-3c and corrected calculations (green corrected and blue uncorrected trace, resp.) is the presence of an intense peak in the uncorrected calculation at 318 cm^{-1} . Moreover, a similar red shift in the far-IR region upon anharmonic correction using the SVWN/DZ level of theory is seen, which also improves the match with the experimental spectrum for the Ace-W_1 cluster in the far-IR significantly. This holds especially for the smaller transitions in the far-IR at around 157 and 218 cm^{-1} .

Figure 4: Experimental (black) infrared spectra of the (a) Ace-W₁ complex, the (b) Ace-W₂ complex and the (c) Ace-W₃ complex. The corrected (green) and uncorrected (blue) PBEh-3c/def2-mSVP calculated infrared spectra are added as well as the B3LYP-D3/6-311++G** (yellow) and SCS(1.1;2/3)-MP2/def2-QZVP (red) calculated spectra. Calculated structures of Ace-W_n (n=1-3) complexes corresponding to the predicted infrared spectra are displayed on the right. The molecular structures are based on the microwave spectroscopy determined structures¹⁴ and re-optimized on the PBEh-3c/def2-mSVP level of theory.

Similar shifts, mostly to the red, are observed between the harmonically and anharmonically calculated spectra for the Ace-W₂ and Ace-W₃ clusters (Fig. 4b-c), where the shifts upon anharmonic correction slightly improves the agreement. The anharmonically corrected PBEh-3c calculations and experimental infrared spectrum of the Ace-W₂ complex show good agreement for the largest experimental transitions at 1600 cm⁻¹ (see supplementary information Fig. SI.2b) and 779 cm⁻¹ originating from CH out of plane and CC stretch modes, respectively. However, the transitions observed in the far-

infrared, below 700 cm⁻¹, cannot be assigned based on either the PBEh-3c calculations nor the B3LYP and SCS (see below) calculations. Most remarkable is the fact that the intensities are predicted to be relatively high, however, we do not observe this in our experiments. The anharmonic corrections seem to be small, and in the region above 650 cm⁻¹ they lead to an improved agreement with the experimental spectrum.

The Ace-W₃ complex has more atoms and thus more degrees of freedom than the Ace-W₁ and Ace-W₂ complexes. This leads to more transitions in the far-IR (see Fig. 4c). As was

Figure 5: Far-infrared jet cooled gas phase action spectra of (a) Ace complexed with a water trimer Ace- W_3 , (b) Ace₂ complexed with a water trimer: Ace₂- W_3 and (c) Ace₂. Vertical red lines indicate vibrational bands originating from Ace₂. The green vertical lines mark vibrational bands involving (H₂O)₃ complexed to either Ace or Ace₂.

observed for the Ace- W_1 and Ace- W_2 complexes, the largest transition is found at 791 cm⁻¹ and originates from the CH wagging. The band at 552 cm⁻¹ is very broad, but at lower energies the line widths decrease. Therefore, the broadening is most probably due to dynamics of the Ace- W_3 complex. Since no good agreement can be found between any level of calculations and the experiment, no conclusive assignment based on the calculated infrared spectra has been made.

B3LYP-D3/6-311++G.** The B3LYP-D3 calculations (yellow trace in Fig. 4a-c) show a good agreement for the homogeneous Ace_n clusters (see supplementary information Fig. S.I.3). However, they perform poorly at predicting the vibrational frequencies of complexes involving water molecules; Ace_n- W_m . For the Ace- W_1 complex (Fig. 4a), the B3LYP-D3 has a poorer agreement than the PBEh-3c method in both peak positions as well as in intensities. On the contrary, for the Ace- W_2 complex (Fig. 4b), the B3LYP-D3 method results in an almost identical spectrum as the uncorrected PBEh-3c calculated spectrum. The only difference between the two is the appearance of a peak at 284 cm⁻¹ that was not predicted in the PBEh-3c calculations. This transition is associated with the water twisting mode. When comparing the B3LYP-D3 and PBEh-3c calculated spectra for the Ace- W_3 complex, all peaks are significantly red-shifted.

SCS(1.1;2/3)-MP2/def2-QZVP. The SCS-MP2 calculations (red spectra in Fig. 4a-c) predict for all measured Ace- W_m ($m=1-3$) complexes a large number of peaks in the region below 300 cm⁻¹. These are not observed experimentally nor predicted by the DFT methods and they are associated with modes involving both the water molecule(s) and the Ace molecule simultaneously. This is contrary to what the previously described DFT methods predict, where the modes of the water molecule(s) and the Ace molecule were mostly decoupled (see also discussion below).

PAH-water interactions

Fig. 5a-c compares the experimental Ace- W_3 , Ace₂- W_3 and Ace₂ spectra, respectively. This comparison will aid us to understand

the spectral signatures resulting from Ace, water and their interactions. It also helps elucidate the extent of the perturbation that the Ace molecules have on the structure of the water complexes. The vertical dotted lines are added to the spectra presented in Fig. 5 to highlight the similarities between different spectra; the green dotted lines correspond to transitions that originate from the pure water cluster signatures, while the red dotted lines correspond to modes from the Ace “platform”.

Following the red dotted lines from Ace₂ (Fig. 5c) to the Ace₂- W_3 (Fig. 5b) cluster, we can directly assign which IR signatures in the IR spectrum of the Ace₂- W_3 cluster originate from the Ace₂ platform. The peaks resulting from the Ace₂ platform appear in both spectra at similar or slightly shifted frequencies. The peak at 413 cm⁻¹ might either be blue-shifted or buried underneath the broad peak of the Ace_n- W_3 complex from 387 to 418 cm⁻¹. The peak at 785 cm⁻¹ in the Ace₂- W_3 spectrum is thought to be composed of the peaks at 791 and 779 cm⁻¹ from the Ace₂ and Ace- W_3 respectively and is therefore broader. By excluding the IR transitions of Ace₂ and by comparing the IR spectra of Ace- W_3 and Ace₂- W_3 , we are able to identify the IR signatures arising from the (W_3)-part of the Ace₂- W_3 cluster as indicated by the green lines in the Ace_n- W_3 spectra in the 100-700 cm⁻¹ region. We have also made the attempt to find a correlation between the Ace_n- W_3 spectra and the calculated spectra of the pure (H₂O)₃. However, large variations (of more than 25 %) in frequencies between the SCS-MP2 and PBEh-3c and other⁶⁵ levels of theory prohibit us to correlate the calculated W_3 to the experimental Ace_n- W_3 spectra. The present spectral analysis indicates that an additional Ace molecule does not affect the W_3 -infrared bands in our Ace_n- W_3 complexes. Even in the far-IR, where the weaker interactions in the structure are probed, the modes involving water are similar when either complexed to Ace or Ace₂. The perturbative effect of the Ace platform, be it Ace or Ace₂, seems therefore small leading to uncoupled vibrations in the water and Ace units. The non-directional dispersive force locking the water complexes to Ace is estimated to be insignificant compared to the hydrogen bonding interactions between the water molecules since the complexation of a second Ace molecule to the Ace- W_3 cluster does not perturb the modes originating from the W_3 (green dotted lines). The interaction seems to have a very limited perturbative effect even though this particular PAH contains two out of plane hydrogens, whereas most astronomically relevant PAHs are considered to possess only in-plane hydrogens. Regarding the small perturbative effect and with retrospect to the poor agreement with theory discussed in Fig. 4, we conclude that the hydrogen bonding in the W_3 is the main reason for the large discrepancy between theory and experiment in that region.

The finding that the PAH has a very limited perturbative effect on the water complexes is in agreement with the parallel study in the microwave range where it is shown that the O-O bond distance in the water complexes is only minimally distorted¹⁴. We confirm the non-perturbative effect of the PAH platform and elucidate on the implications on infrared spectroscopic signatures.

4 Conclusions

Infrared ion dip and UV excitation spectra of neutral acenaphthene, acenaphthene clusters, and microhydrated acenaphthene complexes are presented in this paper and discussed using various levels of theory. Homogenous clusters with up to seven monomer units of acenaphthene are detected and UV and IR absorption spectra are measured up to the trimer. It is shown where spectral changes upon complexation of PAHs manifest in the IR range, and it is discussed how complexation may be crucial to assign the diffuse interstellar bands (DIBs). UV and infrared spectra of microhydrated PAH complexes with up to three water molecules are presented. The far-infrared spectra of the $\text{Ace}_n\text{-W}_m$ ($n=1-3$, $m=1-3$) show distinct features originating either from the pure Ace-cluster or from the pure water-clusters, rather than strong shifts from PAH-water interactions. Hence, the water clusters seem to be locked with negligible perturbation to the PAH structures, which is in line with the findings in the parallel study in the broadband microwave range¹⁴. DFT calculations involving both dispersive interactions and hydrogen bonds are still challenging, though anharmonic corrections lead to slight improvements, especially in the CH out of plane bending and C-C stretch region.

Conflicts of interest

There are no conflicts to declare

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