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

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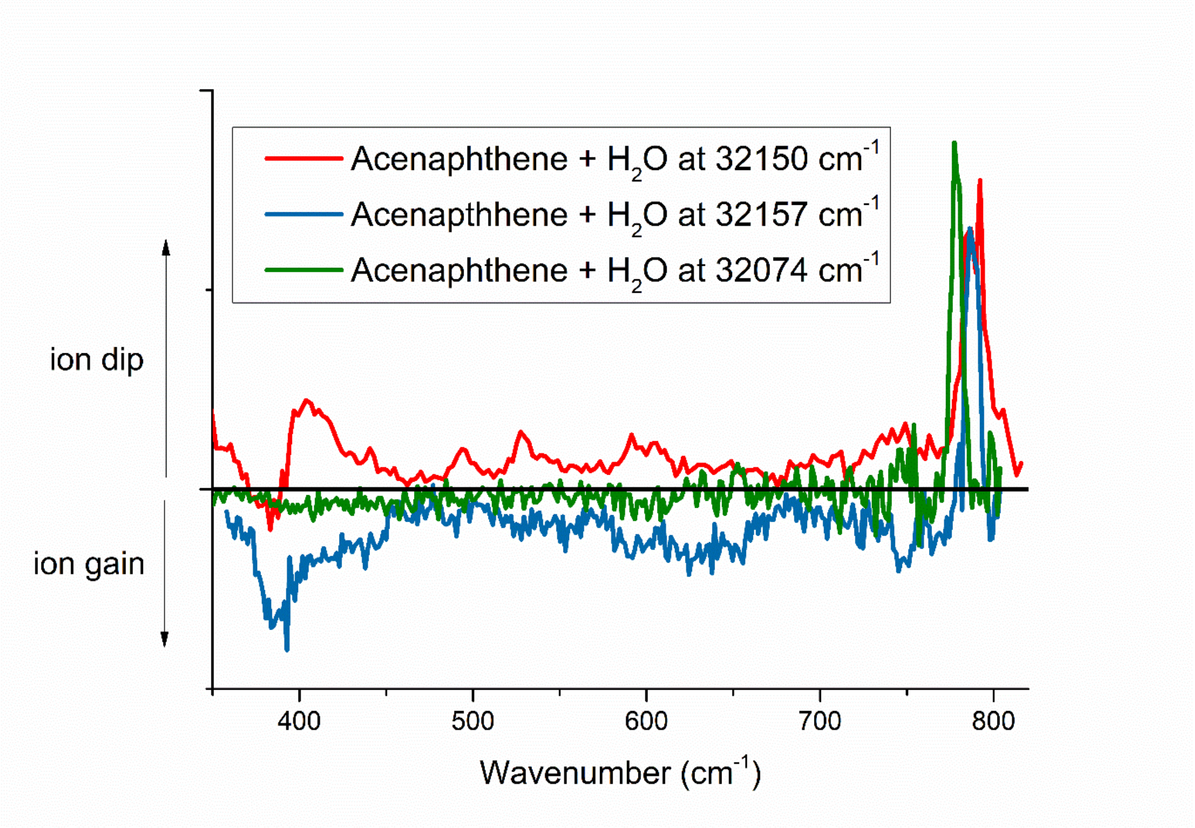

Figure S.I.1: Far-IR spectra recorded in the mass channel of Ace_1-W_1 *recorded using different UV wavelengths. The green trace is recorded at a UV wavelength where predominantly the* Ace_1-W_1 *complex is absorbing, thus recording a clean* Ace_1-W_1 *infrared spectrum. Keeping in mind that light can also have a perturbative effect on the complexes (dissociative) and if UV wavelengths are used where also* Ace_1-W_3 *is absorbing (blue/red), than IR absorption of higher order complexes can appear in the mass channel of the* Ace_1-W_1. In the case of the red trace, additional absorption peaks are observed due to ground state depletion of Ace_1-W_{1+x} *complexes by infrared absorption. The* Ace_1-W_{1+x} *is subsequently not fragmented under UV radiation in the* Ace_1-W_1 *channel anymore due to a change in FC overlap, leading to the additional absorption peaks. Infrared ion gain is observed (blue trace) as* Ace_1-W_{1+x} *complexes dissociate to* Ace_1-W_1 *complexes under infrared radiation and are still ionized using UV radiation thereby resulting in an increase of ions in the* Ace_1-W_1 *channel.*

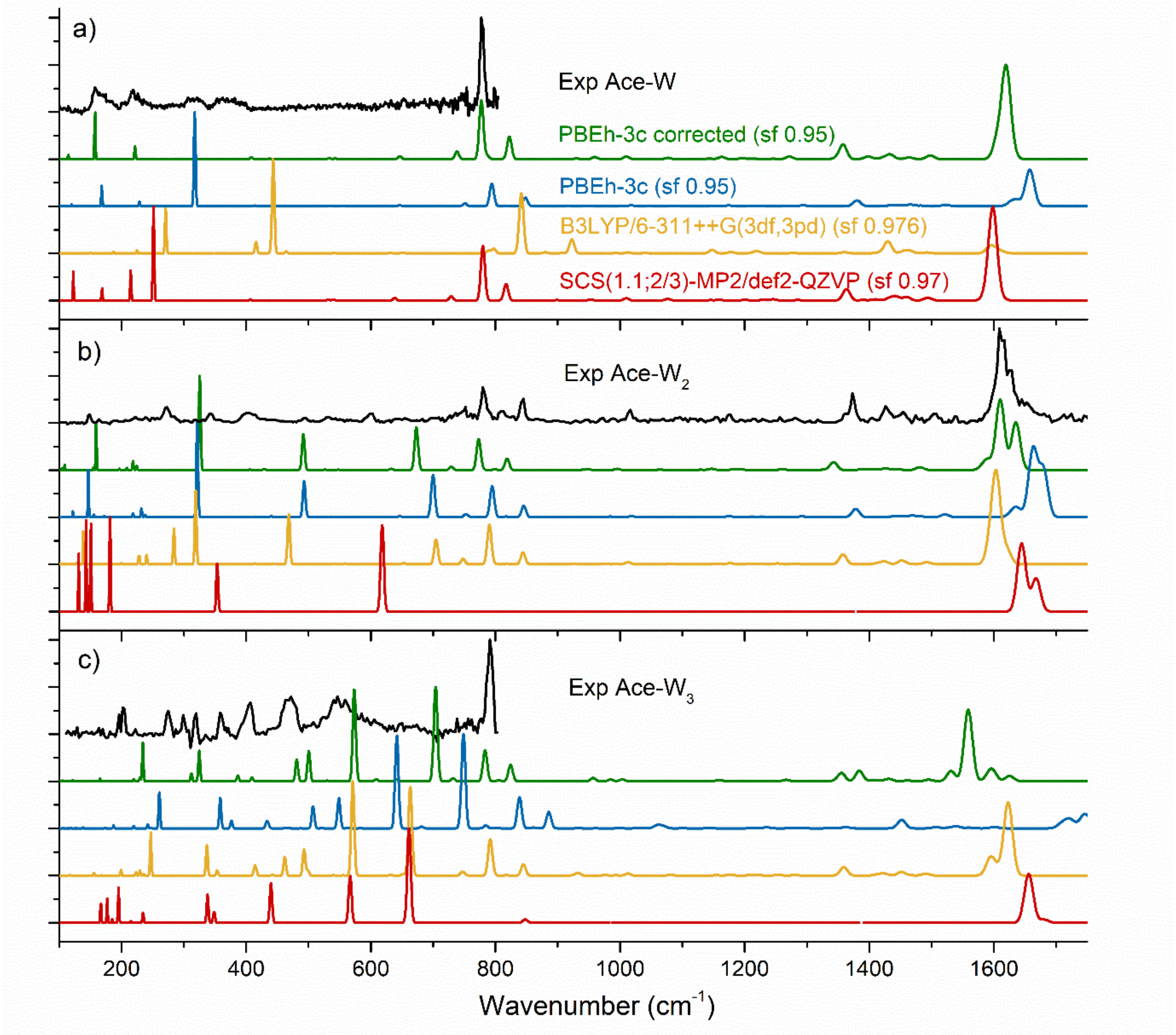

Figure S.I.2: Experimental (black) infrared spectra of the (a) Ace$_1$*-W*$_1$ *complex, the (b) Ace*$_1$*-W*$_2$ *complex and the (c) Ace*$_1$*-W*$_3$ *complex (bottom segment). The corrected (green) and uncorrected (blue) PBEh-3c/def2-mSVP calculated infrared spectra are added as well as the B3LYP-D3/6-311++G*** *(yellow) and SCS(1.1;2/3)-MP2/def2-QZVP (red) calculations. The figure is complementary to Fig. 5, where in this figure a larger infrared range is shown for the Ace*$_1$*-W*$_2$ *complex. The larger range shows the improvement by the anharmonic correction of the PBEh-3c functional for the peak at 1609 cm*$^{-1}$*.*

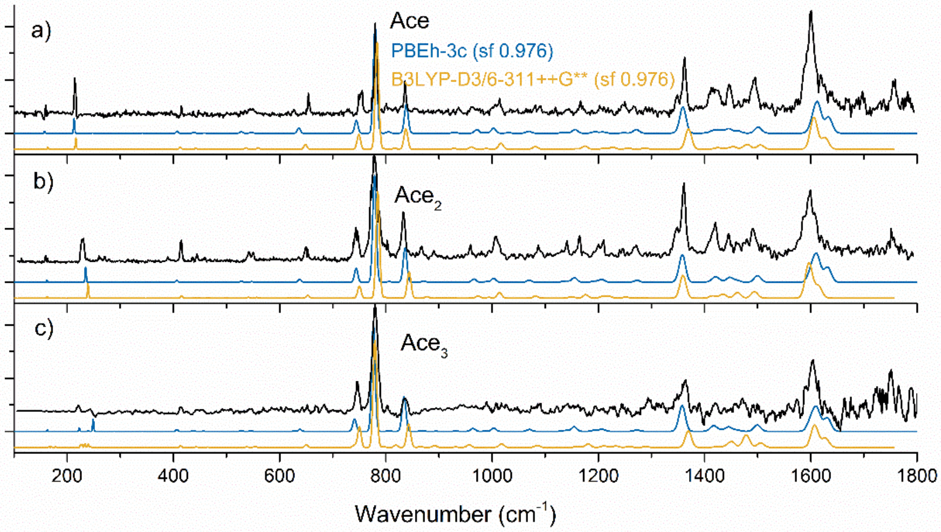

Figure S.I.3: Mid- to far-infrared gas phase action spectra of jet cooled Ace$_n$ *(n=1-3) complexes in black (segment a-c respectively). In blue the corresponding calculated spectra on the PBEh-3c/def2-mSVP level of theory (uncorrected). In this figure B3LYP-D3/6-311++G*** *calculations are added with respect to Fig. 3 to illustrate that a good agreement with theory is also achieved using the B3LYP functional for the homogeneous Ace complexes which is not the case for the Ace*$_1$*-W*$_m$ *(m=1-3) complexes.*

Table S.I.1: UV frequencies used in the IR-UV ion dip spectra reported throughout this paper.

Ace$_1$	31474 cm^{-1}
Ace$_2$	31374; 31637.5 and 31358 cm^{-1}
Ace$_3$	31374; 31637.5 and 31358 cm^{-1}
Ace$_1$-W$_1$	32074 cm^{-1}
Ace$_1$-W$_2$	31536 cm^{-1}
Ace$_1$-W$_3$	32157 and 32126 cm^{-1}
Ace$_2$-W$_3$	31367 cm^{-1}