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

Alexander K. Lemmensa,b, Sebastien Gruetc,d,e, Amanda L. Steber*c,d,e, Jens Antonyf, Stefan Grimmef, Melanie Schnellc,d,e and Anouk M. Rijsa

aRadboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands.
bVan ’t Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
cDeutsches Elektronen-Synchrotron, Notkestrasse 85, D-22607 Hamburg, Germany
dInstitut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Strasse 1, D-24118 Kiel, Germany
eThe Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, D-22761 Hamburg, Germany
fMulliken Center for Theoretical Chemistry, University of Bonn, Beringstr. 4, D-53115 Bonn, Germany

Corresponding Authors
*a.rijs@science.ru.nl, amanda.steber@desy.de

Table of contents

Figures

Fig S.I. 1 Undesired gain/depletion effects
Fig S.I. 2 Large range Ace1-W2 infrared spectrum
Fig S.I. 3 Ace_n compared to B3LYP-D3 calculations

Tables

Table S.I. 1 UV frequencies used in IR-UV ion dip experiments
Figures

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$_2$-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) Ace1-W1 complex, the (b) Ace1-W2 complex and the (c) Ace1-W3 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 Ace1-W2 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$_n$-W$_m$ (m=1-3) complexes.

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

<table>
<thead>
<tr>
<th></th>
<th>cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ace$_1$</td>
<td>31474</td>
</tr>
<tr>
<td>Ace$_2$</td>
<td>31374; 31637.5 and 31358</td>
</tr>
<tr>
<td>Ace$_3$</td>
<td>31374; 31637.5 and 31358</td>
</tr>
<tr>
<td>Ace$_1$-W$_1$</td>
<td>32074</td>
</tr>
<tr>
<td>Ace$_1$-W$_2$</td>
<td>31536</td>
</tr>
<tr>
<td>Ace$_1$-W$_3$</td>
<td>32157 and 32126</td>
</tr>
<tr>
<td>Ace$_2$-W$_3$</td>
<td>31367</td>
</tr>
</tbody>
</table>