ELECTRONIC SUPPORTING INFORMATION

Stepwise Microhydration of Aromatic Amide Cations:
Water Solvation Networks Revealed by Infrared Spectra of Acetanilide\(^+\)-(H\(_2\)O)\(_n\) Clusters (n ≤ 3)

Johanna Klyne,\(^a\) Matthias Schmies,\(^a\) Mitsuhiko Miyazaki,\(^a,b\) Masaaki Fujii,\(^b\) Otto Dopfer\(^a*\)

\(^a\) Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
\(^b\) Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan.

* Corresponding author: Fax: (+49) 30-31423018, E-Mail: dopfer@physik.tu-berlin.de

Table S1. Calculated and experimental proton donor stretch frequencies of the acidic NH group (\(\nu_{\text{NH}}\) in cm\(^{-1}\)) and corresponding frequency red shifts (\(\Delta \nu_{\text{XH}}\) in cm\(^{-1}\)) of H-bonded AA\(^+\)-L(NH) and FA\(^+\)-L(NH) clusters as well as proton affinities (PA, in kJ mol\(^{-1}\)) of the ligands (L=Ar, N\(_2\), H\(_2\)O, and (H\(_2\)O)\(_2\)).

<table>
<thead>
<tr>
<th>(A)</th>
<th>Monomer</th>
<th>(L = \text{He})</th>
<th>(L = \text{Ar})</th>
<th>(L = \text{N}_2)</th>
<th>(L = \text{H}_2\text{O})</th>
<th>(L = (\text{H}_2\text{O})_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>178</td>
<td>369</td>
<td>494</td>
<td>691</td>
<td>808</td>
<td></td>
</tr>
<tr>
<td>(\nu_{\text{NH}})</td>
<td>(\nu_{\text{NH}})</td>
<td>(\Delta \nu_{\text{XH}})</td>
<td>(\Delta \nu_{\text{XH}})</td>
<td>(\Delta \nu_{\text{XH}})</td>
<td>(\Delta \nu_{\text{XH}})</td>
<td>(\Delta \nu_{\text{XH}})</td>
</tr>
<tr>
<td>AA</td>
<td>3385</td>
<td>3385</td>
<td>0</td>
<td>-2</td>
<td>-12</td>
<td>-65</td>
</tr>
</tbody>
</table>
**Figure S1.** Structures of neutral c-/t-AA and most stable isomers of t-AA-H$_2$O calculated at the ωB97X-D/aug-cc-pVTZ level. Relevant structural, energetic, and vibrational parameters are listed in Table 2. Relative energies (E$_0$) and binding energies (D$_0$) are given in cm$^{-1}$, while intermolecular (red) and intramolecular N-H, C=O, and O-H (black) bond lengths are given in Å.

**Figure S2.** Structure of the t-AA$^+$-H$_2$O(NH)-Ar(π) isomer calculated at the ωB97X-D/aug-cc-pVTZ level. Relevant structural, energetic, and vibrational parameters are listed in Table 2. Binding energies (D$_0$) are given in cm$^{-1}$, while intermolecular (red) and intramolecular N-H, C=O, and O-H (black) bond lengths are given in Å.

**Figure S3.** IRPD spectra of AA$^+$-H$_2$O and AA$^+$-H$_2$O-Ar in the X-H stretch range compared to linear IR absorption spectra of t-AA$^+$-H$_2$O(NH)(-Ar(π)), t-AA$^+$-H$_2$O(CO), and c-AA$^+$-H$_2$O(NH)(-Ar(π)) calculated at the ωB97X-D/aug-cc-pVTZ level (Table 1). The dashed lines indicate the experimental frequencies of bare t-AA$^+$ (ν$_{NH}$=3385 cm$^{-1}$) and H$_2$O (ν$_{OH}$=3756/3657 cm$^{-1}$). All computed spectra are drawn to the same intensity scale but the intensities of the bound ν$_{NH}$ transition in the c-/t-AA$^+$-H$_2$O(NH) spectra are multiplied by 0.1.

**Figure S4.** REMPI-IR (IR dip) spectra of t-AA$^+$-H$_2$O(NH) and t-AA$^+$-H$_2$O(NH) generated by REMPI$^3$ compared to EI-IR (IRPD) spectra of AA$^+$-H$_2$O and AA$^+$-H$_2$O-Ar employing the EI ion source.

**Figure S5.** IRPD spectra of AA$^+$-H$_2$O-L with L=Ar and N$_2$ in the fingerprint range (loss of L) compared to linear IR absorption spectra of c-/t-AA$^+$-H$_2$O(NH)(-Ar(π)) and c-/t-AA$^+$ calculated at the ωB97X-D/aug-cc-pVTZ level. The positions, widths, and vibrational and isomer assignments of the transitions observed are listed in Table 1. For comparison, the IRPD spectrum of AA$^+$-Ar with the labeling of the transitions is reproduced from Ref. 59.

**Figure S6.** Comparison of the IRPD spectrum of cold cationic AA$^+$-H$_2$O-Ar and the IR dip spectrum measured for neutral t-AA-H$_2$O(NH) and t-AA-H$_2$O(NH) and their corresponding linear IR absorption spectra calculated at the ωB97X-D/aug-cc-pVTZ level.

**Figure S7.** Comparison of the IRPD spectra of AA$^+$-L$_n$ with L=He, Ar, N$_2$, and H$_2$O obtained in the X-H stretch range.

**Figure S8.** NBO charge distribution (in me) of t-AA$^+$ and c-AA$^+$ in the S$_0$ and D$_0$ state calculated at the ωB97X-D/aug-cc-pVTZ level.
FIGURE S1

t-AA

\[ E_0 = 0 \]

\[ D_0 = 1852 \]

t-AA-H\(_2\)O(CO)

\[ D_0 = 1364 \]

t-AA-H\(_2\)O(NH)

\[ D_0 = 1686 \]

t-AA-H\(_2\)O(CO-II)

\[ D_0 = 1752 \]
FIGURE S2
FIGURE S4

\[ AA^+ - H_2O(NH) \]

\[ AA^+ - H_2O(CO) \]

\[ AA^+ - H_2O \]

\[ AA^+ - H_2O-Ar \]

\[ Y_4 \]

\[ Y_3 \]

\[ Y_2 \]

\[ Y_1 \]

\[ Z_2 \]

\[ Z_1 \]

\[ X \]

\[ E \]

\[ B \]

\[ A \]

Wavenumber / cm\(^{-1}\)
FIGURE S5
FIGURE S6

$\text{t-} \text{AA-H}_2 \text{O(NH)}$

$\text{l}_{\text{IR}} \text{ / km mol}^{-1}$

$\text{l}_{\text{ION}} \text{ / a. u.}$

$\text{AA-H}_2 \text{O(NH)}$

$\text{t-} \text{AA-H}_2 \text{O(CO)}$

$\text{l}_{\text{IR}} \text{ / km mol}^{-1}$

$\text{l}_{\text{ION}} \text{ / a. u.}$

$\text{AA-H}_2 \text{O(CO)}$

$\text{t-} \text{AA}^+ \text{-H}_2 \text{O(NH)-Ar(}\pi\text{)}$

$\text{l}_{\text{IR}} \text{ / km mol}^{-1}$

$\text{l}_{\text{ION}} \text{ / a. u.}$

$\text{AA}^+ \text{-H}_2 \text{O-Ar}$

\text{wavenumber / cm}^{-1}
FIGURE S8

t-AA (S₀)
t-AA⁺ (D₀)

c-AA (S₀)
c-AA⁺ (D₀)