Microsolvation of the acetanilide cation (AA$^+$) in a nonpolar solvent: IR spectra of AA$^+$–L$_n$ clusters (L = He, Ar, N$_2$; n ≤ 10)$^\dagger$

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Infrared photodissociation (IRPD) spectra of mass-selected cluster ions of acetanilide (N-phenylacetamide), AA$^+$–L$_n$, with the ligands L = He (n = 1–2), Ar (n = 1–7), and N$_2$ (n = 1–10) are recorded in the hydride stretch (amide A, $\nu_{NH}$, $\nu_{C\equiv N}$) and fingerprint (amide I–III) ranges of AA$^+$ in its $^{2}\text{A}^\text{g}$ ground electronic state. Cold AA$^+$–L$_n$ clusters are generated in an electron impact ion source, which predominantly produces the most stable isomer of a given cluster ion. Systematic vibrational frequency shifts of the N–H stretch fundamentals ($\nu_{NH}$) provide detailed information about the sequential microsolvation process of AA$^+$ in a nonpolar (L = He and Ar) and quadrupolar (L = N$_2$) solvent. In the most stable AA$^+$–L$_n$ clusters, the first ligand forms a hydrogen bond (H-bond) with the N–H proton of AA$^+$, whereas further ligands bind weakly to the aromatic ring ($\pi$-stacking). There is no experimental evidence for complexes with the less stable cis-AA$^+$ isomer. Quantum chemical calculations at the M06-2X/aug-cc-pVTZ level confirm the cluster growth sequence derived from the IR spectra. The calculated binding energies of $D_e$(H) = 720 and 1227 cm$^{-1}$ for H-bonded and $D_e$(n) = 585 and 715 cm$^{-1}$ for $\pi$-bonded Ar and N$_2$ ligands in t-AA$^+$–L are consistent with the observed photofragmentation branching ratios of AA$^+$–L$_n$. Comparison between charged and neutral AA$^{+}$(–L)$_n$ dimers indicates that ionization switches the preferred ion–ligand binding motif from $\pi$-stacking to H-bonding. Electron removal from the HOMO of AA$^+$ delocalized over both the aromatic ring and the amide group significantly strengthens the C=O bond and weakens the N–H bond of the amide group.

1. Introduction

The intermolecular interaction of aromatic molecules with surrounding solvent molecules plays an important role in chemical and biological recognition.$^5$–$^7$ A molecular-level understanding of these phenomena requires the knowledge of the intermolecular potential energy surface describing the interaction between aromatic molecules and the solvating ligands. It is well established that the fruitful combination of spectroscopy and quantum chemical techniques applied to isolated and size-selected clusters provides direct access to this potential.$^3$–$^{11}$

In these A–L$_n$ clusters, the aromatic chromophore (A) can be solvated by a well-defined and adjustable number (n) of ligands (L). Here, we investigate the interaction of the acetanilide (AA, N-phenylacetamide, C$_8$H$_9$N, Fig. 1) cation with He, Ar, and N$_2$ ligands in the size range n ≤ 10 to probe the initial steps of the microsolvation process of this elementary ion in a nonpolar and quadrupolar solvent. Acetanilide is the simplest aromatic amide with a –NH–CO– peptide linkage, in this case connecting a phenyl with a methyl group. Hence, AA is frequently used as a model system to characterize the biophysically relevant interaction of aromatic peptides with their surrounding environment. In addition, AA and its derivatives, such as paracetamol or phenacetin, are important drug components in pharmaceutical applications.$^{12}$

The AA$^{+}$–L$_n$ complexes with L = He, Ar, and N$_2$ studied in the present work belong to the class of acidic aromatic molecules interacting with nonpolar ligands. Such aromatic molecules with acidic functional groups, here the N–H bond of the amide group, offer at least two competing principal ligand binding sites, namely hydrogen bonding to the acidic group (H-bond) and $\pi$-stacking to the aromatic ring ($\pi$-bond). In the
pheno\textsuperscript{(\(\pm\))}-Rg\textsubscript{n} clusters (Rg = Ar, Kr), this \(\pi \rightarrow H\) rearrangement reaction has recently been monitored in real time by picosecond time-resolved IR spectroscopy, providing for the first time experimental data for intermolecular solvent dynamics in isolated clusters.\textsuperscript{33,36–39} For AA\textsuperscript{(\(\pm\))}–L\textsubscript{0} clusters with L = Rg and N\textsubscript{2}, a similar \(\pi \rightarrow H\) switch in the preferred ligand binding site has been anticipated but the only available preliminary IR spectra for L = Ar with \(n \leq 2\) were not conclusive.\textsuperscript{40}

Acetanilide can occur in two different conformations (Fig. 1), namely the more stable trans isomer (t-\text{\textalpha}A, \textit{anti}) and the significantly less stable cis isomer (c-\text{\textalpha}A, \textit{syn}). Whereas nearly all previous studies report the detection of merely the t-\text{\textalpha}A isomer in both the condensed\textsuperscript{41,42} and the gas phase,\textsuperscript{43,44–46} the c-\text{\textalpha}A isomer has only recently been identified for the first time in the ground electronic state (S\textsubscript{0}) by rotational spectroscopy in a molecular beam.\textsuperscript{47} From the observed population ratio of \(\sim 15\), the difference in relative Gibbs energy between c-\text{\textalpha}A and t-\text{\textalpha}A could be estimated as \(\Delta G_{298} = 550\) cm\textsuperscript{−1}, in good agreement with available quantum chemical calculations.\textsuperscript{47} Microwave,\textsuperscript{43,47} IR,\textsuperscript{40,44} and electronic\textsuperscript{40,44–46} spectra reveal that isolated t-\text{\textalpha}A has a “planar” equilibrium structure with \(C_{\infty}\) symmetry with all heavy atoms of the phenyl ring and the methylated amide group lying in the molecular plane, in line with quantum chemical predictions.\textsuperscript{43,44,46,47} One of the H atoms of the CH\textsubscript{3} group faces the C=O bond in the molecular plane, although the three-fold barrier for internal methyl rotation is rather low in S\textsubscript{0} (\(V_{b} < 50\) cm\textsuperscript{−1}).\textsuperscript{13,46,47} The c-\text{\textalpha}A isomer is well separated from the t-\text{\textalpha}A isomer by a large barrier and has a nonplanar equilibrium configuration, \textit{i.e.}, the phenyl plane is twisted from the amide plane.\textsuperscript{47}

Early low-resolution photoelectron spectra\textsuperscript{48,49} demonstrate that the “\text{\textalpha}A” ground electronic state (D\textsubscript{0}) of the AA\textsuperscript{+} cation is generated by removal of one electron from the HOMO, which is the \(\pi\) HOMO of the aromatic ring strongly mixed with the \(\pi\) HOMO of the acetylamino group. The analysis of the charge distribution reveals that \(\sim 0.4\ e\) of the excess positive charge is localized on the methylated amide side chain,\textsuperscript{46} confirming the conclusion of substantial conjugation between the phenyl and amide \(\pi\) orbitals. High-resolution zero kinetic energy photoelectron (ZEKE) spectra of t-\text{\textalpha}A\textsuperscript{+} are consistent with a planar equilibrium structure with a high barrier for internal methyl rotation (\(V_{b} \sim 300\) cm\textsuperscript{−1}) and exhibit a few low-frequency Franck–Condon active vibrational modes (<1000 cm\textsuperscript{−1}).\textsuperscript{46} However, no spectroscopic information is available about the amide I–III and N–H stretch modes (amide A), which are sensitive to secondary structures in proteins. There is also essentially no spectroscopic and theoretical information available for the c-\text{\textalpha}A\textsuperscript{+} isomer.

Here, we report IR spectra and quantum chemical calculations of AA\textsuperscript{+}–L\textsubscript{0} clusters with L = He (\(n \leq 2\)), Ar (\(n \leq 7\)), and N\textsubscript{2} (\(n \leq 10\)) in the hydride stretch and fingerprint ranges. This cluster system was selected for the following reasons. Very limited spectroscopic information is available for AA\textsuperscript{+} and its clusters with nonpolar and polar ligands. The ZEKE spectra of the t-\text{\textalpha}A\textsuperscript{+}–Ar dimer obtained \textit{via} resonance-enhanced two-photon ionization (REMPI) were interpreted with a \(\pi\)-bonded
generated by REMPI exhibit in the N–H stretch range \((v_{\text{NH}})\) doublet absorptions near 3370 cm\(^{-1}\) but the geometry of the complexes could not be assigned and the origin of the splitting \((\sim 10 \text{ cm}^{-1})\) remained unclear.\(^{49}\) In the current study, AA\(^+\)–Ar\(_n\) clusters are generated in an electron ionization (EI) source, which generates predominantly the most stable isomer of a given cluster ion.\(^{5,13}\) Significantly, the IRPD spectrum of AA\(^+\)–Ar generated by EI demonstrates unambiguously that the H-bonded t-AA\(^+\)–Ar(H) dimer, in which Ar binds to the acidic N–H bond of the amide group, is in fact more stable than the t-AA\(^+\)–Ar(\(\pi\)) isomer previously identified by REMPI techniques.\(^{40,50}\) Moreover, the splitting in the N–H stretch range observed previously will be assigned to the \(v_{\text{NH}}\) fundamentals of the t-AA\(^+\)–Ar(H) and t-AA\(^+\)–Ar(\(\pi\)) isomers. So far, no information is available for AA\(^+\)–Ar\(_n\) with \(n \geq 3\) and AA\(^+\)–(\(N_2\))\(_n\) clusters. Thus, the presented IRPD spectra provide for the first time a reliable impression on the microsolvation process of AA\(^+\) in a nonpolar and quadrupolar solvent, in particular with respect to the comparison between various intermolecular binding motifs including H-bonding and \(\pi\)-stacking. Spectra are recorded in the hydride stretch (2800–3600 cm\(^{-1}\)) and fingerprint range (700–1900 cm\(^{-1}\)), covering the important amide A and I–III bands, which are sensitive to secondary protein structure. Comparison with the H-bonded t-AA\(^+\)–H\(_2\)O and t-AA\(^+\)–CH\(_3\)OH dimers characterized previously by ZEKE\(^{51}\) and IRPD\(^{44,40,52}\) spectroscopy will reveal the differences in the interaction of t-AA\(^+\) with polar and nonpolar ligands. As essentially no information is available at all for c-AA\(^+\) and its clusters, we explored also their properties in order to evaluate the effects of cis–trans isomerization on the geometric, vibrational, and electronic structure and the stability of c/t-AA\(^+\) and their clusters. As the EI source might produce a significant population of c-AA\(^+\), its c-AA\(^+\)–L\(_n\) clusters may also be detected in the present experiments. Finally, the IRPD spectra of AA\(^+\)–L\(_n\) recorded in the hydride stretch and fingerprint ranges provide for the first time detailed spectroscopic information on the C–H and N–H stretch modes as well as the amide I–III modes of the bare AA\(^+\) cation. Comparison of these data with the corresponding spectra of neutral t-AA\(^{44}\) will provide experimental information about the effects of ionization on the geometric and vibrational structure of t-AA\(^{1}\), including the important amide group.

2. Experimental and computational techniques

IRPD spectra of mass-selected AA\(^+\)–L\(_n\) cluster ions with L = He, Ar, and N\(_2\) are recorded in a tandem quadrupole mass spectrometer coupled to an electron impact ionization source and an octopole ion trap.\(^{5,53}\) Weakly bound AA\(^+\)–L\(_n\) cluster ions are produced in a pulsed supersonic expansion by electron and/or chemical ionization of AA close to the nozzle orifice and subsequent clustering reactions.\(^{15}\) The expanding gas mixture is produced by passing either He (15–20 bar), Ar (5–7 bar), or N\(_2\) (4–6 bar) carrier gas through a reservoir filled with AA heated to 120–135 °C. AA was purchased from Sigma-Aldrich (>99.9% purity) and used without further purification. A typical mass spectrum of the ion source using N\(_2\) carrier gas is shown in Fig. 2 for the mass range 50–350 u. It is dominated by X\(^+\)–(N\(_2\))\(_n\) cluster series with X\(^+\) = N\(_2\)\(^+\) and N\(_2\)\(^+\) (with the usual strong even/odd intensity alternation, filled circles), AA\(^+\) (m/z 135, filled down triangles), the aniline cation as the major fragment ion of AA\(^+\) arising from elimination of H\(_2\)CCO (F\(^+\), m/z 93, asterisks),\(^{44}\) and X\(^+\) = H\(_2\)O (m/z 18, filled up triangles) arising from water impurity in the gas inlet system.

Fig. 2  Mass spectrum of the EI ion source using N\(_2\) carrier gas, which is dominated by X\(^+\)–(N\(_2\))\(_n\) cluster series with X\(^+\) = N\(_2\)\(^+\) and N\(_2\)\(^+\) (with the usual strong even/odd intensity alternation, filled circles), AA\(^+\) (m/z 135, filled down triangles), the AA\(^+\) dimer cation (m/z 270, open circle), the aniline cation as the major fragment ion of AA\(^+\) arising from elimination of H\(_2\)CCO (F\(^+\), m/z 93, asterisks),\(^{44}\) and X\(^+\) = H\(_2\)O (m/z 18, filled up triangles) arising from water impurity in the gas inlet system.
AA⁺–Ln ions of interest are size-selected by the first quadrupole and irradiated in an adjacent octopole with a tunable IR laser pulse (νIR) generated by an optical parametric oscillator (IR-OPO) pumped by a Q-switched nanosecond Nd:YAG laser. The IR-OPO laser is characterized by a pulse energy of ~0.3–1 and 2–5 mJ in the 1000–2000 and 2800–3500 cm⁻¹ ranges, a repetition rate of 10 Hz, and a bandwidth of 1 cm⁻¹. Calibration of the IR laser frequency accurate to better than 1 cm⁻¹ is accomplished using a wavemeter. Resonant excitation into vibrational resonances induces evaporation of one or several ligands, according to

\[ AA⁺–Ln + h\nu_{IR} \rightarrow AA⁺–L_{m} + (n-m)L \]  

Fig. 3  Mass spectra obtained by mass-selecting the AA⁺–(N₂)₄ parent cluster with m = 4 (off-scale, m/z 247) using the first quadrupole and scanning the second quadrupole. The CID spectrum reveals fragmentation into all possible AA⁺–(N₂)₄ fragment channels with m = 0–3 clearly confirming the composition of the m/z 247 ion as AA⁺–(N₂)₄. The mass spectrum recorded without laser and collisional activation reveals little fragmentation into the m = 3 fragment channel arising from metastable decay (MD) of hot n = 4 parent clusters in the octopole region. As usually observed and in contrast to CID, MD processes lead mostly to the loss of a single ligand, indicating that the clusters produced in the EI source and probed in the octopole are rather cold. Additional fragmentation into the m = 0 and 1 channels arises from laser-induced dissociation (LID) of the n = 4 parent cluster at νNH = 3367 cm⁻¹ (ν(NH)). In general, LID leads to a narrow range of fragment channels, and this information can be used to estimate the binding energies of the ligands. To separate contributions of MD from LID, the ion source is triggered at twice the laser frequency, and signals from alternating triggers are subtracted. This procedure compensates for slow variations of parent ion currents generated in the ion source. Although the IR spectra are not normalized for laser intensity fluctuations monitored by a pyroelectric detector, the relative intensities of widely spaced bands are believed to be accurate to within a factor of 2–3, mainly due to the changes in the spatial overlap between the IR laser and ion beams. The widths of the transitions in the experimental IRPD spectra of AA⁺–Lₙ increase in the order L = He, Ar, and N₂ and decrease somewhat with the cluster size n. For example, the widths of the ν(NH) transitions of the AA⁺–L dimers are 6, 9, and 14 cm⁻¹ for L = He, Ar, and N₂, respectively. The width arises mainly from unresolved rotational substructure and possibly sequence transitions involving low-frequency intermolecular modes. Thus, the widths correlate with the binding energy of the most weakly bound ligand in the complex, which determines the upper limit of the internal energy that can be deposited in the cluster.

The geometry and vibrational frequencies of AA, AA⁺, and their AA⁺–Lₙ clusters are characterized at the M06-2X/aug-cc-pVTZ level to support the vibrational and isomer assignments and to investigate the effects of ionization and complexation on the geometric, vibrational, and electronic structure. Initial calculations at the UMP2/6-311+G(d,p) level revealed rather high spin contamination for the open-shell t-AA⁺ radical cation in its ²A¹ ground electronic state (e.g., ⟨S²⟩ = 0.28 and 0.06 before and after annihilation). Hence, the MP2 level was not considered suitable for a reliable description of AA⁺ and its weak interaction with Rg and N₂ ligands. On the other hand, the M06-2X/aug-cc-pVTZ level has previously been shown to provide a reliable description of the interaction of Ar and N₂ ligands with the phenol and aminobenzonitrile cations in their ground electronic state. Apparently, this level accounts well for the electrostatic, inductive, and dispersion forces present in such aromatic radical cations weakly interacting with nonpolar ligands. Moreover, spin contamination is negligible at the M06-2X level, with values of ⟨S²⟩ = 0.0003 before and after annihilation for t-AA⁺ using the aug-cc-pVTZ basis. In general, all coordinates are relaxed during the search of stationary points on the potential energy surface without any symmetry restrictions. Vibrational analysis is used to establish the nature of the stationary points as minimum or transition state. Interaction energies (Dₑ) are corrected for harmonic zero-point energies (ZPE) to yield binding energies (Dₑ). Harmonic intramolecular frequencies are scaled by a factor of 0.9534 and 0.98 for frequencies above and below 2500 cm⁻¹ to optimize the agreement between the calculated and the measured.
3. Results and discussion

3.1 Quantum chemical calculations

Fig. 1 shows the minimum structures of c/t-\(A^+\) and the most stable c/t-\(A^+\)-L dimer isomers with \(L = \text{Ar} \) and \(N_2\). The corresponding structural, vibrational, and energetic data relevant for the present work are listed in Table 1. These include intramolecular parameters, such as the N–H and C=O bond lengths of the amide group \((r_{\text{NH}}, r_{\text{CO}})\), and the frequencies and IR intensities of the N–H and C–O stretch modes \((v_{\text{NHCCO}}, v_{\text{QC}})\). Also listed are important parameters of the intermolecular bonds, such as bond lengths \((R)\) and bond angles \((\theta_{\text{NH-L}}, \theta_{\text{HN-N}})\) as well as their dissociation energies \((D_{\text{e}})\). The notation of the cluster isomers employed in this work, c/t-\(A^+\)-L, indicates the number of H-bonded \((x)\) and \(\pi\)-bonded \((y)\) ligands \(L\) attached to c/t-\(A^+\), with \(x + y = n\). IR stick spectra of c/t-\(A^+\) and their AA-\(L\) isomers with \(L = \text{Ar}\) and \(N_2\) in the fingerprint and hydride stretch ranges are compared in Fig. 4. These cover the N–H and C–H stretch ranges \((v_{\text{NH/CH}})\), as well as the amide I (C=O stretch, \(v_{\text{CO}}\)), amide II (in-plane N–H bend), and amide III (in-plane N–H bend coupled to C–N stretch) ranges characteristic for the –NH–CO– group. The corresponding geometric, vibrational, and energetic data for neutral c/t-\(A\) and c/t-\(A\)-L are also provided in Table 1.

3.1.1 AA and AA\(^+\) monomers. In line with previous spectroscopic and quantum chemical data, the structure of neutral t-\(A\) with \(C_s\) symmetry features a planar N-phenylamide unit in its ground electronic state \((S_0)\). The N–H bond is rather short \((r_{\text{NH}} = 1.0063 \ \text{Å})\) leading to a relatively high frequency \((v_{\text{NH}} = 3482 \ \text{cm}^{-1})\), in good agreement with experiment \((3472 \ \text{cm}^{-1})\).\(^{44}\) On the other hand, the C=O bond is relatively weak \((v_{\text{CO}} = 1.2103 \ \text{Å})\) and associated with a lower stretching frequency \((v_{\text{CO}} = 1773 \ \text{cm}^{-1})\), again consistent with experiment \((1728 \ \text{cm}^{-1})\).\(^{44}\) The calculated rotational constants of 3748, 788, and 654 MHz compare favourably with the measured values of 3675, 781, and 656 MHz, respectively.\(^{47}\) In the neutral c-\(A\) isomer, the phenyl plane is rotated by 35° with respect to the amide plane (dihedral C2–C1–N–H). It is calculated to be \(\Delta E_0 = 757 \ \text{cm}^{-1}\) or \(\Delta G_{298} = 954 \ \text{cm}^{-1}\) less stable than t-\(A\), somewhat higher than the recent rough experimental estimate of \(\Delta G_{298} \approx 550 \ \text{cm}^{-1}\).\(^{47}\) Its N–H and C–O bonds are longer than in t-\(A\) by 3.3 and 1.8 mÅ, leading to frequency redshifts of \(\Delta v_{\text{NH}} = -47 \ \text{cm}^{-1}\) and \(\Delta v_{\text{CO}} = -13 \ \text{cm}^{-1}\) upon trans \(\rightarrow\) cis isomerization. Thus, the two isomers can readily be distinguished by their IR spectra, although only the IR spectrum of t-\(A\) has been measured yet.\(^{44}\) The rotational barrier for trans \(\rightarrow\) cis isomerization is calculated to be rather high \((V_b > 5000 \ \text{cm}^{-1})\).

The \(2A^+\) ground electronic state of the planar t-\(A^+\) cation with \(C_s\) symmetry is obtained by removal of one electron from...
the highest occupied molecular orbital. This bonding π(a00) orbital is delocalized over the aromatic ring and has also significant electron density on the amide group (Fig. S1 in ESI†). As a consequence, ionization of t-AA induces a remarkable elongation of the N–H bond (ΔrNH = +8 mÅ) and a drastic contraction of the C=O bond (ΔrCO = −21 mÅ). These structural changes translate directly into corresponding frequency shifts of ΔνNH = −97 cm⁻¹ and ΔνCO = +96 cm⁻¹, respectively. The effects of ionization on other ring modes and amide modes of t-AA have been discussed in detail in the previous ZEKE study of t-AA⁺.46 In contrast to neutral c-AA, the c-AA⁺ cation is also predicted to be planar (Cs) and about 1736 cm⁻¹ (21.8 kJ mol⁻¹) less stable than t-AA⁺. It can clearly be distinguished from the t-AA⁺ cation by its very different geometrical and vibrational structure of the amide group (Fig. 4). For example, both the C=O and N–H bonds of c-AA⁺ are slightly longer than in t-AA⁺ by 1.3 and 4.3 mÅ, leading to lower νCO and νNH frequencies (by 19 and 57 cm⁻¹). These differences arise from different degrees of π-conjugation in both isomers, as indicated by the NBO charge distribution discussed below. The adiabatic ionization energies of c-AA and t-AA are calculated as IE = 66 656 and 65 677 cm⁻¹. The latter value agrees remarkably well with the measured value of 65 537 cm⁻¹ available from the ZEKE spectra,46 indicating that the chosen theoretical approach reliably describes the electronic structure of both the neutral and the cationic ground state of AA⁺. Similarly, the calculated intramolecular frequencies of the amide torsion, amide in-plane bend and in-plane C–N stretch modes (48, 181, 890 cm⁻¹) of t-AA⁺ compare favourably with those extracted from the ZEKE spectra (43, 181, 878 cm⁻¹).46

To investigate the potential energy surface for cis–trans isomerization, energies have been optimized for internal rotation around the amide HN–CO bond (Fig. 5). The amide

![Fig. 4](image-url) IR stick spectra of c/t-AA⁺ and c/t-AA⁺–L dimer isomers (L = Ar/N₂) in the fingerprint and hydride stretch range obtained at the M06-2X/ aug-cc-pVTZ level (Table 1 and Fig. 1).

![Fig. 5](image-url) Potential for cis–trans isomerization of AA⁺ derived at the M06-2X/ aug-cc-pVTZ level. All coordinates are relaxed for each amide dihedral angle θ (H–N–C–O), which varies between 180° (t-AA⁺, θ = 0°) and 0° (c-AA⁺, θ = 1622 cm⁻¹) in steps of 3.6°. The barrier occurs at θ ~ 77° with Vθ = 1116 cm⁻¹ from c-AA⁺.
dihedral angle \( \theta \) (H–N–C–O) varies between 180° (t-AA) and 0° (c-AA) in steps of 3.6°. At this level, c-AA is 1622 cm\(^{-1}\) less stable than t-AA, and c-AA \( \rightarrow \) t-AA isomerization involves a significant barrier of \( V_b = 1116 \text{ cm}^{-1} \) at \( \theta \approx 77° \). As a consequence, if both isomers were produced in the supersonic plasma expansion they may easily be trapped and cooled down in their respective potential wells. As expected, the isomerization barrier in the open-shell cation ground state is much lower in their respective potential wells. Thus, the aromatic ring as well as the highly positively charged amide group \((-\text{AA}^+)\) is more neutral \((0.06 \text{ e})\) than in \(-\text{AA}^+-\text{Ar}(\text{H})\), and also have slightly higher interaction energies \(D_b=325 \text{ cm}^{-1}\) for neutral ligands, leading to the formation of intermolecular \(\pi\)-bonds and H-bonds, respectively. Similar arguments apply to the N–H bends \(\delta_\text{NH}^0 = 10\text{ cm}^{-1}\) measured by ZEKE spectroscopy.\(^{50}\) Intermolecular \(\pi\)-stacking of \(\text{Ar}\) has essentially no effect on the geometric and vibrational properties of the \(\text{N–H}\) and \(\text{C–O}\) bonds, with \(\Delta \delta_\text{NH}^0 < 3 \text{ cm}^{-1}\) and \(\Delta \delta_\text{CO}^0 < 3\%.\) Similar arguments apply to the N–H bonds \(\beta_\text{NH}^0\) and \(\gamma_\text{NH}^0\). Isomerization between the \(\pi\)-bonded local minimum and the \(\text{H-bonded global minimum involves significant barriers of } V_b(\pi \rightarrow \text{H}) = 195 \text{ cm}^{-1}\) and \(V_b(\text{H} \rightarrow \pi) = 226 \text{ cm}^{-1}\), suggesting that both isomers can readily be trapped in their respective minima once they are formed in the supersonic plasma expansion. Barriers of similar magnitude have previously been calculated for related \(\text{Ar}\) complexes with acidic aromatic cations.\(^{14,25,27,57}\) The calculated IE shift upon \(\text{Ar}\) complexation, \(\Delta \text{IE} = \Delta D_b = 548–325 = 223 \text{ cm}^{-1}\), corresponds to the increase in the binding energy of t-AA\(^{-}\text{Ar}(\pi)\) upon ionization and is compatible with the value measured by ZEKE spectroscopy (142 cm\(^{-1}\)). The binding energy in c-AA\(^{-}\text{Ar}(\pi)\) is slightly weaker than in t-AA\(^{-}\text{Ar}(\pi)\), \(D_b = 519 \text{ vs. } 548 \text{ cm}^{-1}\). In addition to the global H-bonded and \(\pi\)-bonded minima, further less stable local minima have been considered for t-AA\(^{-}\text{Ar}\), including those in which \(\text{Ar}\) binds in the molecular plane to either the CH\(_3\) group or the aromatic CH bond in para position. Both structures with \(C_s\) symmetry have relatively low dissociation energies, \(D_b(\text{CH} \_3) = 140 \text{ cm}^{-1}\) and \(D_b(\text{CH} \_p) = 51 \text{ cm}^{-1}\) (Table 1), and are thus not considered in detail further. Although the potential energy surface of the t-AA\(^{-}\text{Ar}\) dimer has been explored in some detail, there might be more local minima than those identified here. However, spectroscopically relevant for the current study are only the by far most stable H-bonded and \(\pi\)-bonded ones. Thus, the preferred cluster growth is predicted to start with the formation of the t-AA\(^{-}\text{Ar}(\pi)\) bonded dimer core and then proceed via attachment of subsequent...
ligands to the aromatic ring. The NBO analysis reveals only minor charge transfer from Ar to the \( t\AA^- \) cation for any of the considered dimer isomers \( (q_{\text{Ar}} < 0.015 \) e\), in line with the view of mainly inductive and dispersive intermolecular attraction for H-bonding and \( \pi \)-stacking, respectively.

In general, the interaction of \( \AA^- \) with \( \text{N}_2 \) is stronger than with Ar due to its additional quadrupole moment and higher parallel polarizability.\(^9\)\(^{58,59}\) As a result, complexation with \( \text{N}_2 \) has an enhanced impact on the intramolecular structural and vibrational properties as compared to Ar, in particular for the H-bonded isomer. The planar H-bonded \( t\AA^-\text{N}_2(\text{H}) \) dimer corresponds to the most stable structure. The nearly linear H-bond is characterized by a binding energy of \( D_0 = 977 \) cm\(^{-1}\), an intermolecular separation of \( R = 2.23 \) Å, a bond angle of \( \theta_{\text{NHN}} = 176^\circ \), and intermolecular frequencies of \( \beta' = 29 \), \( \beta'' = 38 \), \( \gamma' = 106 \), \( \gamma'' = 129 \), and \( \sigma = 88 \) cm\(^{-1}\), respectively. The anisotropy of the charge-induced dipole and charge–quadrupole interaction favors a linear over a T-shaped approach of the \( \text{N}_2 \) ligand toward a positive charge.\(^9\)\(^{27,58,60–67}\) The N–H donor bond leading to a redshift of \( \Delta \nu_{\text{NH}} \) by \( 3 \) mÅ upon formation of the H-bond with \( \text{N}_2 \), again nearly unaffected. Due to the slightly weaker H-bond in \( \text{c-\AA}^-\text{N}_2(\text{H}) \), the monomer deformation upon complex formation is correspondingly smaller.

The \( \pi \)-bonded \( \AA^-\text{N}_2(\pi) \) local minima are substantially less stable than the corresponding H-bonded global minima. For example, the \( \pi \)-bond in \( t\AA^-\text{N}_2(\pi) \) is characterized by \( D_0 = 320 \) cm\(^{-1}\), an \( \text{N}_2 \)-ring separation of \( R = 3.15 \) Å, and intermolecular frequencies of \( \beta_x = 13 \), \( \beta_y = 26 \), \( \gamma_x = 78 \), \( \gamma_y = 71 \), and \( \sigma = 56 \) cm\(^{-1}\), respectively. The \( \text{N}_2 \) ligand points toward the C-atom in \text{ipso} position with respect to the amide group, because this atom carries the highest positive partial charge on the ring skeleton. Similar to Ar, \( \pi \)-bonding of \( \text{N}_2 \) has essentially no effect on the geometric and vibrational properties of the N–H and C==O bonds, with \( \Delta \nu_{\text{NHCO}} \approx 5 \) cm\(^{-1}\). Interestingly, the \( \text{N}_2 \) ligand in \( \text{c-\AA}^-\text{N}_2(\pi) \) is more displaced toward the amide group leading to a slightly stronger interaction than in \( t\AA^-\text{N}_2(\pi) \). The \( \pi \)-bonded \( \AA^-\text{N}_2(\pi) \) structures are only shallow local minima. Due to the much larger well depths at the N-bonded minima, the population of the \( \pi \)-bonded dimers in the supersonic plasma expansion is predicted to be small, and the cluster growth is expected to begin with H-bonding to the NH group for the first \( \text{N}_2 \) ligand followed by attachment to less stable \( \pi \)-binding sites. Similar to the Ar complexes, the NBO analysis reveals only minor charge transfer from \( \text{N}_2 \) to the \( \AA^- \) cation, with \( q_{\text{N}_2} < 0.02 \) e for all structures.

### 3.2 Experimental IRPD spectra

#### 3.2.1 Hydride stretch range

Fig. 7 compares the IRPD spectra of the \( \text{AA}^-\text{L} \) dimers with \( L = \text{He}, \text{Ar}, \) and \( \text{N}_2 \) in the spectral range between 2800 and 3600 cm\(^{-1}\). This spectral range covers mainly the N–H and C=H stretch fundamentals of \( \text{AA}^- \) (amide I, \( \nu_{\text{NH}}, \nu_{\text{C=H}} \)) and the assignment of the spectral features is guided by comparison with the linear IR absorption spectra calculated for the \( t\AA^- \) and \( \text{c-\AA}^- \) monomer isomers and their H-bonded \( \AA^-\text{L}(\text{H}) \) dimers. Corresponding IR spectra of larger \( \text{AA}^-\text{L}_n \) clusters with \( L = \text{He} \) \((n \leq 2)\), \( \text{Ar} \) \((n \leq 7)\), and \( \text{N}_2 \) \((n \leq 10)\) recorded in the dominant fragment channel are shown in Fig. S3 and S4 in ESL.\(^\dagger\) As \( \nu_{\text{NH}} \) (amide A) is most sensitive to the cluster size, an enlarged view of the cluster spectra in this spectral range is offered in Fig. 8. The peak positions observed in the experimental spectra of \( \text{AA}^-\text{Ar/N}_2 \) are listed in Table 2 along with their vibrational and isomer assignments.

The IRPD spectra of \( \text{AA}^-\text{He} \) and \( \text{AA}^-\text{He}_2 \) exhibit a single band (denoted A/B) in the N–H stretch range at 3385 and 3384 cm\(^{-1}\), respectively, with a width of \( \approx 6 \) cm\(^{-1}\). This transition can safely be assigned to the \( \nu_{\text{NH}} \) fundamental of the \( t\AA^-\text{He}_n \) clusters. As the interaction of \( \text{AA}^- \) with He is very weak \((D_0 < 100 \) cm\(^{-1}\)) we cannot draw any reliable conclusion about the binding site of the He ligands \((e.g., \text{H and/or } \pi)\), as the shift will be insignificant at the current spectral resolution for any binding site (Table 1). Thus, the \( \nu_{\text{NH}} \) band of \( \text{AA}^-\text{He} \) at 3385 cm\(^{-1}\) is taken as close approximation of the free \( \nu_{\text{NH}} \) fundamental of the \( t\AA^- \) monomer and has been employed in Section 2 to derive the scaling factor for the high-frequency modes and serves as a reference point for the determination of the \( \Delta \nu_{\text{NH}} \) frequency shifts upon complexation. Although \( \nu_{\text{NH}} \) of \( \text{c-\AA}^- \) is predicted to be 25% stronger than \( \nu_{\text{NH}} \) of \( t\AA^- \), there is no sign of this isomer in the \( \text{AA}^-\text{He} \) spectrum.

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**Fig. 7** IRPD spectra of AA\(^-\)–L dimers with L = He, Ar, and \( \text{N}_2 \) recorded in the C–H and N–H stretch range are compared to the linear IR absorption spectra calculated for \( t\AA^- \) at the M06-2X/aug-cc-pVTZ level. The positions of the transitions for L = Ar and \( \text{N}_2 \) are listed in Table 2 along with their vibrational and isomer assignments.
The most intense feature in the IRPD spectrum of AA$^+$–Ar at 3373 cm$^{-1}$ (band B) is redshifted by $\Delta$\nu$_{NH} = -12$ cm$^{-1}$ from the corresponding AA$^+$–He transition, and is thus safely attributed to $\nu_{NH}$ of the H-bonded t-AA$^+$–Ar(H) dimer. The calculated shift, $\Delta$\nu$_{NH} = -45$ cm$^{-1}$, is somewhat larger than the experimental one, indicating that the computational approach overestimates the frequency shift. Another possibility is that the Fermi resonance interaction of $\nu_{NH}$ with vibrations assigned to band C may push the experimental $\nu_{NH}$ frequency to a higher value. The blueshaded band contour is typical for proton-donor stretch vibrations and thus supports the assignment to the H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer. The observed redshift corresponds to the modest increase in H-bond energy upon H-bonded isomer.

In contrast to AA$^+$–Ar, the IRPD spectrum of AA$^+$–N$_2$ features only a single $\nu_{NH}$ band at 3355 cm$^{-1}$ (band B), and its significant redshift of $\Delta$\nu$_{NH} = -30$ cm$^{-1}$ upon N$_2$ complexation strongly suggests an assignment to the H-bonded t-AA$^+$–N$_2$(H) isomer, with a predicted shift of $\Delta$\nu$_{NH} = -61$ cm$^{-1}$, which similar to t-AA$^+$–Ar(H) is substantially larger than the measured one. The blueshaded band contour is more pronounced than for $\nu_{NH}$ of t-AA$^+$–Ar(H) due to the stronger H-bond with N$_2$ leading to a correspondingly larger $\Delta$\nu$_{NH}$ shift. There is essentially no signal in the spectral range of the free $\nu_{NH}$ mode of t-AA$^+$, indicating that the abundance of the less stable t-AA$^+$–N$_2$(\pi) isomer is below the detection limit. From the achieved signal-to-noise ratio (~50) and the ratio of the predicted IR intensities (~3.6), we can estimate an upper limit for the t-AA$^+$–N$_2$(\pi) population of 7%. This observation clearly confirms that the H-bond in t-AA$^+$–Ar$_n$ clusters is more stable than any other binding site, including the \pi-bond.

The $\nu_{NH}$ bands of the larger AA$^+$–(N$_2$)$_n$ clusters with \( n \geq 2 \) shift in a similar fashion as those of AA$^+$–Ar$_n$, except that the incremental shifts and splittings due to isomers are more pronounced (Fig. 8). Incremental blueshifts of a few cm$^{-1}$ from $\nu_{NH}$ of t-AA$^+$–N$_2$(H) in the size range \( n = 1–5 \) are again followed by a calculated binding energy of \( D_0 = 579 \) cm$^{-1}$, the shift of $\Delta$\nu$_{NH} = -12$ cm$^{-1}$ implies an increase in H-bond energy of only 2% upon $\nu_{NH}$ excitation. In addition, the AA$^+$–Ar spectrum also shows a weak transition at 3385 cm$^{-1}$ (band A), which is essentially unshifted from $\nu_{NH}$ of AA$^+$–He and hence assigned to $\nu_{NH}$ of the \pi-bonded t-AA$^+$–Ar(\pi) dimer. For completeness, we note that the exact position of the Ar ligand in fact cannot be derived from the experimental spectrum in Fig. 8 alone. The only information derived from the vanishing frequency shift is that the Ar ligand is not occupying a H-bonded position. Comparison with related aromatic complexes\(^9\) as well as the current computational studies reveals, however, that the \pi-binding site is by far the most stable non H-bonding site in this type of clusters and is thus the favoured assignment. Using the ratios of the integrated band intensities \( \sim 10 \) and the calculated IR oscillator strengths of $\nu_{NH}$ of the H-bonded and \pi-bonded isomers of t-AA$^+$–Ar (\( \sim 2.6 \)), their relative abundance in the plasma expansion can be estimated, and an upper limit of \( \sim 30\% \) is derived for the population of the AA$^+$–Ar(\pi) isomer under the present experimental conditions. As previous studies demonstrated that the EI ion source predominantly produces the most stable isomer of a given cluster ion, this result clearly indicates that the H-bonded isomer is the global minimum, whereas the \pi-bonded dimer corresponds to a less stable local minimum. This conclusion is further supported by the IRPD spectra of the larger AA$^+$–Ar$_n$ clusters and the quantum chemical calculations.

The most intense transitions in the IRPD spectra of AA$^+$–Ar$_n$ with \( n = 2–7 \) occur within \( \pm 3 \) cm$^{-1}$ from $\nu_{NH}$ of the H-bonded t-AA$^+$–Ar(H) dimer (band B). There are small but noticeable incremental blueshifts in the size range \( n = 1–5 \), which are followed by modest redshifts for \( n = 6–7 \). In addition, the bound $\nu_{NH}$ band exhibits enhanced splittings with increasing cluster size, indicating that the number of isomers increases with \( n \). Although it is difficult to extract more definitive information about the sequential cluster growth from the IR spectral data, they confirm the rough picture that the first Ar ligand is H-bonded to the NH group whereas subsequent Ar ligands occupy less favourable binding sites such as \pi-stacking. Significantly, the AA$^+$–Ar$_n$ spectra with \( n \geq 2 \) do not show any measurable signal in the range of $\nu_{NH}$ of free t-AA$^+$, indicating that the abundance of the t-AA$^+$–Ar$_n$(\pi) isomers is below the detection limit. This observation clearly confirms that the H-bond in t-AA$^+$–Ar$_n$ clusters is more stable than any other binding site, including the \pi-bond.

In contrast to AA$^+$–Ar, the IRPD spectrum of AA$^+$–N$_2$ features only a single $\nu_{NH}$ band at 3355 cm$^{-1}$ (band B), and its significant redshift of $\Delta$\nu$_{NH} = -30$ cm$^{-1}$ upon N$_2$ complexation strongly suggests an assignment to the H-bonded t-AA$^+$–N$_2$(H) isomer, with a predicted shift of $\Delta$\nu$_{NH} = -61$ cm$^{-1}$, which similar to t-AA$^+$–Ar(H) is substantially larger than the measured one. The blueshaded band contour is more pronounced than for $\nu_{NH}$ of t-AA$^+$–Ar(H) due to the stronger H-bond with N$_2$ leading to a correspondingly larger $\Delta$\nu$_{NH}$ shift. There is essentially no signal in the spectral range of the free $\nu_{NH}$ mode of t-AA$^+$, indicating that the abundance of the less stable t-AA$^+$–N$_2$(\pi) isomer is below the detection limit. From the achieved signal-to-noise ratio (~50) and the ratio of the predicted IR intensities (~3.6), we can estimate an upper limit for the t-AA$^+$–N$_2$(\pi) population of 7%. This observation clearly confirms that the H-bond in t-AA$^+$–Ar$_n$ clusters is more stable than any other binding site.

The $\nu_{NH}$ bands of the larger AA$^+$–(N$_2$)$_n$ clusters with \( n \geq 2 \) shift in a similar fashion as those of AA$^+$–Ar$_n$, except that the incremental shifts and splittings due to isomers are more pronounced (Fig. 8). Incremental blueshifts of a few cm$^{-1}$ from $\nu_{NH}$ of t-AA$^+$–N$_2$(H) in the size range \( n = 1–5 \) are again followed...
by smaller redshifts for \( n = 6-10 \). The \( \nu_{\text{NH}} \) bands also display progressing splittings with increasing cluster size and also intensity variations of the individual subcomponents, indicating that there are several routes for cluster aggregation. Again, although it is difficult to extract more definitive information about the sequential cluster growth from the IR spectral data, they confirm the view that the first \( N_2 \) ligand is strongly H-bonded to the NH group and subsequent ligands form weaker bonds to the \( AA^+\text{--}N_2 \) dimer core. Significantly, the \( \nu_{\text{NH}} \) shifts of the \( n = 2 \) cluster disfavour an assignment to a trimer structure, in which two \( N_2 \) ligands bind to the NH group resulting in a bifurcated double H-bond. Such structures were previously observed for \( N_2 \) clusters of the indole and tryptamine cations. However, the calculations show that such a binding motif is less stable for \( t\text{--}AA^+\text{--}N_2 \).

The IRPD spectra of \( AA^+\text{--}L_n \) with \( L = \text{He, Ar, and } \text{N}_2 \) do not provide any evidence for the presence of cluster ions with \( c\text{--}AA^+ \). The \( \nu_{\text{NH}} \) mode of \( c\text{--}AA^+ \) is predicted at \( 3328 \text{ cm}^{-1} \) with high IR oscillator strength (126 km mol\(^{-1}\)). One might speculate that band \( C \), which occurs in this frequency range in the spectra with \( L = \text{Ar and } \text{N}_2 \) may in fact arise from \( \nu_{\text{NH}} \) of \( c\text{--}AA^+\text{--}L_n \) clusters. However, in marked contrast to \( \nu_{\text{NH}} \) of \( t\text{--}AA^+\text{--}L_n \) the position of band \( C \) does not depend much on the ligand \( L \) and the cluster size \( n \). Thus, an assignment of band \( C \) to a Fermi resonance component of \( t\text{--}AA^+\text{--}L_n \) is clearly favoured over an assignment to \( \nu_{\text{NH}} \) of \( c\text{--}AA^+\text{--}L_n \) (vide infra). The absence of any spectral signatures of \( c\text{--}AA^+\text{--}L_n \) is also consistent with the IRPD spectra recorded in the fingerprint range (Section 3.2.2).

In general, the frequency redshifts of proton donor stretch vibrations in H-bonded AH\(^+\)–L dimers are correlated with the proton affinity (PA) of the ligand \( L \). Fig. 9 shows the measured and calculated \( \nu_{\text{NH}} \) frequencies of \( t\text{--}AA^+\text{--}L \) dimers as a function of the proton affinity (PA) of the ligand \( L \). The IRPD spectra of \( AA^+\text{--}L \) dimers (filled circles) as a function of the proton affinity (PA) of the ligand \( L \) for \( L = \text{He, Ar, } \text{N}_2, \text{ and } \text{H}_2\text{O} \) compared to shifts for \( t\text{--}AA^+\text{--}L \) calculated at the M06-2X/aug-cc-pVTZ level (crosses).
−12 cm⁻¹ is rather small and comparable to aniline cations. Despite its weak proton donor ability, the H-bonded t-AA°–Ar(H) dimer is still more stable than the π-bond in t-AA°–Ar(π), indicating that the preference for H-bonding over π-stacking in Ar complexes of acidic aromatic cations holds even for low acidity.

In addition to νNH (bands A and B), the IRPD spectra of AA°–L with L = Ar and N₂ in Fig. 7 and Fig. S3 and S4 in ESI† reveal three less intense transitions (denoted C–E) in the 2800–3600 cm⁻¹ range. Band E occurs between 2932 and 2936 cm⁻¹ for all AA°–L clusters considered and can readily be assigned to the symmetric C–H stretch mode of the CH₃ group of t-AA° in t-AA°–L (ν(CH₃)) by comparison with the spectrum calculated for the t-AA° monomer (ν(CH₃) = 2925 cm⁻¹). This mode is the lowest C–H stretch frequency and has a significant IR intensity (18 km mol⁻¹). The fact that there is little variation in frequency and IR intensity as a function of L and n suggests that the CH₃ group does not belong to the favourable ligand binding sites of t-AA°. Band D of all AA°–L clusters is observed between 3136 and 3142 cm⁻¹ and can readily be attributed to the isolated aromatic C–H stretch of the ortho CH group of the phenyl ring (ν(CH₉) in trans position of the NH group, which has a calculated frequency of ν(CH₉) = 3103 cm⁻¹ for t-AA° and appreciable IR activity (30 km mol⁻¹). All other aromatic and aliphatic C–H stretch fundamentals of the CH₄ and C₆H₆ groups in t-AA° are predicted between ν(CH₄) = 2925 and ν(CH₆) = 3103 cm⁻¹ but their IR oscillator strength appears to be too low (<8 km mol⁻¹) to be detected in the IRPD spectra of AA°–L in the fingerprint range. Clearly, the appearance of the IRPD spectra of AA°–L in the C–H stretch range is compatible with clusters of only the t-AA° isomer (e.g. intense ν(CH₆) and ν(CH₉) transitions), and no sign of the presence of c-AA°–L clusters is visible.

In addition to νNH (A/B) and νCH fundamentals (D/E), the IRPD spectra of AA°–L show several absorptions in the frequency range 3320–3340 cm⁻¹ summarized as band C. These transitions are outside of the range of the C–H stretch fundamentals (ν(CH) = 2900–3150 cm⁻¹). In addition, their IR activity seems to be strongest for those AA°–L clusters with the lowest νNH frequency, e.g. for t-AA°–N₂(H). Hence, they are attributed to overtone and/or combination bands, which gain their oscillator strength via anharmonic coupling (Fermi resonance) with the strongly IR active νNH fundamental. At present, it is unclear whether the various components of band C arise from several vibrational modes or just from a single vibrational mode of the various isomers of a single AA°–L cluster size. The IR spectrum of neutral t-AA also shows a Fermi doublet in the N–H stretch range at 3440 and 3472 cm⁻¹ and the first component was assigned to the first overtone of the C=O stretch, 2νC=O. However, the νCC fundamentals of the t-AA°–L clusters are observed near 1820 cm⁻¹, i.e. the 2νCC overtone cannot account for the Fermi multiplets near 3330 cm⁻¹. In contrast, the only other first overtone of t-AA° calculated in the required frequency range is that of the symmetric aromatic C–C stretch mode 2νCC calculated at 3282 cm⁻¹. However, this mode shows little coupling with the N–H stretch and has little IR activity (13 km mol⁻¹). As a more realistic and currently favoured alternative, band C may be produced by combination bands of the very IR active νCC fundamental (amide I) with other strongly IR active modes near ~1530 cm⁻¹, which all feature strong N–H bend character (amide II) and thus can readily couple to the N–H stretch (amide A).

At this stage, it is noted that the IRPD spectra of larger t-AA°–(N₂)ₙ clusters display additional features [X–Z in Fig. S3 and S4 in ESI†], which increase in intensity as a function of n. At present, it is unclear whether these transitions indeed arise from t-AA°–(N₂)ₙ or whether they are resonances of isobaric X°–(N₂)ₙ clusters with unknown X and p. Such contaminations are possible despite the tandem mass spectrometric approach.²⁴

Comparison of the IR spectra of t-AA°–Ar and t-AA° in Fig. S3 in ESI† reveals the spectroscopic effects of ionization on the properties of the N–H and C–H bonds as discussed in Section 3.1. The calculations predict a redshift of ΔνNH = −97 cm⁻¹, which is consistent with the measured value of ~87 cm⁻¹. The N–H bond in t-AA° becomes much weaker and more acidic in the cation ground state. On the other hand, all aromatic C–H stretch frequencies are predicted to increase upon ionization (by 9–25 cm⁻¹), and indeed the ν(CH₃) frequency measured for t-AA°–L (3139 ± 3 cm⁻¹) is larger than that for t-AA° (3098 cm⁻¹). The predicted aliphatic C–H stretch frequencies of the methyl group in t-AA° are almost not affected upon ionization, and again this trend is confirmed by the small observed redshift of Δν(CH₃) = −8 cm⁻¹.

### 3.2.2 Fingerprint range.

Fig. 10 compares the IRPD spectra of the AA°–L dimers with L = Ar and N₂ in the fingerprint range.
between 700 and 1900 cm\(^{-1}\). Corresponding IR spectra of larger AA\(^{-}\)–L\(_n\) clusters with L = Ar (n ≤ 4) and N\(_2\) (n ≤ 3) recorded in the dominant fragment channels are shown in Fig. S6 and S7 in ESI\(^\dagger\). The peak positions observed in the experimental spectra for n = 1 are listed in Table 2 along with their vibrational and isomer assignments. The strong bands in the AA\(^{-}\)–Ar spectrum in Fig. 10 are saturated as this spectrum has been recorded with high detector sensitivity in order to detect the weak transitions. An unsaturated spectrum is provided in Fig. S6 in ESI\(^\dagger\). A comparison between the IRPD spectrum of AA\(^{-}\)–Ar with the IR spectrum of neutral t-AA is given in Fig. S8 in ESI\(^\dagger\). The fingerprint range covers mainly the amide I–III bands of the amide group including its C–O stretch and N–H bend fundamentals (v\(_{\text{CO}}\), \(\tilde{\nu}_{\text{NH}}\)) as well as C–H bend and rock vibrations of the aromatic ring skeleton and the CH\(_3\) group. The assignment of the spectral features is again guided by comparison with the linear IR absorption spectra calculated for the t-AA\(^+\) and c-AA\(^-\) monomer isomers (Fig. 10) and the H-bonded AA\(^{-}\)–L(H) dimers (Fig. 4). In general, the coarse structure of all AA\(^{-}\)–L\(_n\) spectra is very similar in the fingerprint range, and the major variations are found in the amide II region near 1500 cm\(^{-1}\) (Fig. S9 in ESI\(^\dagger\)). From the comparison of the spectra in Fig. 10, it is again immediately obvious that only dimers with t-AA\(^-\) contribute to the measured AA\(^{-}\)–L spectra. For example, spectra calculated for c-AA\(^-\) (L) predict the strongest transition near 1200 cm\(^{-1}\) (amide III band, \(\tilde{\nu}_{\text{CN}}\) stretch), while the experimental spectra display their most intense bands near 1500 cm\(^{-1}\), in good agreement with the spectra calculated for t-AA\(^-\)\(\text{–(L)}\).

The single intense and quite isolated transition at 1818 cm\(^{-1}\) (band F) in the amide I region of the AA\(^+\)–L\(_n\) clusters does not show any significant dependence on the ligand L and the cluster size and can safely be assigned to the \(\nu_{\text{CO}}\) fundamental of the t-AA\(^+\) rotamer. The somewhat higher frequency calculated for t-AA\(^-\) (1869 cm\(^{-1}\)) implies that the harmonic approach at the M06-2X/aug-cc-pVTZ level using a scaling factor of 0.98 overestimates the measured fundamental frequency by about 51 cm\(^{-1}\). In the case of neutral t-AA, this theoretical approach overestimates \(\nu_{\text{CO}}\) by a similar amount of 45 cm\(^{-1}\), indicating that this level might have some problems in describing the C–O bond properties. Ionization of t-AA strengthens the C–O bond, and the resulting observed frequency increase of \(\Delta\nu_{\text{CO}} = +90 \text{ cm}^{-1}\) is compatible with the predicted change of +96 cm\(^{-1}\). The \(\nu_{\text{CO}}\) frequency of c-AA\(^-\) is predicted to be significantly lower than that of t-AA\(^+\) (by 19 cm\(^{-1}\)). As no second intense transition is detected in the \(\nu_{\text{CO}}\) range in the IRPD spectra of AA\(^{-}\)–L\(_n\), this result provides further evidence that these spectra are largely dominated by clusters of the t-AA\(^-\) cation, a conclusion already suggested from the analysis of the spectra measured in the hydride stretch range.

Inspection of the amide II range reveals strong transitions (bands L = H, I) between 1480 and 1550 cm\(^{-1}\) assigned to modes involving strong N–H in-plane bend contributions more or less coupled to C–C stretch modes of the phenyl ring. These transitions dominate the fingerprint range, and their positions and intensities are well reproduced by the calculations. These amide II modes are also the transitions in the fingerprint range that are most sensitive to the type and number of ligands (Fig. S9 in ESI\(^\dagger\)), with shifts of up to 10 cm\(^{-1}\) for the cluster sizes investigated. The two weak transitions M and O as well as the strong band Q arise from asymmetric and symmetric C–H bends of the methyl group. In contrast to neutral t-AA, the intensity of the amide III transition (band S) is quite weak in the IR spectra of t-AA\(^-\)–L\(_n\). There are a number of modes of the phenyl ring, for which we adopt the notation of Wilson.\(^{71}\) These include the in-plane C–H bends \(\nu_{19\text{b}}\text{(P)}, \nu_{19\text{i}}\text{(R)}, \text{and} \nu_{19\text{ai}14}\text{(T/U)},\) the out-of-plane C–H bend \(\nu_{17}\text{(Z)},\) and the symmetric ring C–C stretch \(\nu_{5}\) which is strongly coupled to the amide C–N stretch (Y). Further bands of the amide group include the C–C stretch (X) and the asymmetric C–N–C stretch (Y). In general, all intense bands predicted by the calculations for t-AA\(^-\) are observed in the IRPD spectrum of AA\(^-\)–Ar and agree well with respect to their frequencies and relative IR intensities, supporting the vibrational and isomer assignment. Apart from the lower signal-to-noise ratio, the IRPD spectra of AA\(^-\)–(N\(_2\))\(_n\) are quite similar to those of AA\(^-\)–Ar. The comparison of the IR spectra of t-AA\(^-\)–Ar and neutral t-AA–Ar in Fig. S8 in ESI\(^\dagger\) illustrates the drastic changes in the geometric and vibrational structure of t-AA induced by ionization for the phenyl, amide, and methyl groups. These changes are well reproduced by the calculations.

3.3 Photofragmentation branching ratios and binding energies

In this section, we derive experimental binding energies (\(D_{\infty}\)) from observed photofragmentation branching ratios and compare these to calculated values listed in Table 1 (\(D_{\text{cvo}}\)). We consider both theoretical values (\(D_{\text{cvo}}\)) because the computational M06-2X approach substantially overestimates the contribution of ZPE arising from the highly anharmonic intermolecular modes.\(^{21}\)

Table 3 summarizes the photofragmentation branching ratios observed in the IRPD process of AA\(^-\)–L\(_n\) clusters described in eqn (1) using the \(\nu_{\text{NH}}\) resonance of the most stable isomer of a given cluster size. In agreement with previous observations for related systems, all AA\(^-\)–L\(_n\) cluster sizes investigated exhibit a

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\(^a\) Only channels contributing more than 5% are listed. Uncertainties are estimated as 5%. \(^b\) Measured at resonances in the fingerprint range.
rather narrow range of fragment channels \(m\) upon LID of a parent cluster \(n\), and this information can be used to extract ligand binding energies within the framework of a simple model. This model relies on the following rough approximations. (i) The difference in the internal energies of the parent cluster and the fragmentation products as well as the kinetic energy release is neglected. (ii) Only single ligands are evaporated, and those with smaller binding energies are evaporated first. (iii) Three-body forces are assumed to be small. (iv) The whole absorbed photon energy under the current single-photon absorption conditions \((\hbar \nu_\text{HI} \sim 3355-3385 \text{ cm}^{-1}\)) is available for ligand evaporation. (v) Ligands at similar binding sites are assumed to have the same binding energy, which are classified as \(D_\text{a}(H)\) and \(D_\text{a}(\pi)\). Moreover, we infer from the IRPD spectra that \(D_\text{a}(H) \geq D_\text{a}(\pi)\) for \(L = \text{Ar}\) and \(D_\text{a}(H) \gg D_\text{a}(\pi)\) for \(L = \text{N}_2\). Additional information comes from the IRPD spectra in the fingerprint range recorded in different fragment channels, which allow for extracting further thresholds for dissociation energies. For example, Fig. 11 shows the IRPD spectra of \(\text{AA}^-\text{Ar}_2\) recorded in the AA' and AA'–Ar fragment channel, indicated as \(n-m = 2-0\) and 2–1, respectively. The vibrations of \(\text{AA}^-\text{Ar}_2\) with frequencies below 1385 cm\(^{-1}\) occur only in the 2–1 fragment channel (loss of one Ar ligand), while those above 1150 cm\(^{-1}\) are only detected in the 2–0 channel (loss of two Ar ligands). From these thresholds, we can infer that the total binding energy of the two Ar ligands in \(\text{AA}^-\text{Ar}_2\), \(D_\text{a}(\text{H} + \text{D}_\text{a}(\pi))\), lies in the interval 1150–1385 cm\(^{-1}\).

Analysis of all available photofragmentation data of \(L = \text{Ar}\) yields rough estimates of \(D_\text{a}(\pi) < 700 \text{ cm}^{-1}\) and \(570 < D_\text{a}(\text{H})/\text{cm}^{-1} < 880\), i.e. \(D_\text{a}(\text{H}) \approx 730 \pm 160 \text{ cm}^{-1}\), with the additional restriction \(D_\text{a}(\text{H}) > D_\text{a}(\pi)\). Using the assumption \(D_\text{a}(\text{H}) \approx D_\text{a}(\pi)\), as suggested from the calculations, we obtain \(570 < D_\text{a}(\text{H})/\text{cm}^{-1} < 700\), in agreement with the calculated values of \(D_{\text{e}0}(\pi) = 585/548 \text{ cm}^{-1}\) and \(D_{\text{e}0}(\text{H}) = 720/579 \text{ cm}^{-1}\), respectively. This matches the threshold values predicted by the M06-2X/aug-cc-pVTZ level provides a reliable prediction of the AA'–Ar interaction in both the H-bonded and \(\pi\)-bonded parts of the potential. Initial calculations at the lower M06-2X/6-311+G** level resulted in the reversed order \(D_{\text{e}0}(\pi) = 588/595 \text{ cm}^{-1} > 543/400 \text{ cm}^{-1} = D_{\text{e}0}(\text{H})\), which is not compatible with experiment for both the \(D_\text{a}\) and \(D_\text{e}\) values.

For neutral \(t\text{-AA}\text{-Ar}\), the binding energies for the two considered isomers are calculated as \(D_\text{a}(\pi) = 325 \text{ cm}^{-1}\) and \(D_\text{a}(\text{H}) = 220 \text{ cm}^{-1}\), i.e., in the \(S_0\) state the \(\pi\)-bond is clearly more stable than the H-bond. All spectroscopic data are consistent with a \(\pi\)-bonded \(t\text{-AA}\text{-Ar}(\pi)\) global minimum in \(S_0\),\(^{50}\) and no evidence for a less stable H-bonded local minimum was reported. While the attraction in \(t\text{-AA}\text{-Ar}(\pi)\) is dominated by dispersion forces between Ar and the highly polarizable \(\pi\) electrons of the aromatic ring, ionization increases its binding energy due to additional charge-induced polarization forces. The calculated increase in binding energy upon ionization, \(\Delta D_\text{a}(\pi) = 223 \text{ cm}^{-1}\), is compatible with the value of 142 cm\(^{-1}\) extracted from the ZEKE spectra.\(^{20}\) The H-bond in neutral \(t\text{-AA}\text{-Ar}(\text{H})\) is predicted to be weak in \(S_0\), \(D_\text{a}(\text{H}) = 220 \text{ cm}^{-1}\), but gains substantial stabilization upon ionization, \(\Delta D_\text{a}(\text{H}) = 359 \text{ cm}^{-1}\), due to strong charge-induced dipole forces arising from the large positive partial charge on the N–H proton. Hence, clearly ionization induces a \(\pi \rightarrow H\) switch in the preferred ion–ligand binding motif of \(t\text{-AA}^{(+)}\text{-Ar}\).

Analysis of the photofragmentation data of \(L = \text{N}_2\) yields \(D_\text{a}(\text{H}) = 1150 \pm 50 \text{ cm}^{-1}\) and \(D_\text{a}(\pi) = 725 \pm 25 \text{ cm}^{-1}\), consistent with the calculated values of \(D_{\text{e}0}(\text{H}) = 1227/977 \text{ cm}^{-1}\) and \(D_{\text{e}0}(\pi) = 715/520 \text{ cm}^{-1}\). The corresponding calculated values for neutral \(t\text{AA}^-\text{-N}_2\) are \(D_\text{a}(\text{H}) = 247 \text{ cm}^{-1}\) and \(D_\text{a}(\pi) = 449 \text{ cm}^{-1}\). Hence, similar to \(t\text{-AA}\text{-Ar}\), the calculations predict an ionization-induced \(\pi \rightarrow H\) switch in the most stable ion–ligand binding motif also for \(AA^{(+)}\text{-N}_2\). So far, no spectroscopic or quantum chemical data have been available for neutral \(AA^-\text{-N}_2\).

### 3.4 Implications for ionization-induced isomerization

IR spectroscopy and quantum chemical calculations presented here convincingly demonstrate the ionization-induced \(\pi \rightarrow H\) switch in the preferred binding motif for \(t\text{-AA}^{(+)}\text{-Ar}\). The ZEKE spectra of \(t\text{-AA}^-\text{-Ar}\) generated by isomer-selective REMPI of the neutral \(\pi\)-bonded complex have been interpreted with a \(\pi\)-bonded cation isomer, consistent with vertical Franck–Condon factors.\(^{50}\) These threshold ionization spectra do not exhibit any signature of the more stable H-bonded complex, probably due to the modest excess energy used for the ionization step achieved by two-colour two-photon (1 + 1') REMPI. In contrast, IR spectra of the \(t\text{-AA}^-\text{-Ar}_n\) clusters \((n = 1-2)\) produced by one-colour two-photon (1 + 1) REMPI of \(\pi\)-bonded \(t\text{-AA}\text{-Ar}_n\) show the signatures of the H-bonded dimer.\(^{50}\) These REMPI-IR spectra are compared to the current EI-IR spectra in Fig. S10 in ESI.\(^\dagger\) The REMPI-IR spectra display a systematic redshift of \(\sim 7 \text{ cm}^{-1}\) compared to the EI-IR spectra which probably arises from calibration issues in the REMPI-IR study. The accuracy of the calibration of the EI-IR spectra to better than 1 cm\(^{-1}\) is assured by a wavemeter monitored simultaneously with the IR laser scan. The REMPI-IR spectrum of \(t\text{-AA}\text{-Ar}\) shows two peaks in the N–H stretch range with similar intensity and separated by \(\sim 10 \text{ cm}^{-1}.\(^{40}\)

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**Fig. 11** IRPD spectra of \(\text{AA}^-\text{Ar}_2\) recorded in the AA' (bottom) and AA'–Ar (top) fragment channel, indicated as \(n-m = 2-0\) and 2–1, respectively. The positions of the transitions for \(\text{AA}^-\text{Ar}\) are listed in Table 2 along with their vibrational and isomer assignments. The vibrations of \(\text{AA}^-\text{Ar}_2\) with frequencies below 1300 cm\(^{-1}\) occur in the 2–1 fragment channel (loss of one Ar ligand), while those above 1300 cm\(^{-1}\) are detected in the 2–0 channel (loss of two Ar ligands).
In the previous work, this splitting could not be explained. Here, we propose that the two bands arise from the \( \nu_{\text{NH}} \) transitions of \( t\text{-AA}^-\text{Ar}(\pi) \) and \( t\text{-AA}^-\text{Ar}(\text{H}) \), respectively, which are split by \( \sim 12 \text{ cm}^{-1} \) in the corresponding EI-IR spectra. The significant intensity of the \( t\text{-AA}^-\text{Ar}(\text{H}) \) isomer in the REMPI-IR spectrum indicates that after the REMPI process a substantial population of the initially \( \pi \)-bonded isomer has been converted into the \( \text{H}\)-bonded configuration, probably due to the large excess energy available from \( 1 + 1 \) REMPI, which enables at least part of the population to overcome the \( \pi \rightarrow \text{H} \) isomerization barrier. A similar finite \( \pi/\text{H} \) population equilibrium has recently been observed in the REMPI-IR spectra of phenol\(^{-}\)–Rg dimers \( (R_g = \text{Ar and Kr}) \).\(^{17,19,37–39} \) Interestingly, \( \text{Ar} \) dimers of amino-benzonitrile did not show any \( \pi \rightarrow \text{H} \) isomerization yield.\(^{27,28} \)

The REMPI-IR spectra of the \( \pi \)-bonded \( t\text{-AA}^-\text{Ar}_2(2\pi) \) trimer show mainly the \( \nu_{\text{NH}} \) band of the \( t\text{-AA}^-\text{Ar}_2(\pi) \) isomer, indicating nearly unity yield for the \( \pi \rightarrow \text{H} \) isomerization of one of the \( \text{Ar} \) ligands.\(^{33,37,39} \) Again, this result is similar to that observed previously for the phenol\(^{-}\)–\( \text{Ar} \) trimer, for which the isomerization timescale has been measured in real time as \( \sim 7 \text{ ps} \).\(^{33,37} \) The 100% yield for \( \pi \rightarrow \text{H} \) isomerization in complexes with two \( \text{Ar} \) ligands has been explained by fast intracluster vibrational energy redistribution enabled by the presence of the second \( \text{Ar} \) ligand.

No spectroscopic information is available for neutral \( \text{AA}^-\text{N}_2 \)\(_m \) complexes. However, comparison with the related aniline–\( \text{N}_2 \) complex\(^{72} \) strongly suggests that \( \text{AA}^-\text{N}_2 \) dimers have a \( \pi \)-bonded equilibrium structure in the \( S_0 \) state, in line with the present quantum chemical calculations (Table 1). Thus, also the \( \text{AA}^-\text{N}_2 \) cluster is expected to show the ionization-induced \( \pi \rightarrow \text{H} \) site switching in the preferred ligand binding motif.

### 4. Concluding remarks

Size-selected \( \text{AA}^-\text{L}_n \) complexes with \( \text{L} = \text{Ar} \) and \( \text{N}_2 \) have been characterized by IR spectroscopy and quantum chemical calculations to characterize the intermolecular potential of this prototypical aromatic amide cation with a nonpolar and quadrupolar solvent. The data provide a first impression of the microsolvation of an aromatic amide with a hydrophilic environment. Systematic shifts observed in the \( \text{N}–\text{H} \) stretch frequencies \( \nu_{\text{NH}} \) (amide A band) as a function of the type and degree of solvation as well as the analysis of the photofragmentation data provide a quantitative picture of the interaction strengths and the cluster growth sequence, which are fully consistent with the calculations. For both ligands, \( \text{H} \)-bonding to the amide NH group is found to be more stable than \( \pi \)-stacking to the aromatic ring. However, the acidity of the NH group is relatively small. The preferred cluster growth begins with \( \text{H} \)-bonding of the ligands to the NH group and further ligands are attached to the phenyl ring and other less favourable binding sites. This is in contrast to solvation with hydrophilic solvents like water. \( \text{AA}^-\text{(H}_2\text{O})_n \) clusters form structures, in which a \( \text{H} \)-bonded solvent network is strongly \( \text{H} \)-bonded to the NH group.\(^{34,40,72} \) Comparison of the IRPD spectra of \( \text{AA}^-\text{L}_n \) with calculated spectra demonstrates that the experimental spectra are dominated by clusters composed of the \( t\text{-AA}^+ \) rotamer and no indication for the presence of the less stable \( c\text{-AA}^+ \) is obtained. The IRPD spectra of \( \text{AA}^-\text{L}_n \) recorded in the hydride stretch and fingerprint ranges provide for the first time valuable experimental information about the geometric and vibrational properties of \( \text{t-AA}^+ \) in the important amide A and I–III ranges. In particular, comparison with the corresponding neutral \( t\text{-AA} \) species reveals the effects of ionization on structure and bonding. Removal of an electron from the bonding \( \pi \) orbital (HOMO), which is largely delocalized over both the phenyl and amide moieties, strengthens the \( \text{C}–\text{O} \) bond and weakens the \( \text{N}–\text{H} \) bond of the amide. Significantly, ionization changes the preferred ion–solvent recognition motif in \( \text{AA}^+\text{Ar/N}_2 \) from \( \pi \)-bonding in the neutral to \( \text{H} \)-bonding in the cation electronic ground state. This \( \pi \rightarrow \text{H} \) change upon ionization was not detected in previous photoionization spectra of \( \text{t-AA}^+\text{-Ar} \),\(^{30} \) which do not detect the most stable \( \text{H} \)-bound global minimum in the cation due to restrictions from the Franck–Condon principle. Future efforts will concentrate on time-resolved spectroscopic measurements to probe the dynamics of the \( \pi \rightarrow \text{H} \) site-switching reaction in \( \text{AA}^-\text{L}_n \) with \( \text{L} = \text{Ar} \) and \( \text{N}_2 \) in real time, using picosecond pump-probe spectroscopy.\(^{34,36} \)

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### References


