Inner-shell X-ray absorption spectra of the cationic series NH$_y$\textsuperscript{+} (y = 0–3)

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Ion yields following X-ray absorption of the cationic series NH$_y$\textsuperscript{+} (y = 0–3) were measured to identify the characteristic absorption resonances in the energy range of the atomic nitrogen K-edge. Significant changes in the position of the absorption resonances were observed depending on the number of hydrogen atoms bound to the central nitrogen atom. Configuration interaction (CI) calculations were performed to obtain line assignments in the frame of molecular group theory. To validate the calculations, our assignment for the atomic cation N\textsuperscript{+}, measured as a reference, was compared with published theoretical and experimental data.

Introduction

To understand the function of large biomolecules, like amino acids and peptides, one has to study the properties of their fundamental constituents, \textit{i.e.} their electronic and geometric structure,\textsuperscript{1–4} as well as their dynamics.\textsuperscript{5–7} By exploiting the element specificity of inner-shell excitation, X-ray absorption spectroscopy (XAS) is an ideal tool to study the local electronic and geometric structure in the vicinity of a specific element within a molecule. Because of the rather large number of atoms within a biomolecule, photoabsorption spectra can be complex and sophisticated calculations are needed for their interpretation.\textsuperscript{8}

Thus, modelling accurate X-ray absorption spectra for biomolecules is very challenging.\textsuperscript{9,10} Instead of addressing an entire biomolecule, one can interpret the (measured) X-ray absorption spectrum as being composed of the contributions of smaller constituents or building blocks of larger molecules. For example, glycine (NH$_2$–CH$_2$–COOH), the simplest amino acid, connects the amino group NH$_2$ and the carboxyl group COOH via a methylene bridge. Solved in water, like all amino acids, glycine is a zwitterion composed of a protonated amino group R–NH$_3$\textsuperscript{+} and a de-protonated carboxylic acid COO$^-$ at its iso-electric point. Based on the assumption that the X-ray absorption is dominantly determined by the local chemical environment, knowing the XAS of NH$_2$\textsuperscript{+} and COO$^-$ will facilitate the interpretation of more complicated XAS of \textit{e.g.} glycine.

An inherent difficulty of this approach is that both of these building blocks of glycine are transient ionic molecules which are (almost) impossible to prepare as a solid or as a solution in water. However, an ion beam arrangement can be used to deliver ionic samples to the X-ray interaction region to address their absorption spectrum.\textsuperscript{11–15} Mass spectroscopy with high resolving power does not only offer the possibility to prepare a pure, transient molecular ion beam, but additionally provides control about the chemical environment of the molecular ion, enabling or disabling the interaction of chosen elements within the molecule (see Fig. 1). Depending on the number $y$ of hydrogen atoms bound to the central nitrogen atom in NH$_y$\textsuperscript{+}, the electronic structure of the respective molecular ion and hence its absorption features will change. Especially inner-shell resonances, like the nitrogen 1s–2p resonances, are sensitive to the chemical environment of a molecule \textit{see e.g.} ref. 16–18, enabling us to probe the changes in the electronic structure of the respective molecular ions by performing a XAS-experiment.

Whereas there is plenty of previous work on the neutral species of the series NH$_y$\textsuperscript{+} \textit{(y = 1–3)} little work on the cations NH$_y$\textsuperscript{+} \textit{(y = 0–3)} has been published. Theoretical work on the electronic structure of NH$^{+}$\textsuperscript{11,12} and NH$_3$\textsuperscript{+13} has been done calculating molecular potential curves and bonding angles. Experiments on molecular ions addressed the valence electronic structure of NH$_2$\textsuperscript{+} using VUV photoionisation\textsuperscript{14} or the determination of the...
absolute cross section of NH\(^+\) using electron impact ionisation.\(^{35}\) Yet, there is no detailed information available on the inner-shell XAS of the cationic series NH\(^+\)\(^y\) apart from the atomic cation, N\(^+\), which has been studied previously by Gharaibeh \textit{et al.}\(^{36}\).

Furthermore, the role of NH\(_y\) with different numbers \(y\) of hydrogen atoms has recently been studied in the liquid phase by Ekmova \textit{et al.} for alkamines in different solutions.\(^{37,38}\) They show a strong dependence of the N 1s X-ray spectra on the number \(y\) of H atoms and the solution itself.

Here, we report on our systematic investigations on the X-ray absorption for the cationic series NH\(^+\)\(^y\) (\(y = 0–3\)) in a combined experimental and theoretical work.

**Experiment**

The PIPE merged-beams set-up\(^{39,40}\) at the XUV beamline P04\(^{41}\) of PETRA III, DESY, was used to record XAS spectra of NH\(^+\)\(^y\) in the photon energy range of the nitrogen K-edge. Details of the preparation of a molecular ion beam at PIPE have been given in a previous publication.\(^{42}\)

As primary source for the production of the target molecular cations we have used gaseous NH\(_3\). The gas leaked into the plasma chamber of a 10 GHz Electron Cyclotron Resonance (ECR)\(^{43}\) ion source \textit{via} an electronic needle valve keeping the gas pressure in the order of \(2 \times 10^{-5}\) hPa.

Fig. 1 shows the mass spectrum of the molecular cation series of NH\(^+\)\(^y\) (\(y = 0–3\)). As can be seen, the resolving power of the preparation dipole-magnet mass spectrometer is sufficient to distinguish each single ion of the series. Both elements, nitrogen and hydrogen, have two naturally stable isotopes but the abundance ratio for both cases, \(^{14}\)N/\(^{15}\)N and \(^1\)H/\(^2\)H, is in the order of 0.99/0.01.\(^{44}\) Thus, the composition of the mass lines in Fig. 1 can be considered to be almost pure. A possible NH\(_4\)\(^+\) molecular ion has the same mass-to-charge ratio as \(\text{H}_2\text{O}^+\). However, the corresponding absorption spectrum did not show any nitrogen resonances, indicating that no NH\(_4\)\(^+\) molecular ions were produced in our ion source.

A beam of singly charged molecular ions was prepared and accelerated to 6 keV kinetic energy, transported to the interaction region on ground potential and collinearly overlapped with the X-ray photons of P04 along an effective absorption length of 1.7 m. The vacuum chamber base pressure of the interaction region was in the order of \(1 \times 10^{-8}\) hPa.

At the nitrogen K-edge, the X-ray photons create an inner-shell hole in the ionic target which results in subsequent Auger decay. The excitation and ionisation is accompanied by possible shake-off processes and is followed by dissociation producing N\(^+\)\(^q\) (\(q = 2, 3\)) ions. These ions were separated from the target ionic beam with a second magnetic-dipole mass spectrometer. The N\(^+\)\(^q\) (\(q = 2, 3\)) ions have been counted with a channeltron as a function of the photon energy.

The yield of photoexcited ions of an atomic nitrogen ion N\(^+\) target was measured as a reference to help identifying the spectroscopic features for the molecular targets, as recently done for \(\text{H}^+\).\(^{42}\) The X-ray photons delivered by the P04 beamline of PETRA III were dispersed by a 400 lines per mm variable line spacing grating (VLS) favouring high photon flux in the order of \(1 \times 10^{12}\) photons per s to \(7.5 \times 10^{13}\) photons per s for monochromator exit slits from 20 \(\mu\)m to 1500 \(\mu\)m. The molecular ion yields were measured with a monochromator exit slit of 500 \(\mu\)m and for the atomic ion yield a slit width of 50 \(\mu\)m was chosen. This results in an energy bandwidth in the order of \(\Delta E = 0.5\) eV for the molecular spectra and \(\Delta E = 0.05\) eV for the atomic spectrum. The energy axis of the P04 monochromator was calibrated with the known resonance positions of the atomic N\(^+\) 1s \(\rightarrow\) 2p resonance group\(^{36}\) (see Fig. 3a). The resulting uncertainty of the experimental photon-energy scale is estimated to be approximately 0.1 eV.

**Theory details**

To assign the observed ion yield peaks with X-ray absorption resonances, we have conducted X-ray absorption cross section calculations with the XMOLECULE toolkit.\(^{45,46}\) The calculations are based on geometries obtained from geometry optimisation for the respective NH\(^+\)\(^y\) cationic ground state using GAMESS\(^{47}\) on the ROHF/MP2 level employing a 6-311G(d,p) basis set.\(^{48}\) We have calculated the orientation-averaged X-ray absorption cross section,

\[
\sigma = \frac{4}{3} \pi \omega \chi |\langle \psi_i | r | \psi_f \rangle |^2 \delta(\omega - E_{\text{photon}}),
\]

where in eqn (1) \(\omega = E_f - E_i\) and \(|\psi_i\rangle, |\psi_f\rangle\) are the initial and final electronic states with energies \(E_i\) and \(E_f\), respectively. The quantity \(|\langle \psi_f | r | \psi_i \rangle|\) is the transition dipole matrix element between the initial and final electronic state, \(\chi \approx 1/137\) is the fine structure constant, and \(\hbar = 1\). For NH\(^+\)\(^y\) and NH\(_2\)\(^+\), the initial cationic states, \(|\psi_i\rangle\), were described with orbitals obtained from a single-configuration-restricted open-shell Hartree-Fock procedure. The initial states |\psi\rangle for NH\(^+\) and N\(^+\) have been described based on a complete active space self-consistent field calculation with an active space constructed by the 3\(\sigma\) and the two
π orbitals for NH+ and the three atomic 2p orbitals for N+, respectively. These calculations are part of a new implementation in the XMOLECULE toolkit. The final states |ψ_f⟩ in eqn (1) were described in a configuration interaction (CI) calculation employing the same orbitals as for the cationic initial state. The CI calculations included all configurations that are constructed from the cationic reference configurations by promoting a single electron from the K shell to an unoccupied orbital. Moreover, further configurations were included involving an additional excitations of the valence electrons into virtual/singly occupied orbitals. The calculations were conducted using spin- and symmetry-adapted configuration state functions employing the respective discrete point symmetry of the molecule. In cases where the point symmetry of the molecule is not discrete (e.g. D_3h) the irreducible representation of respective states was identified via post-processing of the calculated results. For all the X-ray absorption calculation we used a 6-311G basis set augmented with additional 6 diffuse basis functions of angular momentum s, p, and d, respectively, according to the recipe of Kaufmann et al.9

For efficient integral evaluation XMOLECULE employs the libcint library.50 Although the employed basis set contains many diffuse functions, it becomes insufficient for very high valence excitations approaching the electronic continuum. Therefore, the agreement with experimental spectra is expected to decrease with higher X-ray excitation energies. Apart from this discrepancy there is a certain imbalance in the description of initial and final electronic states. This imbalance leads to a calculated transition energy which is slightly too low. Thus, we obtain calculated X-ray absorption lines that have lower energies by 1 eV to 2 eV compared to the experimental data. For better comparison between experimental and theoretical results, we have shifted the calculated absorption lines to higher values, as specified in detail within the results section. In particular, we find that for all molecules the photon-energy range \( E_{\text{ph}} \) > 405 eV involves a slightly smaller energy shift compared to \( E_{\text{ph}} \) < 405 eV. Furthermore, the applied shift slightly varies along the series NH\(_y^+\) (y = 0–3). We attribute this varying relative shift to slight differences in the orbital relaxation of the different molecules and respective excitation ranges.

A similar approach for calculating X-ray absorption spectra has been employed in earlier works\(^{31,52}\) but with a slightly different configurational space. The mentioned energy shift relative to the experimental data could potentially be avoided by using an orbital set for the final core excited state that has been optimised in the presence of the core hole and might result in an improved modelling of core-hole relaxation effects. However, the calculation of electronic transitions (eqn (1)) becomes computationally very demanding with different orbital sets for initial and final state in combination with a large configuration space. We think that the resulting energy shift of 1 eV to 2 eV is acceptable for the purposes of our study and therefore decided keep a common orbital set.

Results and discussion

The normalised ion yields \( Y \) measured for the target ion series NH\(_y^+\) (y = 0–3) are shown in Fig. 2 from y = 0 (panel a) to y = 3 (panel d).

![Image](https://via.placeholder.com/150)

**Fig. 2** Product ion yields \( Y \) (see eqn (2)) from photoionisation and/or photofragmentation of the target ion series NH\(_y^+\) (y = 0–3) (a) N\(^+\) → N\(^{3+}\), (b) NH\(^+\) → N\(^{2+}\), (c) NH\(_2^+\) → N\(^{2+}\), and (d) NH\(_3^+\) → N\(^{2+}\) measured in the photon energy region of the nitrogen K-edge. The light blue vertical lines mark the energy region of the atomic nitrogen 1s → 2p resonance group in panel (a). For the panels (b)–(d) the shift of the respective molecular resonances to lower excitation energies can be seen. For details of the comparison of the different decay channels of the atomic and molecular targets see the main text.

The curves consist of the N\(^{3+}\) ion yield for the atomic N\(^+\) target and the N\(^{2+}\) ion yield for the molecular targets NH\(_y^+\) (y = 1–3). The N\(^{2+}\) and N\(^+\) product channels, for the N\(^+\) and NH\(^+\) primary beams, respectively, exhibited excessive backgrounds from collisions with residual gas targets such that no meaningful photoinduced ion yields could be measured in these product channels.

The normalised photoinduced ion yield \( Y \) is given by the background-subtracted ion count rate \( R \) measured with the channeltron detector divided by the target ion current \( I_{\text{ion}} \) and photon current \( \phi_{\text{ph}} \),

\[
Y = \frac{R}{I_{\text{ion}} \cdot \phi_{\text{ph}}}
\]

(2)

In principle, the PIPE setup allows one to put the measured ion yields on an absolute cross-section scale.\(^{39}\) However, for the
present experiment, there are two unknown quantities: the transmission of the molecular fragments from their point of origin to the detector as well as the exact branching ratio into the measured fragment channel. Still, we can assume that the normalised ion yield \( Y \) is proportional to the partial absorption cross section of the respective fragment channel \( N \). Upon absorption of an X-ray photon in the energy range of the nitrogen 1s orbital, the ionic targets can either be resonantly excited or, above the threshold, photoionised. In both cases, an inner-shell hole remains which can subsequently decay by an Auger process, thereby changing the charge state of the target. To obtain the observed final fragment charge state \( q \) = 3 after resonant excitation of \( N^- \) two electrons need to be emitted from the resulting \( 1s2s^22p^2np \) configuration. For configurations where a two-step Auger cascade is energetically not allowed, i.e. for \( n = 2 \), in particular, a double Auger process is required. Such processes are known to appear with a probability of a few percent following atomic K shell ionisation of light elements.\(^{40,53–58}\) For the molecular ions \( \text{NH}^y^- \) (\( y = 1–3 \)) there are more pathways, resonant and non-resonant, to create the detected \( N^2+ \) fragment compared to the two ionisation processes needed for the \( N^- \) target to reach \( N^3+ \), since hydrogen partners can leave the system either as neutral atoms or as protons. \( N^2+ \), for instance, can be created from \( \text{NH}^- \) via single Auger decay and release of a neutral hydrogen or via double Auger decay and release of a proton. From \( \text{NH}_2^- \) and \( \text{NH}_3^- \) the creation of \( N^2+ \) ions can be expected to be less likely, since it requires more hydrogen to leave the molecule as neutral atoms. This trend is reflected in our data by a steep drop of the \( N^2+ \) count rate when gradually changing the molecular target from \( \text{NH}^- \) \( \text{NH}_2^- \) and \( \text{NH}_3^- \) (with each additional hydrogen the ion yield drops by an order of magnitude). However, since our experimental set-up does not allow us to detect neutral fragments or \( N^2+ \) ions, we have no measure on competing fragmentation channels.

Distinct characteristic behaviour can be observed in the ion yield spectra of Fig. 2. On the one hand, below the 1s ionisation threshold a strong resonance group is observed in each spectrum which originates in the atomic case from the transition \( 1s \rightarrow 2p \). At higher energies, except for \( \text{NH}^+ \), the first 1s ionisation threshold is visible together with Rydberg resonances. Increasing the photon energy and passing the ionisation threshold one may expect an increase in the ion yield, since the initial absorption leads to emission of an electron. For the \( N^- \), \( \text{NH}_2^- \), and \( \text{NH}_3^- \) cations, such an increase of the ion yield above the threshold is clearly seen. Remarkably, almost no increase in the ion yield is seen for \( \text{NH}^- \) (panel b in Fig. 2). This observation may indicate that the mechanisms that lead to creation of \( N^2+ \) ions via emission of additional electrons and release of hydrogen atoms differ for the above and below threshold regions for \( \text{NH}^- \) and any other ion in the series \( \text{NH}_y^- \).

The blue dashed lines in Fig. 2 mark the energy region of the atomic nitrogen 1s \( \rightarrow 2p \) resonance group. As can be seen in the spectra for the molecular ionic series \( \text{NH}_y^- \) (\( y = 1–3 \)), the respective molecular resonance shifts towards lower energies depending on the number of hydrogen atoms bound to the central nitrogen atom. This is due to increasing hybridisation between the nitrogen valence and hydrogen orbitals. For the atomic nitrogen ion \( N^- \), we observe sharp Rydberg lines below and above the lowest 1s ionisation threshold (Fig. 3b), while for the molecular targets the resonance features are broader and overlap with one another. In the following we discuss the assignments of the X-ray absorption resonances for each target \( \text{NH}_y^- \) (\( y = 0–3 \)) in more detail.

**Atomic target \( N^- \)**

The ground state of the \( N^- \) cation is \( 1s^22s^22p^2{}^3P \). Within the experimental ion beam, a non-statistical mixture of several meta-stable terms exists, as has been pointed out before.\(^{16}\) These various states result in a multitude of multiplet lines as observed in Fig. 3. For comparison of the measured \( N^+ \) ion yield (orange dots in Fig. 3) with the calculated X-ray absorption resonance positions (vertical light blue lines in Fig. 3) we take into account the terms \( 1s^22s^22p^2{}^3P \), \( 1s^22s^22p^2{}^1D, 1s^22s^22p^2{}^3S, \) and \( 1s^22s^2{}^1P^3\Sigma^+ \) with the relative weights of 0.54, 0.11, 0.03, 0.32, respectively, as suggested by Gharai\textit{e}b et al.\(^{16}\) For a better comparison, we have shifted the calculated transition energies by 2.1 eV to higher energies for the region showing \( 1s \rightarrow 2p \) excitations (below 405 eV) and by 1.1 eV for the region showing...
higher excitations above 405 eV. Overall, the calculated data show good agreement with the measured ion yield for the energy position of the resonances values below 427 eV. The discrepancies at photon energies above 427 eV are due to the limited capability of the employed basis set to adequately describe the electronic continuum as discussed in the section Theory Details. For the region below 405 eV, the ion-yield peak heights coincide with the calculated absorption cross section. However, for the region above 415 eV the calculated absorption strength does not always agree with the measured abundance of ions. A particularly drastic disagreement is seen for the $1s^22s^22p^33s^13p^1$ transition at 419 eV. The signal in the measured ion yield is remarkably low (magnified by a factor of 200 in Fig. 3b) in contrast to the relatively strong calculated absorption cross section. The $1s^22s^22p^33p^13p^1$ term, e.g., has a particularly high spin that may lead to blocking of certain Auger decay channels, since the spin of most electrons does not match the spin of the core hole. The production of $N_3^+$ ions might therefore be suppressed for this core excited configuration relative to other core excited configurations.

Our assignment of the individual resonances for the first resonance region is given in Table 1 and compared with previous calculations using the multi-configuration Dirac–Fock (MCDF) method and the $R$-matrix method.36 Most of our results match those of previous calculations, however, there is a slight discrepancy regarding the assignment of the $1s^22s^22p^33s^13p^1$ transition. In the previous work36 this line is, according to the $R$-matrix calculation, associated with the first resonance at 399.8 eV whereas we identify this transition at $\approx$ 401.5 eV (in agreement with the previous MCDF calculation36).

Overall we conclude that the applied calculation procedure is sufficient to conduct assignment of the resonant transitions.

**Molecular target NH$^+$**

The NH$^+$ cation has two close lying nearly degenerate terms$^{31,32}$ that both result in an absorption signal from our ion beam: $1s^22s^22p^33s^12\Sigma^+$ and $1s^22s^22p^33s^11s^22\Sigma^+$.

With our geometry optimisation we obtained a bond distance of 1.065 Å for the $2\Pi$ term and of 1.080 Å for the $2\Sigma^+$ term. Fig. 4 shows the calculated absorption resonances (light blue vertical lines) for the NH$^+$ cation compared to the measured $N_2^+$ ion yield (dark blue dots). In the figure we used 0.8 and 0.2 as weights for the $2\Pi$ and $2\Sigma^+$ terms, respectively. The red dashed line in Fig. 4 is the result of a convolution of the calculated resonances characterised by their positions and absorption oscillator strengths with a 400 meV FWHM Gaussian function.

In the region below 405 eV one can clearly identify four peaks in the experimental spectrum. The weak resonance at 395 eV can be assigned to a $1s^22s^22p^33s^11s^22\Sigma^+$ excitation. In the region 397 eV to 400 eV our calculation predicts four excitation resonances $4\Sigma^+ \rightarrow 4\Pi, 2\Pi \rightarrow 2\Delta, 2\Pi \rightarrow 2\Sigma^+$, and $4\Pi \rightarrow 2\Sigma^+$. However, in the measured ion yield one can clearly resolve three peaks, only. The calculation suggests that the $2\Pi \rightarrow 2\Delta$ transition is hidden between the $4\Sigma^+ \rightarrow 4\Pi$ and the $4\Pi \rightarrow 4\Sigma^+$ resonances. The remaining resonance peak at 399.5 eV can be associated with a $2\Pi \rightarrow 2\Sigma^+$ transition.

Above an excitation energy of 405 eV the resonance structures in the measured ion yield are very broad. This might be attributed to the large broadening due to a steep potential energy curve in the final state. The resonance at 411 eV is rather isolated. According to our calculation, the dominant broad peak around 411 eV can mainly be assigned to a $1s^2 \rightarrow 4\sigma (2\Pi \rightarrow 2\Pi)$ excitation. Above 415 eV we see the ion yield

| Resonance transition | CI present work (eV) | MCDF (eV) | $R$-Matrix (eV) |
|----------------------|---------------------|-----------|----------------|
| $1s^22s^22p^33p^1$  | 399.8               | 399.9     | 399.7          |
| $1s^22s^22p^32s^1$  | 400.1               | 400.6     | 400.2          |
| $1s^22s^22p^3$      | 400.6               | 400.0     | 400.6          |
| $1s^22s^22p^32s^1$  | 400.6               | 400.0     | 400.7          |
| $1s^22s^22p^3$      | 401.5               | 400.8     | 399.9          |
| $1s^22s^22p^3$      | 402.5               | 402.3     | 401.3          |
| $1s^22s^22p^32s^1$  | 403.3               | 402.5     | 402.3          |

Fig. 4 N$^+$ ion yield $Y$ (dark blue dots) for the NH$^+$ cation (a) in the energy region of the $1s \rightarrow 2p$ excitation of atomic nitrogen and (b) in the energy region of the atomic nitrogen K-edge. The light blue vertical bars indicate the calculated absorption resonance positions and are proportional to the oscillator strength. The red dashed line shows the calculated absorption cross section obtained via convolution with a 400 meV (panel a) (FWHM) and 3 eV (panel b) (FWHM) Gaussian function.
Table 2  Resonance positions $E_{res}$ and line assignment of the observed resonances in the NH$^+$ molecular target ion (see Fig. 4). The assignment is done according to the dominant CI configuration. The uncertainty of the experimental values is $\Delta E_{res} = 0.1 \text{ eV}$

| Initial state | PIPE (experiment) (eV) | CI (theory) (eV) |
|---------------|------------------------|------------------|
| $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2 \Sigma^- \rightarrow 3\sigma^2 \Sigma^-$ | 394.9 | 394.8 |
| $1\sigma^2 1\pi^2 \Pi$ | 397.8 | 398.0 |
| $1\sigma^2 4\sigma^2 \Sigma^-$ | 409.3 | 412.4 |
| $1\sigma^2 4\sigma^2 \Sigma^-$ | 414.3 | |
| $1\sigma^2 3\sigma^2 1\pi^2 \Pi$ | 398.8 | 398.2 |
| $1\sigma^2 1\pi^2 \Sigma^-$ | 398.8 | 398.6 |
| $1\sigma^2 1\pi^2 \Sigma^-$ | 399.6 | 399.7 |
| $1\sigma^2 4\sigma^2 \Pi$ | 411.4 | |
| $1\sigma^2 4\sigma^2 \Pi$ | 414.3 | |

decreasing with photon energy, whereas the calculated convoluted absorption cross section suggests rather the opposite trend. The assignments for the dominant transitions in the NH$^+$-XAS are summarised in Table 2.

**Molecular target NH$_3$**

The NH$_3$ molecular cation has $C_2v$ symmetry, but has an almost linear geometry with a very flat bending potential in its ground state. The cationic ground level is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^13B_1$. For the X-ray absorption calculation we also included the closed shell level $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^21A_1$.

From geometry optimisation, we obtain an NH bond distance of 1.03 Å and a bond angle of 150° for the triplet level and a bond distance of 1.05 Å with a bond angle of 107° for the singlet level. Fig. 5 shows the calculated absorption resonance positions (light blue vertical lines) for the NH$_3^+$ cation compared to the measured N$^{2+}$ ion yield (green dots). The orange dashed line is a convolution of the calculated absorption resonance positions and are proportional to the oscillator strength. The orange dashed line shows the calculated absorption cross section obtained via convolution with a 1.0 eV (FWHM) Gaussian function.

**Molecular target NH$_3$**

The neutral NH$_3$ molecule has a pyramidal geometry and hence its symmetry group is $C_3v$. The cation NH$_3^+$ has a planar geometry and thus belongs to symmetry group $D_{4h}$. The electronic ground state of the cation is $(1a_1)^2(2a_1)^2(1e)^4(1a_2)^12A_1^g$. Geometry optimisation gives an NH bond length of 1.024 Å.

**Chemical shift**

As indicated by the light blue dashed lines in Fig. 2, the respective 1s $\rightarrow$ 2p resonances shift to lower excitation energies when going from the atomic cation N$^+$ to the molecular cation NH$_3^+$. For the energies of the 1s $\rightarrow$ 2p resonance peaks, we obtain a systematic sequence of 399.8 eV, 398.8 eV, 396.4 eV,
395.2 eV. With more hydrogen atoms in the molecule, additional electrons contribute to core-hole screening effects\(^2\) and lower the energy of the core excited state. As discussed previously\(^4\), this effect leads to a systematic lowering of core excitation resonances. To further confirm this trend, we calculated the ionisation potential of the molecular cations using a \(\Delta\)SCF calculation, in which the ionisation energy is obtained from separate SCF calculations for the initial and final electronic states, respectively (see Table 5). As can be seen, apart from the metastable configurations that involve vacancies in 2s/3\(\sigma\) orbitals (\(\Sigma^+\) for N\(^+\) and \(\Sigma^-\) for NH\(^+\)), the ionisation potential shifts systematically to lower energies with increasing number of hydrogen atoms.

At 400 eV, in Fig. 2 a clear shift of the resonant structures to lower photon energies with increasing number \(y\) of H atoms is found for the series of free NH\(^y\)\(^+\) ions. This is contrary to shifts found for the alkylamines\(^3\), where the N 1s resonances are shifting to higher photon energy with increasing number of H atoms.

**Absolute count rate for the lower and upper resonance regions**

As indicated by the different scale on the calculated cross section axes in Figs. 3–6(a) and (b), the absorption lines for the higher Rydberg region (> 415 eV) are weaker than for the first resonance region (390 eV to 405 eV). In contrast, the measured N\(^2+\) ion yield is significantly larger in the Rydberg region compared to the first resonance region. This clearly indicates that the relative probability for creating N\(^2+\) ions is larger for the more highly excited resonances than for the resonances with lower excitation energies. The relative production yields of N\(^2+\) subsequent to excitation into these two resonance regions can be read off the relative change of the ion yield/cross section scale in Figs. 3–6. For N\(^+\) we observe a factor \(\approx 5\) higher N\(^2+\) production rate, for NH\(^+\) the factor is \(\approx 1.8\), for NH\(^2+\) the factor is \(\approx 3.7\), and for NH\(^3+\) the factor is \(\approx 2.3\).

### Table 3: Resonance positions \(E_{ph}\) in and line assignments of the observed resonances in the NH\(^2+\) molecular target ion (see Fig. 5) in its cationic ground level \(((3a_1)^2(1b_1)^2(1b_2)^2(3a_2)^2(1b_3)^2B_1)\) or excited level \(((3a_1)^2(2a_2)^2(1b_2)^2(3a_2)^2(3a_3)^2A_1)\). The assignment is done according to the dominant CI configuration. The uncertainty of the experimental values is \(\Delta E_{ph} = 0.1\) eV.

| Resonance assignment | PIPE (experiment) (eV) | CI (theory) (eV) |
|----------------------|------------------------|------------------|
| (3a_1)^2(1b_1)^2B_1 | 396.4                  | 396.1            |
| 1a_1 \rightarrow 3a_1 3b_1 | 396.4                  | 396.5            |
| 1a_1 \rightarrow 1b_1 A_1 | 407.2                  | 407.7            |
| 1a_1 \rightarrow 4a_1 B_1 | 407.7                  | 409.8            |
| 1a_1 \rightarrow 2b_1 A_1 | 409.6                  | 412.8            |
| 1a_1 \rightarrow 5a_1 B_1 | 412.7                  | 412.8            |
| 1a_1 \rightarrow 2b_2 A_2 | 412.8                  | 413.0            |
| 1a_1 \rightarrow 3b_2 A_2 | 413.0                  | 415.6            |
| 1a_1 \rightarrow 2b_3 A_3 | 414.1                  | 416.4            |
| 1a_1 \rightarrow 2b_4 A_4 | 416.1                  | 416.4            |
| 1a_1 \rightarrow 5a_1 A_1 | 416.4                  | 416.4            |

### Table 4: Resonance positions \(E_{ph}\) and line assignments of the observed resonances in the NH\(^3+\) molecular target ion in its ground level \(((1a_1)^2(2a_2)^2(1b_1)^2(1b_2)^2(1b_3)^2(1b_4)^2(1b_5)^2A_1)\) (see Fig. 6). The assignment is done according to the dominant CI configuration. The uncertainty of the experimental values is \(\Delta E_{ph} = 0.1\) eV.

| Assignment | PIPE (experiment) (eV) | CI (theory) (eV) |
|------------|------------------------|------------------|
| 1a_1 \rightarrow 1a_2^2A_1 | 395.2                  | 395.2            |
| 1a_1 \rightarrow 2c^2E^* | 408.1                  | 408.3            |
| 1a_1 \rightarrow 2c^2E^* | 410.8                  | 410.3            |
| 1a_1 \rightarrow 2a_2^2A_1 | 410.8                  | 411.2            |
| 1a_1 \rightarrow 2a_3^2A_1 | 413.9                  | 413.4            |
| 1a_1 \rightarrow 3e^1E^* | 413.9                  | 414.1            |
| 1a_1 \rightarrow 4c^2E^* | 413.9                  | 417.3            |

### Comparison with glycine

Fig. 7 shows a comparison between the absorption spectrum of glycine around the nitrogen K-edge\(^6\) and our measured ion yield of NH\(^2+\). The data of glycine was scaled to match the intensity at energies above the K-edge and the figure is drawn with two different energy axes, because of the different chemical environment of the two molecules. As can be seen, the first...
resonances below the K-edge are prominent in both spectra, but at higher energies the resonances are much smoother in glycine. The three resonances for glycine are assigned to excitations into the 2b2, 2b1, and 1a1 orbitals, respectively.

In contrast, the spectra of glycine show some significant differences compared to the spectra of NH3+. Thus, this comparison between NH3+, NH2+, and glycine demonstrates that the spectra of ionic fragments can be useful to identify building blocks of more complex molecules.

Conclusions

The N2+ ion yields of the target molecular cations NH3+ (y = 1–3) have been measured in the energy range of the nitrogen K-edge and their absorption resonance structure has been determined. We have calculated X-ray absorption cross sections based on the configuration interaction method utilising the XMOLECULE toolkit. Our calculations show excellent agreement with the ion yield data. For most of the observed transitions, the ion yield seems to correlate with the calculated absorption strength. However, we quantify a trend for a lower abundance of N2+ ions for excitation in the first resonance region compared to higher resonances. This trend as well as particular deviations (e.g., the very low ion yield for the N+ 1s22s22p33p5 → 1s22s22p53p1 transition) indicate that the mechanism behind the production of the highly charged ions depends on the specific state populated by the X-ray absorption. In future studies, this effect will be further investigated by comparing the relative ion yields of different fragment charges.

The measured ion yield resonances have been identified by the calculated absorption transitions (see Tables 2–4). Depending on the number of hydrogen atoms bound to the nitrogen atom we report characteristic structures in the X-ray absorption. Each additional hydrogen atom and its electron has a significant impact on the spectral features of the different absorption spectra (Fig. 2). These characteristic resonance structures in the NH3+ series might help to identify different molecular cationic (sub-)groups within larger molecular complexes such as the amino acid glycine, for example. Nevertheless, the comparison of the free ions NH3+ with the amine group in different solutions and molecular environments shows the tremendous influence also of the larger chemical surrounding.

Conflicts of interest

There are no conflicts to declare.

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