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X-ray induced fragmentation of size-selected salt cluster-ions stored in an ion trap

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Supplementary Information

Examples of mass spectra

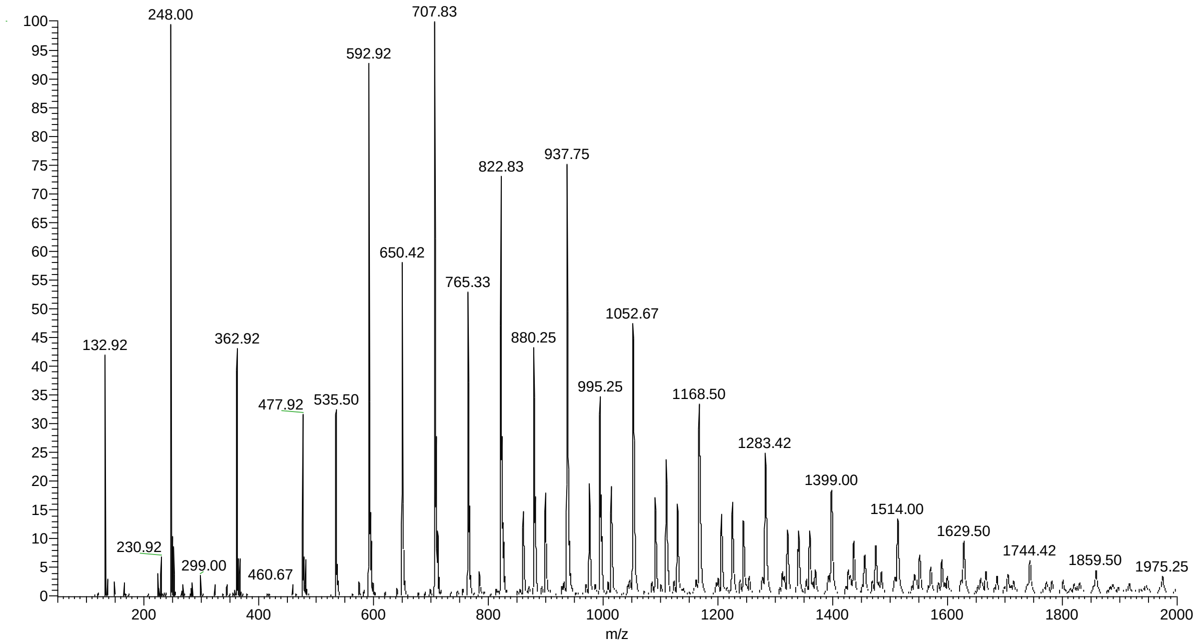

Figure S1. Mass spectrum produced from ammonium sulphate solution displaying peaks before mass selection.

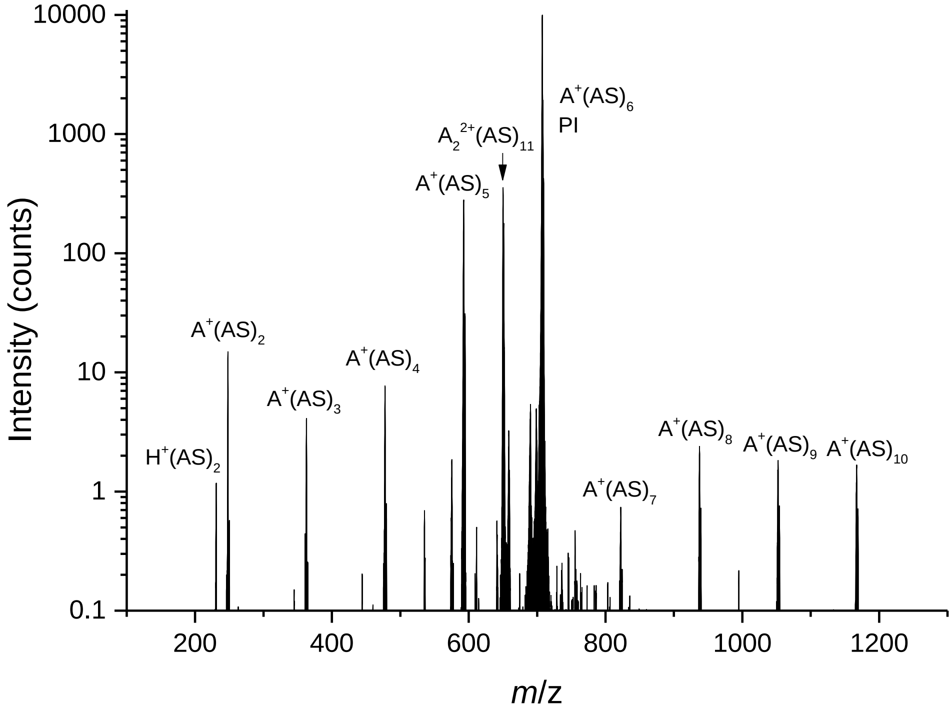

Figure S2. Mass spectrum (on semi-logarithmic scale) showing the abundance of ions after size selection of the cluster $A^+(AS)_6$ and irradiation by 406.8 eV X-rays (N1s range).

The peak $A_2^{2+}(AS)_{11}$ at 650.5 Th in Fig. S2 is formed by loss of an AS unit from the $A_2^{2+}(AS)_{12}$ cluster overlapping the parent ion $A^+(AS)_6$ at 708 Th. The isotope pattern of $A_2^{2+}(AS)_{11}$ observed in the spectrum matches the expected pattern calculated from literature isotope abundances. The peak is not found to be influenced by the X-rays as it maintains a constant ratio to the parent ion over the energy ranges investigated. Thus, it is likely formed by CID from the helium gas, analogous to the formation of $A^+(AS)_5$ from $A^+(AS)_6$ as discussed in the main text. In addition, the singly charged ions formed by fragmentation of $A_2^{2+}(AS)_{12}$, *i.e.*, $A^+(AS)_n$ with n = 7–10 in Fig. 2, did not exhibit any trends indicating that their formation is dependent upon the X-ray photon energy.

The formation of $H^+(AS)_n$ clusters is, as mentioned in the main text, at least an order of magnitude less frequent compared to the formation of corresponding $A^+(AS)_n$ clusters; this can clearly be seen in Fig. S2. However, it should be noted that the relationship between the fragment size and the X-ray dependency of the fragment abundance follows the same general trends as established for $A^+(AS)_n$ fragments. That is, the larger fragments, $H^+(AS)_6$ and $H^+(AS)_5$, show no dependency on photon energy; smaller fragments, $H^+(AS)_4$ and especially $H^+(AS)_3$ and $H^+(AS)_2$, displays the absorption edge.

Model for the relative importance of photoionization and electron-impact ionization of target ions in helium

Introduction

In the present set of experiments, ionic clusters are trapped and stored in a cylindrical ion trap and translationally cooled by helium at a pressure of about 10^{-3} mbar. The subsequent probing of the clusters by means of X-ray radiation inherently induces ionization of helium, and, due to the high helium-to-cluster ratio, photoelectrons from helium may core-excite and core-ionize the clusters by electron impact, in addition to valence ionization. In order to evaluate the relative importance of electron-impact vs. photo-ionization of target ions in a helium atmosphere we will here develop an analytical model that takes into account both the geometry of the experimental setup and the helium pressure. Employing this model with the specific parameter values that applies to our experiments shows that core ionization by electron impact is negligible compared to direct photoionization, and this result is assumed to hold also for the corresponding core excitation processes. In the following, we will first present the assumptions underpinning the model, before deriving the working equations.

Assumptions

We consider an idealized geometry of the ion trap as a cylinder of length L, radius R_t and containing ions and helium at constant number densities ρ_i and $\rho_{He} = p_{He}/\mathrm{k_B}T$, respectively, such that $\rho_i \ll \rho_{He}$. The sample is assumed exposed to a rather narrow beam of X-rays characterized by photon energy E and a uniform flux ϕ_p such that the photon beam is co-centric with the trap and of radius $R_p < R_t$.

Not only target ions but also helium is photoionized by the X-rays. We consider only single ionization of helium, *i.e.*, double ionization is neglected. This is justified by the cross section for double ionization being two orders of magnitude smaller than that of single ionization—rendering single-photon double ionization of little importance here—and by the fact that multi-photon double ionization is negligible at normal photon fluxes at a synchrotron-radiation facility.

The conditions of the trap are assumed such that the photoelectrons originating from helium leave the trap after a single pass and that the electron attenuation length is much longer than the dimensions of the trap. Both of these assumptions are well met under the experimental conditions reported here.

Without loss of generality, we consider unpolarized photons, implying that the photoelectrons are preferentially emitted in the radial direction, *i.e.*, normal to the common axis of the trap and the beam and with an angular distribution of $\sin^2\theta$ in the angle between the beam and the electron momentum. For simplicity, we will assume that ionization of helium only leads to electrons emitted normal to the beam.

Qualitative considerations

With the assumptions and simplifications stated above, photoionization of target ions takes place at a rate of $\eta_i^p = \phi_p \sigma_i^p(E)\rho_i V_p$, where $V_p = \pi R_p^2 L$ is the trap volume that is illuminated by X-rays and $\sigma_i^p(E)$ is the cross section of ionization of target ions at a photon energy of E. Correspondingly, helium is photoionized at a rate of $\eta_{He}^p = \phi_p \sigma_{He}^p(E)\rho_{He} V_p$, where $\sigma_{He}^p(E)$ is the photoionization cross-section of helium. The photoelectrons originating from helium have kinetic energy $E - I_{He}$, where I_{He} is the first ionization energy of helium. At a sufficiently high pressure of helium, the high-energy photoelectrons may compete with photons with respect to ionizing the target ions. Factors that favour electron-impact ionization are (i) the possibility that the cross-section for electron-impact ionization may be significantly larger than that for the photon-induced ionization, *i.e.*, $\sigma_i^e(E - I_{He}) \gg \sigma_i^p(E)$, and (ii) that the number of target ions exposed to photoelectrons may be much larger than the number of ions exposed to photons, by a factor of $(R_t/R_p)^2$. While the first item is difficult to assess precisely due to lack of absolute cross sections of either kind, it is possible to form a conservative upper bound. The second factor will surely be modified by reduction in the electron flux with the distance from the photon beam and it is clearly desirable to have access to a model that provides the combined effects of cross sections and geometry on the relative importance of photon- and electron-impact ionization of target ions.

Derivation of an analytical model

In order to obtain an analytical model that contains the important physical aspects, we will make use of the simplifying assumption that ionization of helium only leads to electrons emitted normal to the beam. One may then consider photoionization of helium and target ions, and also electron-impact ionization of target ions, within thin disks of thickness Δz of the cylindrical beam and trap volumes, obtained by slicing the trap volume perpendicularly to the symmetry axis. The total rate of electron-impact ionization may then be obtained by integration over the disks.

Focusing on a single thin disk, we first consider the electron flux in the radial direction at position $\vec{r}_1$, denoted by $\phi_e(\vec{r}_1)$, due to photoionization of a helium atom at $\vec{r}$. We will use cylindrical coordinates (x, φ, z) with the distance from the cylindrical axis denoted by *x*, the azimuthal angle about the symmetry axis denoted by φ, and the position of the disk along the axial direction of the trap denoted by *z*. Using subscripted coordinates for the point of evaluation of the electron flux $\phi_e(\vec{r}_1)$, we find

$$\phi_e(\vec{r}_1) = \int_0^{R_p}\int_0^{2\pi}\int_z^{z+\Delta z} \frac{\phi_p \sigma_{He}^p(E)\rho_{He}}{2\pi|\vec{r}-\vec{r}_1|\Delta z} dz d\varphi x dx$$
$$= \int_0^{R_p}\int_0^{2\pi} \frac{d\varphi x dx}{2\pi\sqrt{x_1^2 + x^2 - 2xx_1\cos(\varphi-\varphi_1)}} \phi_p \sigma_{He}^p(E)\rho_{He}$$
$$= \int_0^{R_p} \frac{xdx}{\pi}\int_0^{\pi} \frac{d\varphi}{\sqrt{x_1^2 + x^2 - 2xx_1\cos\varphi}} \phi_p \sigma_{He}^p(E)\rho_{He}$$

The angular integral may be recast in terms of the elliptic integral of the first kind, F, or alternatively, in the complete elliptic integral K (Ref. [1], Eqns. 2.597, 8.111 and 8.112), as follows:

$$\phi_e(\vec{r}_1) = \int_0^{R_p} \frac{2xdx}{\pi|x-x_1|}\int_0^{\pi/2} \frac{du}{\sqrt{1+\frac{4xx_1}{(x-x_1)^2}\sin^2 u}} \phi_p \sigma_{He}^p(E)\rho_{He}$$
$$= \frac{2}{\pi}\int_0^{R_p} \frac{x}{x+x_1} F\left(\frac{\pi}{2}, \frac{2\sqrt{xx_1}}{x+x_1}\right) dx\, \phi_p \sigma_{He}^p(E)\rho_{He} =$$
$$= \frac{2}{\pi}\int_0^{R_p} \frac{xdx}{x+x_1} K\left(\frac{2\sqrt{xx_1}}{x+x_1}\right) \phi_p \sigma_{He}^p(E)\rho_{He} = \frac{2}{\pi}\int_0^{R_p} \frac{x}{x_>} K\left(\frac{x_<}{x_>}\right) dx\, \phi_p \sigma_{He}^p(E)\rho_{He}$$

In the last step, use has been made of the identity $K\left(\frac{2\sqrt{xx_1}}{x+x_1}\right) = \frac{2(x+x_1)}{x+x_1+|x_1-x|} K\left(\frac{x+x_1-|x_1-x|}{x+x_1+|x_1-x|}\right)$ (Ref. [1] Eq. 8.126) Expanding K in terms of positive powers (Ref. [1] Eq. 8.113), one has that

$$K\left(\frac{x_<}{x_>}\right) = \frac{\pi}{2}\sum_{k=0}^{\infty} A_k \left(\frac{x_<}{x_>}\right)^{2k} = \frac{\pi}{2}\left(1 + \frac{1}{4}\left(\frac{x_<}{x_>}\right)^2 + O\left(\left(\frac{x_<}{x_>}\right)^4\right)\right),$$

where $A_k = [(2k)!/2^{2k}(k!)^2]^2 \sim {}^1/_{\pi k}$ for large values of *k*.

At positions not illuminated by X-rays, *i.e.*, $x_1 > R_p$, the electron flux is given by

$$\phi_e(\vec{r}_1) = \phi_p \sigma_{He}^p(E)\rho_{He}\frac{R_p^2}{2x_1}\sum_{k=0}^{\infty} A_k \frac{1}{k+1}\left(\frac{R_p}{x_1}\right)^{2k} = \phi_p \sigma_{He}^p(E)\rho_{He}\frac{R_p^2}{2x_1}\left[1 + \frac{1}{8}\left(\frac{R_p}{x_1}\right)^2 + ..\right]$$

whereas for $x_1 < R_p$,

$$\phi_e(\vec{r}_1) = \phi_p \sigma_{He}^p(E)\rho_{He}R_p \sum_{k=0}^{\infty} A_k \frac{1}{1-2k}\left(\frac{x_1}{R_p}\right)^{2k} = \phi_p \sigma_{He}^p(E)\rho_{He}R_p\left[1-\frac{1}{4}\left(\frac{x_1}{R_p}\right)^2 ..\right]$$

The infinite series that appear in the expressions for the electron flux converge slowly when $x_1 \approx R_p$. However, the flux is continuous at the border of the photon beam, and by explicit summation one finds the approximate limit of 0.6366 $\phi_p \sigma_{He}^p(E)\rho_{He}R_p$.

With the electron flux at hand, one may obtain the rate of target ionization due to electron impact as

$$\eta_i^e = \int_0^{R_t}\int_0^{2\pi}\int_0^L \phi_e \sigma_i^e(E-I_{He})\rho_i \, dz d\varphi x_1 dx_1 = 2\pi L \int_0^{R_t} \phi_e(x_1)x_1 dx_1 \sigma_i^e(E-I_{He})\rho_i$$

where

$$\begin{aligned}\int_0^{R_t} \phi_e(x_1)x_1 dx_1 \\ &= \phi_p \sigma_{He}^p(E)\rho_{He}\left\{\int_0^{R_p}\sum_{k=0}^{\infty} A_k \frac{-1}{2k-1}\left(\frac{x_1}{R_p}\right)^{2k} x_1 dx_1 \right.\\ &\left.+ \frac{R_p^2}{2}\int_{R_p}^{R_t}\sum_{k=0}^{\infty} A_k \frac{1}{k+1}\left(\frac{R_p}{x_1}\right)^{2k} dx_1\right\} \\ &= \phi_p \sigma_{He}^p(E)\rho_{He}\frac{1}{2}R_p^2 R_t \sum_{k=0}^{\infty} A_k \frac{1}{(1-2k)(k+1)}\left(\frac{R_p}{R_t}\right)^{2k}\end{aligned}$$

Introducing the auxiliary function $S\left(\frac{R_p}{R_t}\right) = \sum_{k=0}^{\infty} A_k \frac{1}{(1-2k)(k+1)}\left(\frac{R_p}{R_t}\right)^{2k}$ one obtains

$$\eta_i^e = \sigma_i^e(E-I_{He})\rho_i \phi_p \sigma_{He}^p(E)\rho_{He}V_p R_t S\left(\frac{R_p}{R_t}\right)$$

and

$$\eta_i^e/\eta_i^p = \frac{\sigma_i^e(E-I_{He})\rho_i \phi_p \sigma_{He}^p(E)\rho_{He}V_p R_t S\left(\frac{R_p}{R_t}\right)}{\phi_p \sigma_i^p(E)\rho_i V_p} = S\left(\frac{R_p}{R_t}\right)\frac{\sigma_i^e(E-I_{He})}{\sigma_i^p(E)}\sigma_{He}^p(E)\rho_{He}R_t$$

The function $S(\frac{R_p}{R_t}) = \sum_{k=0}^{\infty} \frac{\left[(2k)!/2^{2k}(k!)^2\right]^2}{(1-2k)(k+1)}\left(\frac{R_p}{R_t}\right)^{2k} = 1-\frac{1}{8}\left(\frac{R_p}{R_t}\right)^2 - O\left(\frac{R_p}{R_t}\right)^4$ decreases slowly and monotonously from a value of 1 at $R_p = 0$ to (approximately) 0.8488 for $R_t = R_p$. For the purpose of estimating the relative importance of ionization by electron impact and by photon absorption, it is clearly sufficient to retain the leading term, giving the expression that is used in the main text: $\eta_i^e/\eta_i^p = \frac{\sigma_i^e(E-I_{He})}{\sigma_i^p(E)}\sigma_{He}^p(E)\rho_{He}R_t$.

References:

1. I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products. Corrected and Enlarged Edition*, Academic Press, New York, 1980.