Multiple ionization of atom clusters by intense soft X-rays from a free-electron laser

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Intense radiation from lasers has opened up many new areas of research in physics and chemistry, and has revolutionized optical technology. So far, most work in the field of nonlinear processes has been restricted to infrared, visible and ultraviolet light[1], although progress in the development of X-ray lasers has been made recently[2]. With the advent of a free-electron laser in the soft-X-ray regime below 100 nm wavelength[3], a new light source is now available for experiments with intense, short-wavelength radiation that could be used to obtain deeper insights into the structure of matter. Other free-electron sources with even shorter wavelengths are planned for the future. Here we present initial results from a study of the interaction of soft X-ray radiation, generated by a free-electron laser, with Xe atoms and clusters. We find that, whereas Xe atoms become only singly ionized by the absorption of single photons, absorption in clusters is strongly enhanced. On average, each atom in large clusters absorbs up to 400 eV, corresponding to 30 photons. We suggest that the clusters are heated up and electrons are emitted after acquiring sufficient energy. The clusters finally disintegrate completely by Coulomb explosion.

Short-wavelength radiation, namely vacuum-ultraviolet (VUV) radiation and soft and hard X-rays, is a very powerful tool for studying the properties of matter—such as geometrical and electronic structure, chemical composition and magnetic structure. The ability to ionize matter allows direct insight into electronic structure and element composition because the binding energies of electrons are characteristic of the individual elements. Diffraction of hard X-rays is very important because it allows for structure determination in complex systems with atomic resolution. Free-electron lasers (FELs) for soft X-rays based on the principle of self-amplification of spontaneous emission (SASE) are now becoming available for experiments. These lasers combine the advantages of short-wavelength sources (like synchrotron radiation) with those of lasers; for example, short pulse length, high peak power, coherence and diffraction-limited collimation[4]. Short-wavelength X-ray FELs are therefore expected to open the way to new types of experiments[5,6], such as the study of chemical reactions in real time with element selectivity[7], or structure determination of single biomolecules[8].

Here we report the study of the interaction of intense soft X-rays from an FEL with matter. Xe atoms and clusters are chosen because they can be ionized even by single 12.7-eV photons (the ionization potential of Xe atoms is 12.1 eV). The experiments were performed by irradiating atoms and clusters with ~100-fs-long FEL pulses at 98 nm wavelength and a power density of up to $7 \times 10^{13}\,\mathrm{W\,cm^{-2}}$. The resulting ions are detected with a time-of-flight (TOF) mass spectrometer.

TOF mass spectra for different cluster sizes recorded at $2 \times 10^{13}\,\mathrm{W\,cm^{-2}}$ are shown in Fig. 1 (experimental details are given in the legend). The most striking result is the surprisingly different ion signal from atom and cluster beams. Whereas only singly charged ions are observed after irradiation of isolated atoms, atomic ions with charges up to 8+ are detected if clusters are irradiated. Doubly charged ions resulting from ionization of isolated Xe atoms are not detected above the noise level of ~1%. Clusters absorb many photons, and completely disintegrate into singly and multiply charged ions. The mass peaks are very broad, indicating that the ions have a high kinetic energy. This can be understood in terms of a Coulomb explosion process. The population of different ion states and their kinetic energy strongly depends on the power density. This is shown in Fig. 2 for clusters comprising 1,500 atoms. At the highest power level of $7 \times 10^{13}\,\mathrm{W\,cm^{-2}}$, charge states up to 8+ are detected. Lowering the power density strongly reduces the intensity of highly charged ions. At $2 \times 10^{11}\,\mathrm{W\,cm^{-2}}$, only singly charged Xe ions with high kinetic energy can be detected. The high kinetic energy of the ions

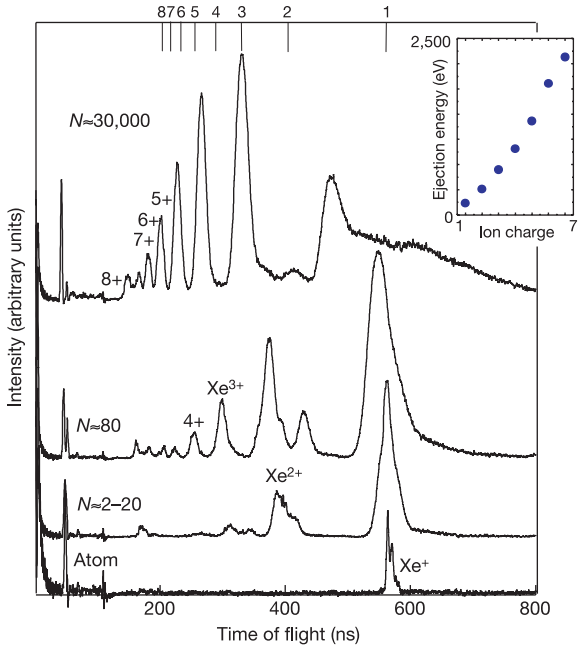

Figure 1 Time-of-flight (TOF) mass spectra of ionization products of Xe atoms and clusters. The spectra were recorded after ionization with soft X-rays (98 nm wavelength) at an average power density of $2 \times 10^{13}\,\mathrm{W\,cm^{-2}}$. The atomic spectrum (bottom trace) shows a splitting into several lines owing to the different isotopes. After irradiation of clusters, highly charged ions are observed. The mass peaks are rather broad and displaced with respect to the calculated flight times indicated by thin vertical lines (different charge states) in the uppermost part of the figure. This indicates that the ions have high kinetic energies. *N* is the number of atoms per cluster. Inset, the kinetic energy of ions as a function of the charge for $N = 1{,}500$. The experiments are performed as follows. A pulsed beam of atoms or clusters was prepared by expanding Xe gas at high pressure (0.1–30 bar) through a small conical nozzle (0.1 mm diameter, 15° half-angle). The composition of the beam and the size of the clusters could be controlled by varying the gas pressure[28,29]. The cluster beam passed through a small skimmer into the main chamber. Soft X-rays from the FEL[4] with 98 nm wavelength (bandwidth 0.5 nm) were focused with an elliptical mirror onto the atom or cluster beam. The pulse energy was measured with a carefully calibrated channel-plate detector, which detects a well-defined percentage of FEL light scattered from a wire. The diameter of the focal spot was ~20 μm. The power density is calculated assuming a pulse length of 100 fs. The ions produced in the interaction zone were detected with a TOF detector mounted perpendicular to the polarization direction and with a digital sampling oscilloscope operating at a 1-Hz repetition rate.

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and the absence of molecular fragments (Xe_2^+, Xe_3^+, Xe_4^+,...) indicates that the clusters completely disintegrate even at reduced power density. Further reducing the intensity by lowering the gain of the FEL results in a decreasing signal and simultaneously a change of the kinetic energy of Xe^+ (lowest curve in Fig. 2).

The strong dependence on the power density is a clear sign that optical nonlinear processes dominate the ionization of the clusters at the power levels used. If the power density is increased from 2×10^{11} to 7×10^{13} W cm^{-2}, the mean charge state increases from 1 to ~2.5. Therefore, we conclude that at the highest power density each atom in the cluster of 1,500 atoms loses on average 2–3 electrons. The average kinetic energy per ion is derived from the measured flight time in Figs 1 and 2. It varies strongly with the charge state and the cluster radius. For Xe^+ the kinetic energy increases almost linearly with the cluster radius, whereas for high charge states it starts to saturate for large clusters (H.W., manuscript in preparation). For Xe^{7+}, kinetic energies of more than 2 keV were observed. In small clusters, the kinetic energy increases quadratically with the charge state (see Fig. 1 inset). This behaviour is a clear signature of a Coulomb explosion[9]. From the results presented in Fig. 1 we conclude that an energy of up to several hundred eV per atom is taken from the FEL beam.

Coulomb explosion of clusters is not a new phenomenon[10]. Clusters irradiated with infrared light at $>10^{16}$ W cm^{-2} completely disintegrate[11–13]. The interaction of intense lasers with clusters has attracted great interest, and has been extensively studied experimentally[14,15] and theoretically[16–21] in the past few years. The interpretation of the heating mechanism and of the explosion dynamics, especially if driven by the thermal expansion of the electron gas, is still a subject of discussion[9]. On the other hand, it is agreed that the experimental findings are explained by field ionization of the atoms and the clusters by the strong electric field of the infrared laser[18,20].

The effects observed here when clusters are exposed to short-wavelength radiation are somewhat surprising, because Coulomb explosion starts at 10^{11} W cm^{-2}; this is much lower than the power density needed to induce Coulomb explosion in the infrared. Moreover, the frequency ω of the FEL is so high that the direct effect of the laser field on the electron movement is expected to be small[22]. Whether field ionization is efficient can be estimated from textbook formulas[23]. Field ionization by the laser field dominates if the Keldysh parameter γ is smaller than 1. Under our conditions, γ varies between 8 (Xe atoms, ionization potential $I_p = 12.1$ eV) and ~100 (electrons bound to highly charged Xe clusters) and therefore field ionization can hardly account for the observations. Consequently, additional processes have to be considered for the understanding of absorption, ionization and explosion dynamics with short-wavelength radiation. Three questions have to be answered. (1) What is the ionization mechanism that causes the massive electron ejection? (2) How can the high charge states of the

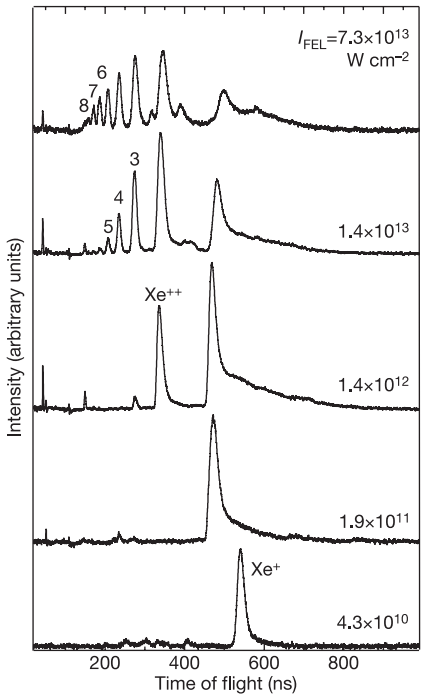

Figure 2 TOF mass spectra recorded after irradiation of 1,500-atom Xe clusters as a function of power density. The power density (I_{FEL}) is given next to each trace. The spectrum at the bottom was recorded at a reduced gain of the FEL. The intensity of highly charged ions increases with increasing power density. Experimental details: the intrinsic pulse energy of the ~100-fs-long SASE-FEL pulses[4] typically varied between 1.5 and 25 μJ. The spectra with power densities of (1.9×10^{11})–(7×10^{13}) W cm^{-2} were taken with pulses of 25 μJ energy. The power density could be lowered to 10^{10} W cm^{-2} at 1.5 μJ by moving the cluster beam out of the focus.

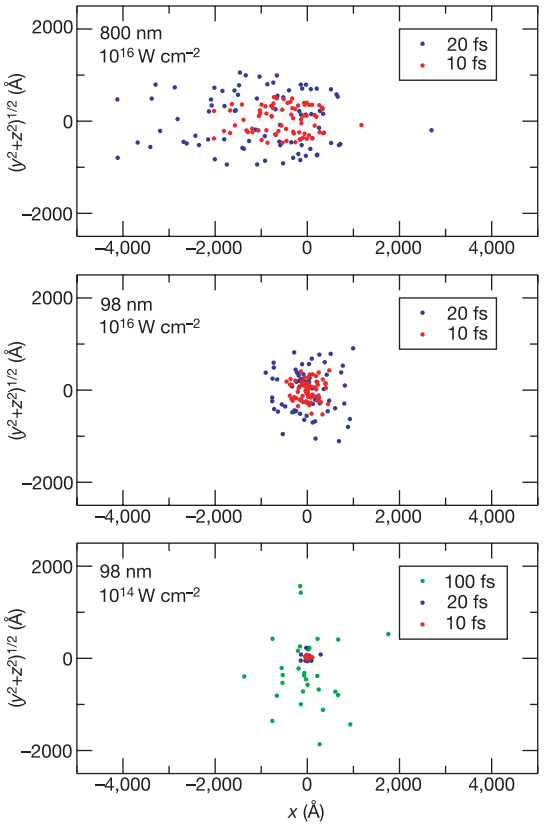

Figure 3 Classical simulations of the electron motion and ionization for Xe_{13} clusters after irradiation with infrared radiation and soft X-rays. Electron trajectories were calculated for 100-fs-long pulses of constant intensity. The position of the electrons is shown 10, 20 and 100 fs after the onset of a light pulse. The position of the ions is that of the neutral cluster and kept fixed during the simulation. The radiation field is polarized in the x direction. The vertical scale $(y^2 + z^2)^{1/2}$ shows the vertical distance of the electrons from the cluster. The uppermost plot corresponds to typical conditions for infrared lasers (800 nm wavelength, power density 10^{16} W cm^{-2}). Most electrons leave the cluster during the first optical cycle into the polarization direction of the light owing to field ionization. At 98 nm wavelength, the electrons are emitted isotropically by thermionic emission. Details of the calculation will be published elsewhere (H.W., manuscript in preparation). Further calculations were performed assuming that at least one electron per atom is unbound owing to inner ionization by the FEL photons. The number of unbound electrons is varied between 1 and 6 per atom in view of the high charge states seen in the experiment. At 98 nm wavelength and a power density of 1×10^{14} W cm^{-2}, up to 29 electrons can leave the cluster.

fragments and their high kinetic energy be explained? (3) Which process allows the cluster to absorb such large amounts of energy?

To help the understanding of these findings, we recall that the binding energy of electrons in clusters increases strongly with the charge of the cluster. The total energy needed to remove N electrons from a cluster comprising N atoms is approximately proportional to N^2, and can be as large as 10^7 eV for $N = 30{,}000$ if the radius of the cluster remains unchanged during ionization. We assume that the ionization of the cluster is a two-step process, as in the case of irradiation with infrared light[17,20]. In a first step, atoms inside the cluster lose at least one electron, which then can move almost freely inside the cluster. This process is called inner ionization. In a second step, the electrons are removed from the cluster to infinity. This process is called outer ionization. Inner ionization of the electrons can be easily explained, because the energy of the FEL photons exceeds the ionization energy of Xe atoms. Therefore, we assume that valence electrons in the cluster are promoted to excited states (conduction band). At a power level of a few times 10^{13} W cm^{-2}, this takes place in the first few femtoseconds of the FEL pulse because the cross-section is large[24] (30–50 Mbarn).

To explain the outer ionization, we have performed simulations of the electron movement in Xe_{13} and Xe_{55} clusters using a classical model similar to that in ref. 17 in order to get insight into the absorption and ionization processes. The motion of unbound electrons inside the clusters is simulated under the action of the forces of the ions and the electrons in the cluster and of the FEL field. The results are presented in Fig. 3. At 98 nm wavelength and a power density of 10^{14} W cm^{-2} or 10^{16} W cm^{-2}, the electrons are emitted isotropically, whereas at the typical conditions of optical laser experiments (800 nm, 10^{16} W cm^{-2}) the electrons are preferentially emitted into the polarization direction of the electric field of the laser. The latter is a clear signature of field ionization. The isotropic emission of electrons at 98 nm shows that field ionization does not play a role. A close examination of the electron trajectories shows (H.W., manuscript in preparation) that the electrons are scattered many times before they leave the cluster. The clusters are heated, and electrons escape once sufficient energy is acquired. The steps of the proposed ionization process are illustrated in Fig. 4. We assume that highly charged ions are formed at the cluster surface by field ionization in the strong Coulomb field of the ions inside the clusters[16,18]. The electric field at the surface of large highly charged Xe clusters calculated by Coulomb's law is typically 10–50 V Å^{-1}. This is up to 20 times larger than the maximum field strength of the FEL at 10^{14} W cm^{-2}. 30 V Å^{-1} are sufficient[25] to produce Xe^{8+}, giving a straightforward explanation for the presence of high charge states.

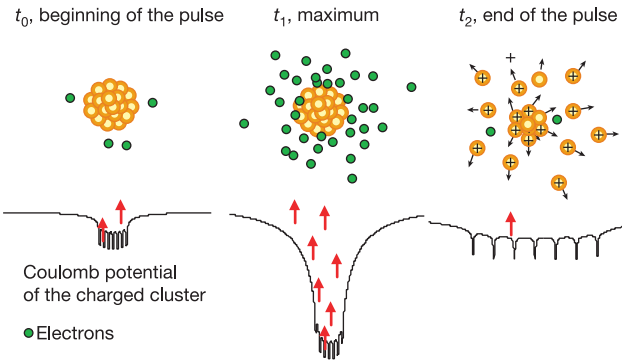

Figure 4 Schematic illustration of the ionization of Xe clusters and a subsequent Coulomb explosion. The Coulomb potential of the clusters is shown at the beginning of the FEL pulse, at its maximum and at the end of the pulse. Photons are indicated by arrows. Ionization proceeds in steps. In the first step—depending on the size of the cluster—a few electrons are directly ejected from the cluster because their binding energy is smaller than the energy of the FEL photons. However, once the charge of the cluster has reached a critical value, the binding energy of the electrons becomes larger than the photon energy. At that stage, only hot electrons in excited states can leave the cluster, but electrons in the valence band and in excited states can absorb photons. We assume that after a few femtoseconds a nanoscale plasma is formed, which is confined by the Coulomb potential of the positive charge in the cluster. The radius of the electron cloud can be considerably larger than the cluster radius because the Coulomb potential is long range. As a result we expect that the electrons have a high probability of being outside the cluster. These loosely bound electrons can be removed from the cluster by the absorption of additional photons or by collisions with other electrons in the presence of ions close by. Once a high number of electrons have left, the clusters start to disintegrate as a result of the Coulomb repulsion of the ions ('Coulomb explosion'). At the same time outer ionization becomes easier because the Coulomb potential gets weaker[18].

We now discuss further the mechanisms that allow the cluster to absorb such a high amount of energy. The energy released in the Coulomb explosion corresponds to the absorption of many photons. This number is estimated by dividing the average kinetic energy of the ejected ions by the photon energy. For clusters comprising 1,500 atoms, approximately 400 eV per atom are absorbed at 7×10^{13} W cm^{-2}, corresponding to ~30 photons per atom. The absorption of 30 photons at 7×10^{13} W cm^{-2} corresponds to an average cross-section of 10 Mbarn if we assume that the photons are absorbed sequentially. The absorption can not be explained by simple ionization of Xe atoms. Although 100 photons per shot fall into the absorption cross-section (50 Mbarn) for the initial ionization, the energy of a single photon is not sufficient to excite or ionize further Xe ions inside the cluster. Therefore, other absorption mechanisms have to be considered.

The standard inverse bremsstrahlung model describes successfully the absorption of infrared light by ionized clusters. Our estimates (H.W., manuscript in preparation) for 98 nm wavelength based on the work in ref. 12 give only 15 eV per atom for singly charged ions, which is substantially lower then the experimentally derived value. At 98 nm the absorption by inverse bremsstrahlung is inefficient because the ponderomotive energy is small (<150 meV), and the oscillation amplitude of electrons heating the cluster is only 0.01 nm and thus much smaller than the diameter of the clusters (1–5 nm). Our classical simulations for Xe_{55} in the geometry of the neutral cluster predict an absorption of 30 eV per atom in 100 fs if an average charge state 1 per atom is considered. It increases to 85 eV per atom for an average charge state of 2 per atom. In agreement with recent theoretical work[17], the simulations show a strong wavelength-dependent resonance behaviour that is due to oscillations of unbound electrons in the entire cluster and to plasmon absorption. In contrast to experiments with infrared lasers, under our conditions the plasma frequency is always smaller than the laser frequency. For Xe clusters the plasma frequency shifts from 2.7 eV for singly charged atoms to 6.6 eV for six charges per atom. Even if a strong broadening of the plasmon absorption due to damping of the electron motion by collisions is considered, the absorption is approximately 5–10 times less efficient than experimentally observed (H.W., manuscript in preparation). Other approaches, such as Brunel absorption[26], also cannot account for the strong absorption because the FEL frequency is much larger than the plasma frequency.

Two different effects may account for the efficient absorption. The model calculation gives absorption rates that depend on cluster size. According to recent theoretical work[27], the absorption of a cluster plasma confined by a strong Coulomb potential is enhanced compared with that of an infinite plasma. This enhancement compared with conventional inverse bremsstrahlung is due to collisions of the electrons with the whole cluster ion[27]. Whether this effect can explain the enhanced absorption could be checked by calculations for larger clusters. Furthermore, we note that a classical modelling of the absorption process is limited, because enhancements due to resonant intermediate states are not included. The photon energy of the FEL is of the same order of magnitude as the

level spacing in Xe atoms and Xe ions. It is therefore quite likely that a quantum mechanical description of the absorption process which includes resonant intermediate states could give larger absorption than the classical model.

In conclusion, absorption of short-wavelength radiation and subsequent ionization in clusters differs considerably from that in the optical spectral range. Absorption and ionization start by single-photon absorption as described by quantum mechanics. After many unbound electrons are created, a plasma is formed. Our experimental results give evidence that absorption in such cluster plasma is stronger than predicted by calculations with classical models. We assume that quantum-mechanical modelling is needed at these short wavelengths to explain the efficient energy deposition seen in the experiment. On the other hand, the classical simulation clearly shows that electrons can leave the cluster by a photon-assisted thermionic emission. Field ionization, the dominant ionization process at optical frequencies, does not contribute to cluster ionization. □

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Non-framework cation migration and irreversible pressure-induced hydration in a zeolite

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Zeolites crystallize in a variety of three-dimensional structures in which oxygen atoms are shared between tetrahedra containing silicon and/or aluminium, thus yielding negatively charged tetrahedral frameworks that enclose cavities and pores of molecular dimensions occupied by charge-balancing metal cations and water molecules[1]. Cation migration in the pores and changes in water content associated with concomitant relaxation of the framework have been observed in numerous variable-temperature studies[2–5], whereas the effects of hydrostatic pressure on the structure and properties of zeolites are less well explored[6–8]. The zeolite sodium aluminosilicate natrolite was recently shown to undergo a volume expansion at pressures above 1.2 GPa as a result of reversible pressure-induced hydration[9]; in contrast, a synthetic analogue, potassium gallosilicate natrolite, exhibited irreversible pressure-induced hydration with retention of the high-pressure phase at ambient conditions[10]. Here we report the structure of the high-pressure recovered phase and contrast it with the high-pressure phase of the sodium aluminosilicate natrolite. Our findings show that the irreversible hydration behaviour is associated with a pronounced rearrangement of the non-framework metal ions, thus emphasizing that they can clearly have an important role in mediating the overall properties of zeolites.

The pressure-induced changes of the unit cell parameters of a powder sample of the potassium gallosilicate form of natrolite (K-GaSi-NAT) reveal a volume expansion of about 1.0% between 1.2(1) and 1.7(1) GPa (numbers in parentheses are errors on measured pressures) (Fig. 1a)[10]. Structurally, this expansion differs from that observed in the sodium aluminosilicate form of natrolite (Na-AlSi-NAT): in K-GaSi-NAT, the *c*-axis, along which the rigid T_5O_{10} (T = Al, Si, Ga, and so on) tetrahedral building units join to form a chain (Fig. 1b), expands by about 0.4%, whereas it