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Unusual under-threshold ionization of neon clusters studied by ion spectroscopy

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Abstract
We carried out time-of-flight mass spectrometry for neon clusters that were exposed to intense free electron laser pulses with the wavelength of 62 nm, which induce optical transition from the ground state ($2s^2\ 2p^6$) to an excited state ($2s^2\ 2p^5\ nl$) in the Ne atoms. In contrast to Ne^+ ions produced by two-photon absorption from isolated Ne atoms, the Ne^+ ion yield from Ne clusters shows a linear dependence on the laser intensity (I). We discuss the ionization mechanisms which give the linear behaviour with respect to I and expected features in the electron emission spectrum.

(Some figures may appear in colour only in the online journal)

1. Introduction

'More is different' is a famous phrase given by Anderson [1], who proposed that, as the number of constituent atoms increases, new phenomena could emerge. In this work, we investigate ionization processes of clusters irradiated by free electron laser (FEL) pulses. Here, 'More is different' has two aspects: we can control not only the number of constituent atoms but also the number of photons over a wide range. Multi-photon absorption by a single atom, which leads to the production of a highly charged ion, is a well-known example for varying the number of photons, while the shift of the ionization potential (IP) with cluster size is an example for varying the number of atoms e.g. in the case of the single-photon absorption. A particularly intriguing situation is encountered when a cluster is exposed to photons whose energy is lower than the IP. In this case, if any ionization event (i.e. under-threshold ionization) takes place, it must be an effect of 'More is different', either due to the number of photons or to the number of atoms. Furthermore, if the photon energy is tuned to the Rydberg states or exciton levels, various auto-ionization processes such as an interatomic Coulombic decay (ICD) [2, 3] and other phenomena like the exciton–Mott transition (EMT) [4] are expected to occur.

The ICD in general is induced by a two-centre energy transfer, and conventionally it is triggered by ionizing an

inner-valence electron. The ICD was proposed by Cederbaum and has been verified experimentally in rare-gas clusters [5–8] and molecular clusters [9, 10]. Recently, Kuleff *et al* [11] proposed a novel ICD mechanism, in which two electrons are photo-excited from outer valence orbitals to the Rydberg states and one of them is then emitted by using the relaxation energy from the other. EMT is defined as an insulator-to-metal transition, in which the electron–hole correlation plays a crucial role: an exciton gas that was created by an optical means can be transformed to an electron–hole plasma when the exciton density is high enough to induce screening effects by the overlap of the wavefunctions. In the rare-gas cluster, the evolution of the Rydberg excited states to the excitons has been investigated as a function of cluster size [12, 13], but the EMT has not been reported.

In this study, we adopted neon clusters with an average size $\langle N \rangle$ of 1000 atoms and exposed them to extreme ultraviolet free electron laser (EUV-FEL) pulses with a wavelength of 62 nm, which corresponds to the optical transition from the ground state ($2s^2\ 2p^6$) to an excited state ($2s^2\ 2p^5\ nl$) in the Ne atom [14]. We found that, whereas the Ne^+ ion yield from the uncondensed Ne gas shows a quadratic dependence on the laser intensity (I), indicating two-photon absorption, the Ne^+ ion yield from Ne clusters shows a linear dependence on the laser intensity. We discuss possible ionization mechanisms which give rise to such a linear behaviour and predict expected features in the electron emission spectrum.

2. Experiment

The experiments were performed at the SPring-8 Compact Self Amplified Spontaneous Emission (SASE) Source (SCSS) test accelerator in Japan [15]. Our experimental setup was almost the same as the one reported in [16, 17]. Briefly, the cluster beam crossed the FEL beam at 45° in the horizontal plane. The photon energy was tuned to 20 eV (62 nm). The FEL beam was partially blocked by a 1.5 mm wide horizontal beam stopper before the ionization region, so that the unfocused beam did not irradiate the cluster beam directly. The FEL beam was focused back onto the cluster beam by a multi-layer focusing mirror fabricated at the Lawrence Berkeley National Laboratory, which was the same as used in [16]. Taking all the optical elements (deflecting and focusing mirrors, etc) between the radiation source point and the ionization volume into account, we estimated the power density in the focus spot to be at most $\sim 3 \times 10^{14}$ W cm^{-2} at full power of the FEL, assuming a diffraction limited focus size of 3 μm in diameter and a pulse length of 30 fs [18]. The measured spectral fluctuation of the FEL was 0.3 eV (FWHM) in this experiment.

The cluster beam was prepared by the adiabatic expansion of a Ne gas through a pulsed 250 μm nozzle. The stagnation pressure was 4.6 bar and the nozzle temperature was 80 K [19]. The average cluster size $\langle N \rangle$ was estimated to be 1000 atoms according to scaling laws [20, 21]. To avoid space–charge effects due to the ionization of a background gas, the pulsed gas jet was cut to 0.6 mm width and 0.4 mm height with knife-edge slits and travelled to the focus spot located at 1.7 m downstream from the nozzle.

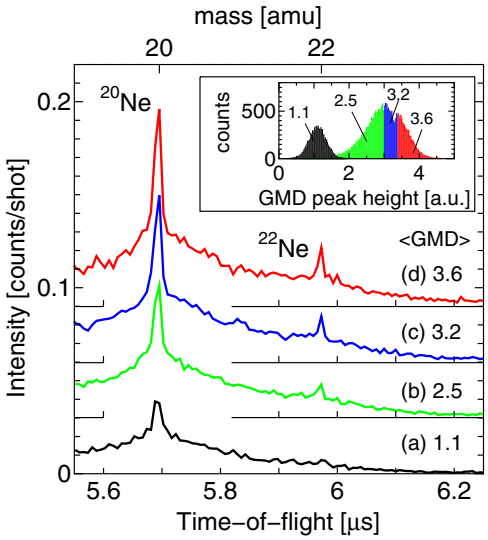

Figure 1. Ion TOF spectra of a Ne_{1000} cluster beam irradiated by 62 nm FEL pulses. The numbers in the figure denote the peak height of the gas monitor detector (GMD). The inset shows the power distribution in the GMD for the full and for one-third of the laser power. Colour areas correspond to the laser power distributions for each TOF spectrum.

We measured time-of-flight (TOF) spectra with our momentum imaging spectrometer [16, 17]. Fragment ions were vertically extracted by a uniform electrostatic field. They travelled through an extraction region (75 V cm^{-1} electric field strength, 40 mm in length), an acceleration region (110 V cm^{-1} electric field strength, 52 mm in length) and a field-free region (308 mm), and were finally detected by a microchannel-plate (MCP) detector equipped with a three-layer delay-line anode (RoentDek HEX120) [22].

The measurements were carried out with the full laser power and with one-third of it. In the latter case, the intensity was attenuated by transmitting the laser pulses through a gas chamber filled with Ar. Since the pulses from the SASE source fluctuate shot to shot, we measured the intensity of each pulse by a gas monitor detector (GMD). At the same time, the TOF spectrum was also measured for each laser shot. Both signals were recorded by an eight-channel digitizer (Acqiris DC282×2), and the timing signals were extracted by a software constant fraction discriminator [23]. This procedure enabled us to deduce precise laser-power dependences of the TOF spectra. In this study, we discuss the FEL intensity dependence based on the GMD pulse height which is proportional to the photon number in each FEL pulse because of the uncertainty in estimating the focal size of FEL.

3. Results

In figure 1, spectrum (a) displays the TOF spectrum accumulated during the experiment with one-third of the full laser power. The corresponding power distribution is shown as a black area in the inset of figure 1 as a function of the GMD peak height. For the one-third power, the weighted average of the GMD peak height is 1.1. Since the power

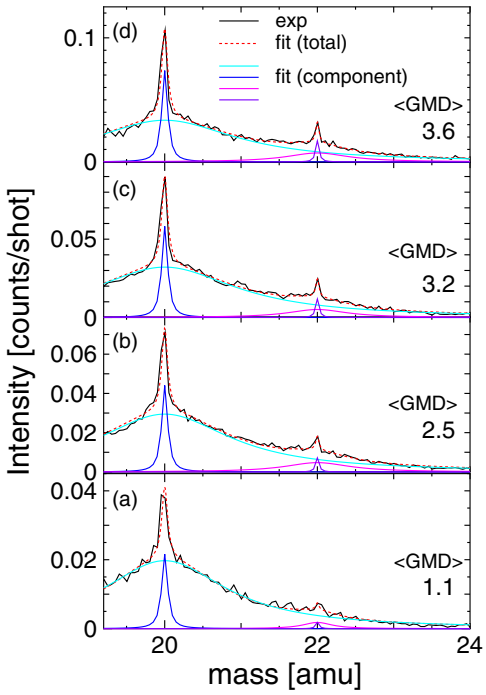

Figure 2. Decomposition of the TOF spectrum into four Lorentzian curves: $^{20}Ne^{+}$ from the uncondensed gas and from the cluster, and $^{22}Ne^{+}$ from the uncondensed gas and from the cluster.

distribution is much wider for the full power experiment, we have divided the data into three parts: (b) below 3.0, (c) from 3.0 to 3.4 and (d) above 3.4 (green, blue and red areas). The average peak height is 2.5 for (b), 3.2 for (c) and 3.6 for (d). In each corresponding TOF spectrum, a prominent peak is observed at the mass-to-charge ratio m/q of 20, and a smaller one at $m/q = 22$, corresponding to $^{20}Ne^{+}$ and its isotope $^{22}Ne^{+}$, respectively. In addition, broad distributions centred at $m/q = 20$ and $m/q = 22$ are also seen. The broad features are due to the fragments from clusters, whereas the sharp peaks correspond to ions from the uncondensed gas, because large fragment energies resulting in a broad TOF distribution can only be produced by Coulomb repulsion between ions from the cluster. No multiply charged ions such as Ne^{2+} were observed.

We now examine the laser intensity dependence of the ion yield to clarify the multiphoton ionization mechanism. For this purpose, we decompose the TOF spectra into a sum of two narrow and two wide Lorentzian curves, as displayed in figure 2. The height and width parameters were determined by a least-squares fitting. In the fitting procedure, the m/q region below 20 was eliminated, because the MCP signal in this region was contaminated by H_2O. We analysed the apparent ratio of $^{20}Ne^{+}$ to $^{22}Ne^{+}$ for uncondensed atoms as a function of FEL intensity and found a progressive deviation from the natural abundance (about 9:1) with an increase of the laser power. Thus, we use the data for $^{22}Ne^{+}$ hereafter. The benefit of using the $^{22}Ne^{+}$ isotope for a quantitative analysis was demonstrated in a previous paper [24].

In figure 3, the $^{22}Ne^{+}$ yield is plotted versus the laser power. The directly measured GMD signal is shown on the abscissa. The integrated intensity of the sharp peak exhibits a quadratic dependence on the laser intensity, indicating that the ionization of isolated atoms was due to two-photon absorption as expected. In contrast, the ion yields from the clusters show a linear dependence on the laser intensity. To check the influence of the choice of how the data are divided, results of the other such choices, in which the full power data are divided into two parts, are displayed by diamonds in figure 3(a).

4. Discussion

These experimental results suggest that the ionization process is qualitatively different between free neon atoms and neon atoms embedded in clusters. Two-photon ionization was observed for Ne atoms, while an unexpected linear dependence of the ion yield on the FEL intensity was found for Ne clusters. Although it is difficult to clarify the ionization process based only on these results of ion spectrometry alone, we try here to discuss the possible cluster ionization mechanisms and predict the expected features of the electron emission spectrum in each case.

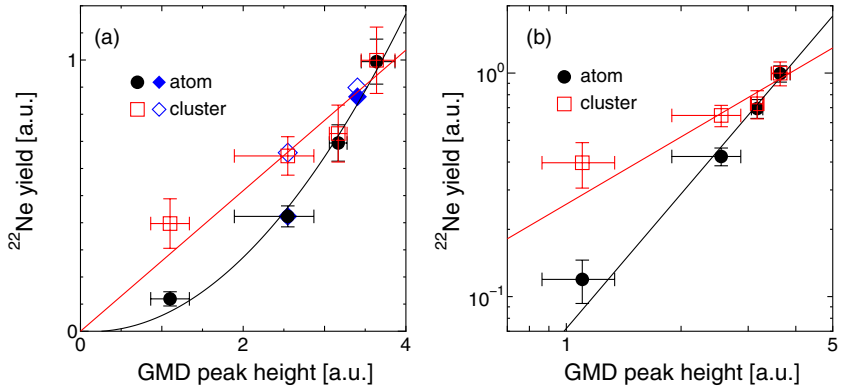

Figure 3. (a) $^{22}Ne^{+}$ yield from uncondensed atoms (closed symbols) and from clusters (open symbols) as a function of the GMD peak height. The intensities of these two components are re-normalized at the highest point of the GMD scale. The horizontal error bars denote the standard deviation, and the vertical error bars denote the statistical errors, which are defined by the square root of the integrated number of $^{22}Ne^{+}$. The line guides a quadratic dependence on the laser power for atoms and a linear dependence for clusters. (b) Log–log plot of the $^{22}Ne^{+}$ yields. The lines are guides for the eyes the same as (a).

In the infrared spectral region, tunelling ionization followed by plasma heating is known to give efficient cluster ionization even if the photon energy is much smaller than the IP [25, 26]. In such a case, the ponderomotive energy should be several electron volts or more, and the intensity dependence of the ion yield would be nonlinear, contrary to what we observe here. Therefore, we can safely ignore the ionization of the cluster induced by the electric field of the laser.

The first candidate for the ionization mechanism of neon clusters is the direct two-photon ionization of the constituent atoms. In this case, the intensity dependence of the ion yield should be quadratic, which is however inconsistent with our experimental results. It should be noted that the linear intensity dependence could be observed even in such a two-photon process when the saturation of ionization is reached for each constituent atom [16, 27]. Such saturation effects can however be excluded in this experiment, since the simultaneously measured atomic ionization shows a quadratic intensity dependence. Since the cross-section of the two-photon ionization of the cluster constituent atoms is expected to be of the same order of magnitude as that of an isolated atom, the two-photon route could be excluded as an ionization process of neon clusters based on the FEL intensity dependence of the ion yield.

Thus, we have to search for alternative ionization mechanisms in which the number of emitted ions is proportional to the number of photon-absorbing atoms.

As a candidate of such an ionization process, a novel ICD mechanism via resonant excited states is proposed by Kuleff [11]. When many Rydberg excited atoms are formed within a cluster, energy transport by the exchange of a virtual photon becomes possible between the excited states of two neighbouring atoms, and hence one atom can ionize another atom utilizing this transition energy. In this case, the number of generated ions is expected to be approximately one-half of the number of excited atoms. Since the number of excited atoms would be proportional to the FEL intensity, this type of ICD is consistent with our experimental results. If this is the case, the ICD electron should appear as a peak in the electron emission spectrum.

Let us consider a situation where one single ion is created in the cluster. The creation of this single ion can be either due to the direct two-photon ionization of a single atom in the cluster or due to the ICD following the sequential excitation of two atoms by two photons. Since the binding potentials of atoms in the cluster are distorted by the Coulombic potential of a single neighbouring ion, the sequential excitation of other atoms leads to the delocalization of excited electrons and to the production of nano-plasma. This is the same effect as the ionization barrier suppression found in the inner ionization of the cluster [28]. In this case, the ion yield will linearly depend on the FEL intensity too, since the number of ions is expected to be proportional to the number of excited atoms. The electron emission spectrum should be dominated by thermal electrons from nano-plasma with an additional peak of 'the first ionizing atom' at about 18 eV ($= 2\,h\nu - IP$), independent of whether the first electron emission is due to direct two-photon ionization or double excitation ICD.

Now, if the multiple excitation takes place before the first electron ejection as discussed above, the excited electrons will be delocalized also because of the lowering of the inner IPs [28]. As briefly noted in the introduction, the delocalization of the excited electrons can be viewed as the EMT, which has been intensively studied for bulk silicon [29]. When a sufficient number of excitons are created in bulk silicon, it is well known that the bound electrons are spontaneously delocalized and transformed to a plasma state by the overlap of the exciton wavefunctions. Also in this case of a neon cluster, if the FEL irradiation achieves a high enough exciton density, electrons will be liberated by the thermoelectronic emission from the nano-plasma produced by EMT. Then, as in the previous case, the electron emission spectrum is expected to show an exponential component corresponding to thermal electrons. The only difference from the previous case would be the lack of a sharp peak corresponding to the direct two-photon ionization of a single atom or a double excitation ICD.

5. Summary

We carried out time-of-flight mass spectrometry on neon clusters that were exposed to intense free electron laser (FEL) pulses with the wavelength of 62 nm, which induce transitions from the ground state ($2s^2\ 2p^6$) to an excited state ($2s^2\ 2p^5\ (2P_{1/2,3/2})\ 3d$) in a Ne atom. In contrast to isolated Ne atoms, in which a Ne^+ ion is produced by two-photon absorption, the Ne^+ ion yield from Ne clusters shows a linear dependence on the laser intensity. We have considered possible ionization mechanisms consistent with the experimentally observed FEL intensity dependence of the ion yields and discussed the expected electron emission spectrum for each case. We believe that the additional information obtainable from electron emission spectra will be helpful to decide the underlying mechanism.

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