Ion pair formation in the NeAr dimer irradiated by monochromatic soft X-rays

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A B S T R A C T

We investigated Ne−–Ar+ ion-pair formation which follows irradiation of the NeAr dimer by monochromatic soft X-rays. Using momentum-resolved electron-ion multicoincidence spectroscopy, we could unambiguously identify that the formation of the ion pair at photon energy of 200.5 eV proceeds via interatomic Coulombic decay (ICD) of the Ne+(2s/C01)Ar inner-valence ionized and NeAr+(3p/C025d) ionization satellite states. Photoabsorption at higher photon energies of 268.2 eV and 888.7 eV leads to the emission of core electrons of Ar and Ne respectively, and to the subsequent local Auger decay process. We demonstrate that at these energies the ion pair formation originating in the doubly ionized Ar L-MM and Ne K-LL Auger final states proceeds mostly via radiative charge transfer and charge transfer driven by non-adiabatic coupling mechanisms.

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1. Introduction

Absorption of monochromatic soft X-ray radiation causes inner-shell ionization of atoms or molecules if its energy is higher than the respective electron binding energies. The inner-shell ionization is usually followed by the electronic decay, whereby additional electrons are emitted. The electronic decay in question is known as the Auger process [1] whose final states are usually dicatonic ‘two-hole’ states. In the case of diatomic molecules, such as N2, these two hole states mostly dissociate into N+ and N+. The situation may be different for van der Waals rare-gas dimers, such as Ar2, where the interatomic distances are significantly larger [2] (three times larger in Ar2 than in N2). The Auger spectra in weakly bound systems are generally considered as ‘self imaging’, i.e. imaging the atom where the inner-shell hole is created (see for example [3] and references therein). If we apply this self-imaging picture to Ar2 after 2p ionization, the ‘atomic’ Ar L-MM Auger takes place, creating two holes in one Ar site. Such dicatonic states are not necessarily dissociative [4]. Saito et al. [5], however, elucidated using electron-ion-ion coincidence momentum imaging methods that Ar−–Ar+ charge separation takes place from the electronically stable Ar2(3p−2–3s2)–Ar states, which are the majority products of the Ar L-MM Auger decay. The ab initio study of the electronic structure of doubly ionized Ar2 [6] concluded that the only possible mechanism of this charge separation is radiative charge transfer (RCT) [7]. The investigation by Kreidi et al. [8] of the charge separation processes which follow the K-LL Auger decay in the Ne dimer showed that in the lower lying states of the Ne2−–Ne character the charge separation proceeds via RCT and charge transfer through non-adiabatic transitions resulting in the two Ne+ ions.

In the case of inner-valence ionized atoms or molecules Auger decay is not allowed energetically. However, in weakly bound clusters (e.g. van der Waals or hydrogen-bonded) the inner-valence ionized species can relax electronically transferring the energy to a neighbor and ionizing it. Thus, the absorption of a photon...
ultimately leads to the production of an ion pair. This process is called interatomic/intermolecular Coulombic decay (ICD) [9–11]. Marburger et al. [12] observed ICD for the first time in Ne clusters whereas Jahnke et al. [13] unambiguously identified ICD in Ne₂ detecting Ne⁺–Ne⁺ ion pair and low energy ICD electrons in coincidence, after 2s inner-valence ionization of Ne.

Ion pairs are produced not only in the absorption of an energetic photon but also following the scattering of energetic electrons or ions off rare-gas dimers. Thus, ion pair formation following electron impact was observed in Ar₂ [14,15] and the ICD and RCT contributions unambiguously identified [15]. Titze et al. demonstrated the interplay of charge transfer and ICD in the experiment where α-particles were scattered off He₂ inducing production of two He⁺ ions [16]. ICD was also shown to play a major role in multiple ionization of and ion pair formation in Ne₂ and Ar₂ following the impact of positively charged ions [17,18]. Finally, both ICD and RCT are among the processes responsible for the ion pair formation in Ar₂ in ultrashort intense laser pulses [19]. This experimental evidence indicates that ICD and charge transfer processes are prominent in effecting charge redistribution in systems subjected to the action of ionizing radiation.

In the present work, we investigated Ne⁺–Ar⁺ pair formation from NeAr irradiated by monochromatic soft X-rays at three different photon energies: 200.5 eV, 268.2 eV, and 888.7 eV. Measuring kinetic energies of the two ions and electrons using electron-ion coincidence momentum imaging methods we could identify the mechanisms responsible for the pair production at each photon energy. In what follows we show that these mechanisms strongly depend on the energy of the exciting photon with ICD being predominant at the lowest energy and charge transfer processes which follow the L-MM Auger decay in Ar and K-LL in Ne taking precedence at higher energies.

2. Experiment

The experiment was carried out on the C-branch of the beam line BL27SU [20–22] at SPring-8. The photon beam was focused to a size of less than 0.2 mm in height and 0.5 mm in width at the point of crossing with the cluster beam. The measurements were performed at photon energies of 200.5 eV, 268.2 eV, and 888.7 eV. The photon energies of 268.2 eV and 888.7 eV are ~18 eV above Ar 2p and Ne 1s ionization thresholds, respectively. With those photon energies, the photoelectrons do not overlap with the ICD electrons which may be emitted. The value of 200.5 eV was chosen as a photon energy at which no core-level ionization occurs. The storage ring was operated in several-bunches mode providing 53 single bunches (4/58 filling bunches) separated by 82.6 ns for the measurements at photon energies of 200.5 eV and 888.7 eV, and in several-bunches mode providing 26 single bunches (2/29 filling bunches) separated by 165.2 ns for the measurements at a photon energy of 268.2 eV.

The heteronuclear dimers NeAr were produced by expanding a mixture of Ne and Ar gases at a flow-rate ratio of 70 : 1 and a total stagnation pressure of 0.12 MPa at temperature of 103 K through a pinhole of 80 μm diameter. Under these conditions the cluster beam contains monomers (Ne and Ar), homonuclear dimers (Ne₂ and Ar₂), heteronuclear dimers (NeAr), and a small fraction of larger clusters. The cluster beam was directed vertically and crosses the incident radiation at right angles.

Our momentum-resolved electron-ion multicoincidence [23,24] is equivalent to cold-target recoil-ion momentum spectroscopy or reaction microscope [25] and is based on recording times of flight (TOFs) for electrons and ions with two position and time sensitive multi-hit-capable detectors (Roentdek HEX120 for electrons and HEX80 for ions). Knowledge of the position and arrival time on the particle detectors, (x, y, t), allows us to extract information about the 3D momentum of each particle. The electron and ion TOF spectrometers were placed face to face. The spectrometer axis was horizontal and perpendicular to both the incident radiation and the cluster beam. Detailed geometric descriptions and typical field conditions of the spectrometers were given elsewhere [24]. The TOFs of electrons and ions were recorded with respect to the bunch marker of the light source using multi-hit time-to-digital converters (Roentdek TDC8HP), selecting by logic gating only electron signals synchronized with the single bunches.

3. Computational methods

The NeAr electronic ground state potential energy curve (PEC) was computed by the Møller-Plesset second order perturbation theory (MP2) implemented in the MOLPRO 2010.1 quantum chemistry package [26]. The PECs for the doubly ionized states were obtained by adding the corresponding double ionization energies to the energy of the NeAr electronic ground state. The double ionization energies were in turn computed within the framework of the Algebraic Diagrammatic Construction (ADC) scheme based on the perturbational expansion of the two-particle propagator, complete up to second order in perturbation theory (ADC(2)) [27]. The NeAr reference electronic state, molecular orbitals and electron integrals required by the ADC calculations were computed by the restricted Hartree-Fock method as implemented in the MOLCAS 7.4 package [28].

We furthermore calculated rates of RCT of NeAr²⁺ and Ne₂²⁺ states into Ne⁺–Ar⁺ states by means of the multireference configuration interaction (MRCI) method including single and double excitations as implemented in the MOLPRO 2010.1 package [26]. The reference space comprised 2h configurations with respect to the NeAr ground state Hartree-Fock determinant. The active orbital space contained 2s and 2p orbitals of Ne and 3s and 3p orbitals of Ar. In all ab initio calculations we used the aug-cc-pVQZ basis sets on neon and argon atoms [29,30].

4. Results and discussion

4.1. Photon energy 200.5 eV: interatomic Coulombic decay

Fig. 1 depicts the ion-ion coincidence TOF spectrum recorded at photon energy of 200.5 eV. The horizontal and vertical coordinates
correspond to the TOFs of the first and the second ions of the coincidence pair. Only the Ne$^+$–Ar$^+$ ion pairs satisfying the momentum conservation law within the plane perpendicular to the TOF axis are plotted. The results shown below are further filtered by the momentum conservation parallel to the TOF axis and thus the false coincidences in Fig. 1 are further suppressed. The ion pair Ne$^+$–Ar$^+$ is formed mostly as a result of ICD after double ionization to NeAr$^+(3s^2)$ [31]. The ion pairs Ne$^+$–Ar$^+$ and Ne$^+$–Ar$^+$ are formed mostly as the result of minor processes such as ICD after double ionization to Ne$^+$(2s$^1$2p$^1$)Ar [32] and triple ionization to NeAr$^+(3p^4)$ [33], respectively. Below, we will discuss in detail the ion pair formation channels Ne$^+$–Ar$^+$. In Fig. 1, two isotope components 20Ne$^+$–Ar$^+$ and 22Ne$^+$–Ar$^+$ are seen separately. A correlation line due to 20Ne$^+$–Ar$^+$ appears at the TOF region which corresponds to later times than the strongest correlation line due to 20Ne$^+$–Ar$^+$. There are other weak correlation lines parallel to the 20Ne$^+$–Ar$^+$ line at the TOF region which corresponds to earlier times. These lines are due to Ne$^+$–Ar$^+$ ion pairs produced by the previous synchrotron radiation pulse. In later analysis we use only 20Ne$^+$–Ar$^+$ signals detected at appropriate timing.

Fig. 2 shows the experimental results for Ne$^+$–Ar$^+$ ion-pair formation recorded at photon energy of 200.5 eV. Fig. 2(c) depicts the correlation between the kinetic energy release (KER) of the nuclei, i.e. the sum of the kinetic energies of the Ne$^+$ and Ar$^+$ ions, and the electron energy. These are the energies with respect to the resting laboratory frame. In this two dimensional plot, one can clearly see two islands labeled A and B which correspond to the interatomic decay events. Fig. 2(a) obtained by integrating the map in Fig. 2(c) over the electron energy coordinate depicts the KER in these events. The KER spectrum exhibits a single peak at 4.2 eV. Assuming a pure Coulomb repulsive energy between Ne$^+$ and Ar$^+$, one can estimate the interatomic distance at which the Coulomb explosion takes place as ~3.4 Å. This interatomic distance agrees with the ground state equilibrium distance of the electronic ground state $R_{e0}$ of the NeAr dimer, 3.5 Å [34]. This in turn indicates that the decay processes responsible for both signatures A and B occur at about the equilibrium distance of NeAr. Provided the photoabsorption has led to a vertical transition this indicates that the decay processes are much faster than the characteristic nuclear dynamics in the decaying states. Fig. 2(b) obtained by integrating the map in Fig. 2(c) over the KER coordinate depicts the energy distribution of electrons detected in coincidence with the Ne$^+$–Ar$^+$ ion pair. One can see a pronounced peak at ~7 eV which corresponds to the signature A and a minor peak at ~1 eV which corresponds to the signature B. The structure of the electron spectrum suggests three possibilities. The decay processes resulting in A and B originate from different decaying states, the same state decays into different final channels, or both the decaying and final states of the two processes are different.

The absorption of the photon at the energy of 200.5 eV can lead to the photoemission of 3p- and 3s-electrons of Ar, as well as 2p- and 2s-electrons of Ne. The 2s-ionization of Ne is expected to be followed by ICD as is shown by the following equation:

$$\text{(A) Ne}^+(2s^12S)\text{Ar} \rightarrow \text{Ne}^+(2p^12P)\text{Ar}^+(3p^12P) + \epsilon_{\text{ICD}}.$$ 

If the ICD process takes place, the sum of KER and electron kinetic energy, should be constant due to the energy conservation. For the process in Eq. (A) it is expected to be 11.2 eV. Therefore, one can identify the peak A in Fig. 2(d) as corresponding to this ICD channel. This ICD lifetime of the Ne$^+$(2s$^1$2S)Ar state was found to be less than 100 fs [35], therefore the decay takes place around the equilibrium distance. It is worth noting that it was previously observed by O’Keeffe et al. in NeAr dimer [36] and by Barth et al. in larger NeAr clusters [37] using conventional electron spectroscopy.

$$\text{(B) NeAr}^+(3p^1-1D)\text{Sd}^2S \rightarrow \text{Ne}^+(2p^1-1P)\text{Ar}^+(3p^1-2P) + \epsilon_{\text{ICD}}.$$

The energy levels diagram in Fig. 3(b) shows that the ICD decay from this state becomes forbidden for the interatomic distances between 2.6 Å and 2.8 Å. The ICD rate of such higher lying ionization satellites is usually less than the characteristic vibrational frequencies in the decaying state. Therefore, ICD is accompanied by nuclear dynamics and most of the decay takes place at shorter
interatomic distances [39,40]. In the case of the process in Eq. (8) the shortest distance where the decay can happen corresponds to ICD thresholds which explains why ICD electrons have energies between 0 eV and 1 eV.

The features between peaks A and B in Fig. 2(d) are considered to correspond to the ICD processes from NeAr$^+$ ionization satellite states lying above NeAr$^+$ (3p$^2$ D)$^5 S$ and converging to the doubly ionized states NeAr$^{2+}$ (3p$^2$ 3P), NeAr$^{2+}$ (3p$^{-2}$ 3D) or NeAr$^{2+}$ (3p$^2$ 1S).

4.2. Photon energies 268.2 eV and 888.7 eV: radiative and non-radiative charge transfer

Absorption of a photon at 268.2 eV by NeAr leads mostly to the emission of a 2p-electron of Ar [41,42]. The resulting core-ionized state undergoes local Auger decay populating mostly the following NeAr$^{2+}$ states: NeAr$^{2+}$ (3p$^2$ 3P) (344), NeAr$^{2+}$ (3p$^{-2}$ 3D) (395), NeAr$^{2+}$ (3p$^{-2}$ 1S) (100), NeAr$^{2+}$ (3s$^1$ 3p$^{-1}$ 3P) (73), and NeAr$^{2+}$ (3s$^{-1}$ 3p$^{-1}$ 3P) (60) where the number in parenthesis indicates a relative population of each state [43]. All these states are stable with respect to electronic decay.

Fig. 3(a) depicts the experimental KER of the Ne$^+$–Ar$^+$ pair obtained when the NeAr is irradiated by photons at energy of 268.2 eV. The corresponding ion-ion coincidence TOF spectrum recorded at 268.2 eV has been already published in [31]. One can see four peaks in the KER spectrum at 3.9 eV, 4.4 eV, 4.9 eV, and 6.0 eV. It is possible that the ICD following the 2s-ionization of Ne which gives the peak at 4.2 eV in the KER spectrum (see Fig. 2(a)) contributes to the KER spectrum in Fig. 3(a). However, in the current case the contribution of ICD to the ion pair formation is less significant, since the 2s photoionization cross section of Ne is about 5% of the 2p photoionization cross section of Ar at 268.2 eV [41,42]. Moreover, the peaks in the KER spectrum appear also in the KER spectrum recorded in coincidence with Ar 2p photoelectrons at ~18 eV (not shown here). Therefore, the Ne$^+$–Ar$^+$ ion-pair formation is the result both of ICD after Ne 2s-ionization and, predominantly, of charge transfer after L-MM Auger decay in Ar.

Charge transfer can occur radiatively, RCT, whereby an emitted photon ensures the conservation of energy [5]. Alternatively if the curves corresponding to the one-site dicatonic states and two-site dicatonic states cross the process can proceed via non-adiabatic transitions. Fig. 3(b) shows the ab initio PECs of the NeAr$^{2+}$ one-site dicatonic states predominantly populated in the Auger decay as well as the PECs of the two-site dicatonic Ne$^+$ (2p$^{-1}$ P)Ar$^+$ (3p$^{-1}$ 3P) and Ne$^+$ (2p$^{-1}$ 2P)Ar$^+$ (3s$^{-1}$ 3S) states. The charge transfer in the low lying one-site states can occur only radiatively. Indeed their interaction with the Ne$^+$ (2p$^{-1}$ 2P)Ar$^+$ (3p$^{-1}$ 2P) manifold leads to the avoided crossings and energy gaps larger than 1 eV which makes non-adiabatic transitions improbable. The rate of RCT usually increases exponentially with the decreasing interatomic distance (see e.g. [44]), therefore, it takes place mostly close to the inner turning points of the corresponding PECs. In the current system the interaction of the NeAr$^{2+}$ (3p$^2$ 3P), NeAr$^{2+}$ (3p$^{-2}$ 3D), and NeAr$^{2+}$ (3p$^2$ 1S) states with the Ne$^+$ (2p$^{-1}$ 2P)Ar$^+$ (3p$^{-1}$ 2P) states leads to slower increase in the interatomic dipole transition moment with the decreasing distance. Therefore, RCT can be considerable even some distance away from the turning point leading to smaller KER values. We found that RCT in the NeAr$^{2+}$ (3p$^2$ 3P), NeAr$^{2+}$ (3p$^{-2}$ 3D), and NeAr$^{2+}$ (3p$^2$ 1S) states result in the theoretical KER spectrum shown in Fig. 3(a) which explains the appearance of the peaks at 4.4 eV and 4.9 eV in the experimental spectrum. Expected energies (wavelengths) of photons emitted with the RCT from the NeAr$^{2+}$ (3p$^2$ 3P), NeAr$^{2+}$ (3p$^{-2}$ 3D) and NeAr$^{2+}$ (3p$^2$ 1S) states are 1.0–1.9 eV (1200–650 nm), 2.5–3.4 eV (500–370 nm) and 5.4 eV (230 nm), respectively. The higher lying NeAr$^{2+}$ (3s$^1$ 3p$^{-1}$ 3P) and NeAr$^{2+}$ (3p$^{-3}$ 3p$^{-1}$ 3P) states may also undergo RCT into the Ne$^+$–Ar$^+$ manifold. There are four molecular terms (1Σ, 1Π, 3Σ and 5Π) arising from the NeAr$^{2+}$ (3s$^{3}$ 3p$^{-1}$ 3P) and NeAr$^{2+}$ (3s$^{-3}$ 3p$^{-1}$ 3P) states. Our numerical estimates show that the RCT rate in the 1Σ, 1Π and 3Σ terms close to the respective
inner turning points is an order of magnitude smaller than the rate of local radiative decay in Ar<sup>2+</sup>. Although, the ratio of the RCT to the local radiative rate in the <sup>3</sup>P term reaches 3 : 2 at the respective turning point, this ratio is small for most of the interatomic distances where the dynamics take place. Therefore, we conclude that the excited NeAr<sup>2+</sup> states predominantly relax into the lower lying one-site doubly ionized states, while RCT into the NeAr manifold is insignificant.

As the discussion above shows the peaks at 3.9 eV and 6.0 eV cannot appear in the experimental spectra due to the RCT. The other possibility is the transitions driven by the non-adiabatic coupling between one-site and two-site doubly ionized states. As we explained above there are no suitable crossings between the lowest two-site and one-site states which rules out the non-adiabatic transitions between them. However, the two higher one-site multiplets lie at energies where there are many two-site satellite states of the Ne<sup>−</sup>−Ar<sup>+</sup> character. If no third body, such as a photon or an electron, is emitted the KER following the non-adiabatic transition should be equal to the $E_{\text{fin}}(\infty) - E_{\text{fin}}(\infty) - \Delta E_{\text{fin}}(R_{\text{eq}})$, where $E_{\text{fin}}$ and $E_{\text{ini}}$ are the PECs of the initial and final states, while $\Delta E_{\text{fin}}(R_{\text{eq}})$ is the interatomic binding energy in the initial state at the ground state equilibrium geometry of NeAr. Since the PECs of the NeAr<sup>2+</sup>(3s<sup>−3</sup>3p<sup>−1</sup>) and NeAr<sup>2+</sup>(3s<sup>−1</sup>3p<sup>−1</sup>) states are very weakly bound ($\Delta E_{\text{fin}}(R_{\text{eq}}) \approx 50$ meV) the KER is equal to the difference of the energies of the initial and final states at infinite interatomic separation. Thus we can identify suitable Ne<sup>−</sup>−Ar<sup>+</sup> states from the atomic data. For the NeAr<sup>2+</sup>(3s<sup>−1</sup>3p<sup>−1</sup>1P) state the crossing with the following states will lead to the peaks in the KER spectrum:

(i) NeAr<sup>2+</sup>(3s<sup>−1</sup>3p<sup>−1</sup>1P) → Ne<sup>+</sup>(2p<sup>−1</sup>2P)Ar(3P<sup>−3</sup>2P<sup>−3</sup>)Ar<sup>+</sup>(3P<sup>−2</sup>2F)Ar<sup>+</sup>(3P<sup>−2</sup>2F),

(ii) NeAr<sup>2+</sup>(3s<sup>−1</sup>3p<sup>−1</sup>1P) → Ne<sup>+</sup>(2p<sup>−1</sup>2P)Ar(3P<sup>−3</sup>2P<sup>−3</sup>)Ar<sup>+</sup>(3P<sup>−2</sup>2F),

(iii) NeAr<sup>2+</sup>(3s<sup>−1</sup>3p<sup>−1</sup>1P) → Ne<sup>+</sup>(2p<sup>−1</sup>2P)Ar(3P<sup>−3</sup>2P<sup>−3</sup>)Ar<sup>+</sup>(3P<sup>−2</sup>2F). 

The NeAr<sup>2+</sup>(3s<sup>−1</sup>3p<sup>−1</sup>1P) state can only cross the Ne<sup>+</sup>(2p<sup>−1</sup>2P)Ar(3P<sup>−3</sup>2P<sup>−3</sup>)Ar<sup>+</sup>(3P<sup>−2</sup>2F) which would lead to the KER of 3.9 eV. The KER of the ion pair produced in the charge transfer via non-adiabatic coupling is determined by the energetics at infinite separations. Therefore, the actual shape of the dissociative curve is only important inasmuch as it determines the position of the crossing point. For charge transfer to take place the crossing point should lie approximately between $R_{\text{eq}}$ and the inner turning point. At larger interatomic distances the PECs of the Ne−Ar<sup>+</sup> states behave as $1/R$, while at distances shorter than the spatial extension of an excited electron they behave as $2/R$ or even exponentially. We used this information to estimate the position of the crossing point as is shown in Fig. 3 (a). We would like to remark that non-adiabatic interactions should be strong enough to transfer the charge within a few ns, which is a characteristic radiative lifetime of Ar<sup>2+</sup>(3s<sup>−1</sup>3p<sup>−1</sup>).

Photoabsorption by NeAr at 888.7 eV results in the emission of a 1s-electron of Ne which is followed by the local Auger decay. We are interested in the Ne−Ar<sup>+</sup> pair formation in the NeAr<sup>2+</sup>(2p<sup>−2</sup>1D)Ar and NeAr<sup>2+</sup>(2p<sup>−2</sup>5S)Ar Auger final states (populated in the ratio of 6:1 [45]) which are stable with respect to electronic decay. Higher lying NeAr<sup>2+</sup>(2s<sup>−1</sup>2P<sup>−1</sup>3P)Ar and NeAr<sup>2+</sup>(2s<sup>−1</sup>2P<sup>−1</sup>1P)Ar Auger final states undergo ICD [32] producing a different pair of ions (Ne<sup>−</sup>−Ar<sup>+</sup>).

Fig. 4(a) depicts KER for Ne−Ar<sup>+</sup> ion pair recorded in coincidence with Ne 1s-photoelectrons. One can see three peaks labeled by
interestingly, both rct and the charge transfer via non-adiabatic coupling compete in the case of the ne₂−ar⁺ states. our computations show that the rct lifetime at the inner turning point can be as short as 10 ns. appearance of the peak at 8 ev in the kerr spectra indicate that the other charge transfer mode should be as fast or even faster that the radiative one.

5. summary

we identified ne−ar⁺ ion-pair formation channels in the near dimer irradiated by monochromatic soft x-rays. we observed that the mechanisms, whereby the ion pair is produced strongly depend on the energy of the x-ray photon. at the lowest energy used in the experiment, 200.5 ev, the predominant mechanism of the pair formation was the interatomic Coulombic decay (icd) of the ne²−(2s⁻) ar inner-valence ionized and nea²⁺(3p⁻5d) ionization satellite state produced in photoabsorption. at higher photon energy, 268.2 ev, photoabsorption leads to the emission of a 2p-electron of ar and the auger decay process which populates a manifold of ne₂⁺ states. comparing the theoretical predictions with the experimentally measured kinetic energy release in the ne−ar⁺ coulomb explosion we conclude that two mechanisms are responsible for the ion pair formation. the charge transfer in the lower lying ne₂⁻ states is accompanied by photon emission (radiative charge transfer (rct)). in the higher lying ne₂⁺ states which cross a number of ne₂−satellite states charge transfer is driven by the non-adiabatic coupling. similarly, for the highest photon energy of 888.7 ev a combination of rct and charge transfer via non-adiabatic coupling is responsible for the ne−ar⁺ pair creation from the ne₂−auger final states. the presented results are the first observation of charge transfer and icd in near dimer using momentum-resolved electron-ion multiconfiguration spectroscopy.

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