Radiative charge transfer and interatomic Coulombic decay following direct double photoionization of neon dimers

I Higuchi, T Ouchi, K Sakai, H Fukuzawa, X-J Liu, K Ueda, H Iwayama, K Nagaya, M Yao, D Ding, D Zhang, Y Tamenori and N Saito

1 Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679-5198, Japan
2 Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
3 Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
4 Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, P. R. China
5 National Institute of Advanced Industrial Science and Technology (AIST), NMIJ, Tsukuba 305-8568, Japan

E-mail: fukuzawa@tagen.tohoku.ac.jp

Abstract. We have investigated charge separation Ne\(^+\)-Ne\(^-\) and Ne\(^{2+}\)-Ne\(^+\) from Ne\(_2\) after direct double photoionization and compared them with those after 1s photoionization followed by KLL Auger decay and also with those after 2p photoionization of Ar\(_2\) followed by LMM Auger decay. The Ne\(^+\)-Ne\(^-\) separation takes place via radiative charge transfer from one-site two-hole states Ne\(^{2+}\)(2p\(^4\)) - Ne, whereas the Ne\(^{2+}\)-Ne\(^+\) separation takes place via interatomic Coulombic decay from one-site two-hole states Ne\(^{2+}\)(2s\(^1\)2p\(^5\)) - Ne.

1. Introduction
Both direct double photoionization and core-level photoionization followed by the Auger decay of molecules usually lead to ion-pair formation. The situation may be different for van der Waals rare gas dimers such as Ne\(_2\). Both direct double photoionization and 1s photoionization of Ne\(_2\) followed by KLL Auger decay create two holes in one Ne site. Such dicationic states are not necessarily dissociative [1]. In the present study, we will investigate the fate of such one-site two-hole states of Ne\(_2\) created by direct double photoionization as well as 1s photoionization followed by KLL Auger decay. For comparison, we will also present results for the one-site two-hole states of Ar\(_2\) created by 2p photoionization followed by LMM Auger decay.

For Ar\(_2\), Morishita et al [2] found that Ar\(^{2+}\)(3p\(^3\)3d)-Ar one-site state is subject to interatomic Coulombic decay (ICD) to the Ar\(^{2+}\)(3p\(^5\))-Ar\(^+\) charge-separation channel, using electron-ion multi-coincidence momentum spectroscopy (often called COLTRIMS or reaction microscope). Saito et al [3], on the other hand, elucidated that Ar\(^-\)-Ar\(^+\) charge separation takes place from the Ar\(^{2+}\)(3p\(^4\))-Ar one-site two-hole states, using Auger-electron-Ar\(^-\)-Ar\(^+\) coincidence methods. Considering that the Ar\(^{2+}\)(3p\(^5\))-Ar states are non-dissociative [4], it is concluded that the only possible mechanism of this charge separation is via radiative charge transfer. For Ne\(_2\), Kreidi et al [5] and Yamazaki et al [6] have investigated 1s photoionization of Ne\(_2\) using electron-ion multi-coincidence momentum spectroscopy and found that Ne\(^{2+}\)(2p\(^4\))-Ne\(^+\) charge separation takes place via ICD from one-site state Ne\(^{2+}\)(2s\(^1\)2p\(^3\))-
Ne populated by the KL\textsubscript{1}L\textsubscript{2,3} Auger decay. Kreidi \textit{et al} \cite{7} did further extensive study on charge separation channels that include ICD, radiative charge transfer, and potential curve crossing from many different KLL Auger final states in Ne\textsubscript{2}. In the present paper, we report the first observations of charge-separation via radiative charge transfer and via ICD, after direct double photoionization of Ne\textsubscript{2}, and compare them with those after KLL Auger decay of Ne\textsubscript{2} as well as those after LMM Auger decay of Ar\textsubscript{2}.

2. Experiment

The experiment was carried out on the \textit{c} branch of the soft X-ray photochemistry beam line 27SU at SPring-8 \cite{8-10}. The operation mode of the storage ring was the so called several single-bunches mode, i.e., 26 single-bunches + 2/29 filling mode, with a single-bunch separation of 165.2 ns.

The cluster beam is produced by expanding a mixture of neon and argon gases at a flow rate ratio of 70:1, at a total stagnation pressure of 1.2 \times 10^5 Pa at 103 K, through a nozzle with diameter of 80 \textmu m. Under these conditions, the cluster beam includes Ne and Ar monomers, Ne\textsubscript{2} and Ar\textsubscript{2} dimers, NeAr hetero-dimers, as well as larger clusters. The cluster beam is directed vertically.

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 coincidence measurements described below were performed with the electric vector \(E\) of the linearly polarized light orientated vertically, at a photon energy of 268.24 eV, i.e., 19.61 and 17.46 eV above the atomic Ar 2p\textsuperscript{1} 2P\textsubscript{3/2} and 2p\textsuperscript{1} 2P\textsubscript{1/2} ionization thresholds, i.e., 248.628 and 250.776 eV, respectively \cite{11}, and at photon energy of 888.09 eV, i.e., 17.88 eV above the atomic Ne 1s\textsuperscript{1} ionization thresholds, i.e., 870.21 eV \cite{12}. The photon bandwidth is 0.1 eV and 0.6 eV at 268.24 eV and 888.09 eV, respectively.

Our momentum-resolved electron-ion-ion coincidence spectroscopy \cite{13-19} is based on recording the electron and ion times-of-flight (TOFs) with multi-hit two-dimensional position sensitive detectors \cite{20}. Knowledge of position and arrival time on the particle detectors, \((x, y, t)\), allows us to extract information about the linear momentum \((p_x, p_y, p_z)\) for each particle. The two TOF spectrometers are placed face to face. The TOF spectrometer axis is horizontal and perpendicular to both the photon beam and the molecular beam. The lengths of the acceleration region and the drift region of the electron spectrometer are 33.7 mm and 67.4 mm, respectively. For the ion spectrometer, there are two acceleration regions and no drift region. The length of the first acceleration region is 16.5 mm and that of the second one is 82.5 mm. The TOF spectrometer for the electron is equipped with a hexagonal multi-hit position-sensitive delay-line detector of effective diameter of 120 mm, while that for the ion is of effective diameter of 80 mm.

In the present experiments, the static extraction field was set to 1.5 V/mm. The static field of the second acceleration region for the ions was set to 21 V/mm. A uniform magnetic field of 6.1 G was superimposed to the spectrometer by a set of Helmholtz coils outside the vacuum chamber. Under these conditions, all the electrons up to the kinetic energies of 20 eV and all the ions up to the kinetic energies of 9 eV, both ejected in 4\textpi\,sr, were accelerated onto the MCP detectors. The TOFs of the electrons and ions were recorded with respect to the bunch marker of the synchrotron radiation source using multi-hit time-to-digital converters (Roentdek TDC8HP). Appropriate gates selected only those electron signals synchronized with the single bunches. We recorded only events in which at least one ion and one electron were detected in coincidence.

3. Results and discussion

3.1. Photoion-photoion coincidence (PIPICO) map

Figure 1 shows the PIPICO map, simultaneously recorded for mixture gas of Ne and Ar (1.4 \%) recorded at 268.24 eV. In this map, the horizontal and vertical axes are the TOFs for the first-arrived and second-arrived ions of the detected pairs. Only the Ar\textsuperscript{+}-Ar\textsuperscript{+}, Ar\textsuperscript{+}-Ar\textsuperscript{2+}, Ne\textsuperscript{+}-Ne\textsuperscript{+}, and Ne\textsuperscript{+}-Ne\textsuperscript{2+} pairs satisfying the momentum conservation laws within the plane perpendicular to the TOF axis are plotted.
Other ion pairs arising from hetero-dimers NeAr were also detected and will be discussed elsewhere. Some false coincident events originating from the previous bunch shifted by 165.2 ns are still seen. The results shown below are after imposing also the momentum conservation parallel to the TOF axis and thus all the false coincidences in figure 1 are further suppressed. Coincidence events originating from the $^{22}$Ne isotopes are also seen in figure 1 but were not included in the following analysis.

3.2. \( \text{Ar}^+ - \text{Ar}^+ \) coincident channel

Let us start with the strongest channel in the map of figure 1, i.e., \( \text{Ar}^+ - \text{Ar}^+ \) pair formation. This is the channel intensively discussed [3]. In brief, figure 2 (a) depicts distribution of kinetic energy release (KER), or the sum of the kinetic energies of the two \( \text{Ar}^+ \) ions, recorded in coincidence with the \( \text{Ar} \) 2p photoelectrons at kinetic energy 18 eV. The KER is peaked at 5.1 eV. Assuming a pure Coulomb repulsive energy between the two \( \text{Ar}^+ \) ions, one can estimate the internuclear distance at the Coulomb
explosion to be 2.8 Å. This internuclear distance is much shorter than equilibrium internuclear
distance, 3.8 Å, in the neutral Ar₂ dimers. On the other hand, it is in good agreement with the
equilibrium internuclear distances of the one-site dicationic states Ar²⁺(3p²3P, ¹D, ¹S)-Ar [4]. These
states can be populated via the intra-atomic L₂,3M₂,3 Auger decay in one site, following Ar 2p
ionization. The sum of the branching ratios to these Auger final states is 0.72. These Auger-final states
are, however, not dissociative. The only way to produce Ar⁺-Ar⁺ pair from these Auger-final states is
radiative charge transfer, as discussed previously.

3.3. Ne⁺-Ne⁺ coincident channel

PIPICO map recorded at 888.09 eV, not shown here, exhibits the strong Ne⁺-Ne⁺ coincidence channel.
KER distribution recorded in coincidence with Ne 1s photoelectrons at kinetic energy of 18 eV shown
in figure 2 (b) is peaked at 7.4 eV, illustrating that the charge separation starts to take place at the
internuclear distance of 1.9 Å. This internuclear distance is much shorter than the equilibrium
internuclear distance, 3.1 Å, in the neutral Ne₂ dimers but coincides with the equilibrium internuclear
distances of one-site dicationic states Ne²⁺(3p²3P, ¹D, ¹S)-Ne [1]. Thus, as in the case of Ar₂ discussed
above, Ne⁺-Ne⁺ pair formation is mostly via radiative charge transfer from these one-site states

Figure 3. (a) Kinetic energy release distribution for Ne⁺-Ne⁺ pair coincident formation at the photon energy
of 268.24 eV. (b) Electron kinetic energy spectrum coincident with Ne⁺-Ne⁺ pair at the photon energy of
268.24 eV. (c) Relationship between the electron energy and the KER.
produced via intra-atomic Ne KL$_2$L$_{2,3}$ Auger decay. The sum of the branching ratio to these Auger-final states is 0.70. This channel was observed also by Kreidi et al [5,7] and Yamazaki et al [6].

Let us now discuss the Ne$^+$-Ne$^+$ pair formation at 268.24 eV. Figure 3 (a) depicts KER distributions. Two peaks appear: peak 1 is at 4.8 eV and peak 2 is at 7.1 eV. Assuming a pure Coulomb repulsive energy between the two Ne$^+$ ions, one can estimated the internuclear distances 3.0 Å and 2.0 Å for the peaks 1 and 2, respectively. Figure 3 (b) depicts two electron energy spectra coincident with the Ne$^+$-Ne$^+$ pairs that form the peaks 1 and 2, respectively. The electron spectrum that correlates to peak 1 is peaked at 0.4 eV. Both KER 4.8 eV and the electron energy 0.4 eV well agree with the measurement by Jahnke et al [21], where they identified the interatomic Coulombic decay in the Ne dimer after Ne 2s ionization. The relationship between the electron energy and the KER is shown in figure 3 (c). The tilted island with a slope of -1 around the KER of 4.8 eV and the electron energy of 0.4 eV is providing evidence that Ne$^+$-Ne$^+$ pair formation is via ICD decay following 2s ionization. The energy of the peak 2 coincides with that in figure 2 (b). Furthermore, the corresponding electron spectrum indicates that most of the contributions come from continuous electron emission. These facts indicate that the channels forming the peak 2 with continuous electron emission are mostly attributed to radiative charge transfer after 2p double photoionization. In other words, this is the first evidence of radiative charge transfer that takes place after double photoionization. We note, however, that the energy of the peak 2 also coincides with that of shake-induced ICD observed by Jahnke et al [21]. The intensity of the peak 2 observed in the present experiment is much higher than they observed. Thus, to be exact, the present peak 2 is considered to be the sum of radiative charge transfer from the 2p$^4$ dicationic states the shake-up induced ICD from 2p$^3$2p cationic satellite states

3.4. Ar$^{2+}$-Ar$^+$ and Ne$^{2+}$-Ne$^+$ coincident channels

In figure 4, the panels (a), (b), and (c) depict the KER distributions for Ar$^{2+}$-Ar$^+$ formation at 268.24 eV, Ne$^{2+}$-Ne$^+$ formation at 888.09 eV, and Ne$^{2+}$-Ne$^+$ formation at 268.24 eV, respectively, whereas panels (d), (e), and (f) show the electron energy distributions (< 10 eV) recorded in coincidence with Ar$^{2+}$-Ar$^+$ at 268.24 eV, Ne$^{2+}$-Ne$^+$ at 888.09 eV, and Ne$^{2+}$-Ne$^+$ at 268.24 eV, respectively. As can be seen, low-energy electron yields are common for all these three cases.

Let us first focus on the spectra (a) and (d) for Ar$^{2+}$-Ar$^+$ formation at 268.24 eV. This channel was first discussed by Morishita et al [2]. Ar$^{2+}$-Ar$^+$ formation is mostly due to interatomic Coulombic decay from the Auger final one-site dicaticionic state Ar$^{2+}$(3p$^3$3d)-Ar to the two-site tri-caticionic state Ar$^{2+}$(3p$^3$)-Ar (3p$^4$). The low-energy electrons (~2 eV) in the panel (d) is emitted by this ICD process. The KER distribution in the panel (a) is peaked at 7.4 eV, illustrating that the charge separation starts to take place at the internuclear distance of 3.9 Å, i.e., close to the equilibrium internuclear distance 3.8 Å, and thus that the ICD and Auger take much faster than nuclear motion.

Let us focus on the spectra (b) and (e) for Ne$^{2+}$-Ne$^+$ at 888.09 eV. This channel was again fully discussed by Kreidi et al [5,7] and by Yamazaki et al [6]. Ne$^{2+}$-Ne$^+$ formation is mostly due to interatomic Coulombic decay from the Auger final one-site dicaticionic state Ne$^{2+}$(2s$^2$2p$^5$)-Ne to the two-site tri-caticionic states Ne$^{2+}$(2p$^4$1D)-Ne$^+$ (2p$^5$) and Ne$^{2+}$(2p$^4$1P)-Ne$^+$ (2p$^5$). In the KER distribution in the panel (b), the larger peak at 9.2 eV correspond to the channel to Ne$^{2+}$(2p$^4$1D)-Ne$^+$ (2p$^5$), whereas the smaller peak at 12.5 eV to Ne$^{2+}$(2p$^4$1P)-Ne$^+$ (2p$^5$). The former peak corresponds to the case when the charge separation starts to take place at the equilibrium internuclear distance 3.1 Å of the neutral Ne$_2$ ground state, whereas the latter peak at the case when the charge separation starts to take place at shortened internuclear distance 2.3 Å. In the first case, the spin of the double charged Ne atom is conserved, whereas the spin is not conserved in the second case. These differences come from the different ICD mechanisms. The first type of ICD is caused by the direct Coulomb integral and thus called direct ICD. The second time of ICD is caused by the exchange integral and thus called exchange ICD. Direct ICD dominates at large internuclear distances, whereas exchange ICD becomes effective at short internuclear distances where the wavefunctions overlap. In the present Ne$_2$ case, the direct ICD is energetically closed at the internuclear distances < 2.5 Å. Thus we see clearly the
exchange ICD at internuclear distances < 2.5 Å. The low-energy electrons (~2 eV) in the panel (e) are emitted by these two types of ICD processes.

Now let us focus on the spectra (c) and (f) for Ne\textsuperscript{2+}-Ne\textsuperscript{+} at 268.24 eV. We immediately notice that these spectra well coincide with spectra (b) and (e) just discussed above. Thus the spectra (c) and (f) is considered to be due to ICD from one-site dicationic state Ne\textsuperscript{2+}(2s\textsuperscript{1}2p\textsuperscript{5}\textsuperscript{1}P)-Ne. The only possible mechanism to produce one-site dicationic state Ne\textsuperscript{2+}(2s\textsuperscript{1}2p\textsuperscript{5}\textsuperscript{1}P)-Ne at photon energy 268.24 eV is

![Figure 4.](image-url)
double photoionization that directly creates \( \text{Ne}^{2+}(2s^12p^51P)\)-Ne. Thus this is the first evidence of ICD that takes place after double photoionization.

4. Conclusion
We have observed charge separations \( \text{Ne}^+\)-\( \text{Ne}^+ \) and \( \text{Ne}^{2+}\)-\( \text{Ne}^+ \) from \( \text{Ne}_2 \) after direct double photoionization and after 1s photoionization and compared them with charge separations \( \text{Ar}^+\)-\( \text{Ar}^+ \) and \( \text{Ar}^{2+}\)-\( \text{Ar}^+ \) from \( \text{Ar}_2 \) after 2p photoionization, using electron-ion-ion coincidence momentum spectroscopy. We found that the charge separation \( \text{Ne}^+\)-\( \text{Ne}^+ \) takes place via radiative charge transfer from one-site two-hole states \( \text{Ne}^{2+}(2p^4)-\text{Ne} \) populated via the direct double photoionization as well as via KL(2,3)L(2,3) Auger decay following 1s photoionization, whereas the charge separation \( \text{Ne}^{2+}\)-\( \text{Ne}^+ \) takes place via ICD from one-site two-hole states \( \text{Ne}^{2+}(2s^12p^5)-\text{Ne} \) populated via the direct double photoionization as well as via KL(1)L(2,3) Auger decay following 1s photoionization. These are the first evidences of the radiative charge transfer and ICD after direct double ionization. Measurements of the radiative charge transfer and ICD following direct double ionization of \( \text{Ar}_2 \) at the photon energy below \( \text{Ar} 2p \) ionization threshold would be possible.

Acknowledgements
The experiments were carried out at SPring-8 with approval by JASRI. We are grateful to Lorenz Cederbaum and Alexander Kueff for helpful discussion. The work was partially supported by Grants-in-Aid for Scientific Researches from Japan Society for the Promotion of Science (JSPS) and by the Budget for Nuclear Research from Ministry of Education, Culture, Sports, Science and Technology, based on screening and counseling by the Atomic Energy Commission. DD and DZ thank the hospitality during their staying in SPring-8 and the partial support from NSFC.

References
[1] Stoychev S D, Kuleff A I, Tarantelli F and Cederbaum L S 2008 J. Chem. Phys. 129 074307
[2] Morishita Y et al 2006 Phys. Rev. Lett. 96 243402
[3] Saito N et al 2007 Chem. Phys. Lett. 441 16
[4] Stoychev S D, Kuleff A I, Tarantelli F and Cederbaum L S 2008 J. Chem. Phys. 128 014307
[5] Kreidi K et al 2008 J. Phys. B: At. Mol. Opt. Phys. 41 101002
[6] Yamazaki M et al 2008 Phys. Rev. Lett. 101 043004
[7] Kreidi K et al 2008 Phys. Rev. A 78 043422
[8] Ohashi H et al 2001 Nucl. Instrum. Methods Phys. Res. A 467-468 529
[9] Ohashi H et al 2001 Nucl. Instrum. Methods Phys. Res. A 467-468 533
[10] Ueda K 2003 J. Phys. B: At. Mol. Opt. Phys. 36 R1
[11] King G C et al 1977 J. Phys. B: At. Mol. Phys. 10 2479
[12] Siegbahn K et al 1969 ESCA Applied to Free Molecules (Amsterdam, North-Holland)
[13] Muramatsu Y et al 2002 Phys. Rev. Lett. 88 133002
[14] Fanis A De et al 2001 Phys. Rev. Lett. 89 023006
[15] Ueda K and Eland J H D 2005 J. Phys. B: At. Mol. Opt. Phys. 38 S839
[16] Saito N, Fanis A De, Koyano I and Ueda K 2005 J. Electron Spectrosc. Relat. Phenom. 144-147 103
[17] Morishita Y et al 2006 Radiat. Phys. Chem. 75 1977
[18] Ueda K et al 2007 J. Electron Spectrosc. Relat. Phenom. 155 113
[19] Saito N, Liu X-J, Morishita Y, Suzuki I H and Ueda K 2007 J. Electron Spectrosc. Relat. Phenom. 156–158 68
[20] Jagutzki O et al 2002 IEEE Transact. Nucl. Science 49 2477
[21] Jahnke T et al 2004 Phys. Rev. Lett. 93 163401