Interatomic Coulombic decay and electron-transfer-mediated decay following triple ionization of Ne<sub>2</sub> and NeAr

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**Article info**

**Article history:**
Available online 15 September 2016

**Abstract**

We report observations of the interatomic Coulombic decay (ICD) and electron-transfer-mediated decay (ETMD) from the triply charged states in Ne<sub>2</sub> and NeAr dimers. The ICD processes leading to fragmentation of Ne<sup>3+</sup>-Ne into Ne<sup>2+</sup>-Ne<sup>2+</sup> and Ne<sup>3+</sup>-Ar into Ne<sup>2+</sup>-Ar<sup>+</sup>, and ETMD processes leading to fragmentation of Ne<sup>3+</sup>-Ne into Ne<sup>2+</sup>-Ne<sup>2+</sup> are unambiguously identified by electron–ion-ion coincidence spectroscopy in which the kinetic energy of the ICD or ETMD electron and the kinetic energy release between the two fragment ions are measured in coincidence.

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**1. Introduction**

In 1997, Cederbaum et al. [1] theoretically suggested a new relaxation mechanism of the electronically excited species in the presence of the loosely bound neighboring species. In this mechanism, the excited species decays electronically by ionizing the neighboring species. This new relaxation mechanism is called interatomic/intermolecular Coulombic decay (ICD). Six years later, the first experimental proof for occurrence of ICD was reported for neon clusters [2]. Since then, a number of theoretical and experimental studies on ICD have been carried out in many different systems, as recently reviewed [3]. These studies elucidated ICD plays an important role in chemistry, transferring the energy and the charge from the excited species to the environment surrounding it. It is worth noting also that ICD in hydrogen bonded systems and its role as a source of low energy electrons in biological medium have been discussed in several recent publications [4–9].

Prototype systems where ICD have been studied in details, both experimentally and theoretically, are rare-gas dimers. Let us consider the ICD in a dimer AB illustrated in Fig. 1. An atom A with an inner-valence vacancy transfers its energy to a neighboring atom B which subsequently releases its energy by emitting an electron from its outer-valence orbital (Fig. 1(a)). This energy transfer process corresponds to the direct Coulomb term of the two-electron integral. This term causes an asymptotic behavior of the ICD rate of $R^{-6}$ ($R$ being the internuclear distance) characteristic of dipole–dipole interaction and thus can be viewed as virtual photon exchange [10]. The ICD rate caused by the exchange term (Fig. 1(b)), on the other hand, drops exponentially as a function of $R$. There is another class of ICD-related processes, as illustrated by Fig. 1(c), where the outer-valence electron of the neighboring atom B fills the inner-valence vacancy of atom A and another outer-valence electron of the atom B is emitted. This process is called electron-transfer-mediated decay (ETMD) [11]. ETMD is different from ICD in the final charge states of both atoms. In ETMD, the charge state of the atom A that had the initial vacancy decreases by one while the originally neutral neighboring atom B now becomes doubly charged. The ETMD rate drops exponentially as a function of $R$. ETMD is much slower than ICD at equilibrium.

http://dx.doi.org/10.1016/j.chemphys.2016.09.022
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The internuclear distances of van der Waals clusters in general. For example, in the case of decays from Ne\(^+(2s^{-1})\)-Ar, ICD is at least 10\(^3\) times faster than ETMD at the equilibrium internuclear distance of NeAr and thus the lifetime of Ne\(^+(2s^{-1})\)-Ar is solely determined by the ICD rate \[11\]. ETMD, however, becomes dominant if ICD is energetically closed \[12,13\].

The initial states of ICD and ETMD can be not only inner-valence ionized states \[1,2\] but also resonant neutral states \[14\], ionic satellite states \[15\], Auger final diatomic states \[16,17\], triply ionized states \[12\], etc. In the present work, we have investigated ICD and ETMD from the triply ionized states using homo-nuclear dimers Ne\(_2\) and hetero-nuclear dimers NeAr. In the case of atomic Ne, \(\sim 6\%\) of Ne\(^+(1s^{-1})\) produced by Ne 1s photoionization leads to Ne\(^{3+}\) by double Auger decay \[18,19\]. This double Auger decay was recently investigated by Hikosaka et al. in further detail \[20\]. We detected slow electrons in coincidence with a pair of two atomic ions using momentum-resolved electron–ion-ion coincidence spectroscopy and extracted the correlation between the kinetic energy of the ICD or ETMD electron and kinetic energy release (KER), i.e., the sum of the energies of two dissociating ions.

2. Experiment

The experiment was carried out on the C-branch of the beam line BL27SU \[21–23\] 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 crossing with the cluster beam. The measurements were performed with the linearly polarized light having the electric vector \(E\) in the horizontal direction at a photon energy of 888.7 eV, i.e., 18.5 eV above the atomic Ne 1s ionization threshold \[24\]. The storage ring was operated in several-bunches mode providing 53 single bunches (4/58 filling bunches) separated by 82.6 ns.

The heteronuclear dimers NeAr were produced by expanding a mixture of neon and argon 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 \(\mu\)m in diameter. Under these conditions the cluster beam contains monomers (Ne and Ar), homonuclear dimers (Ne\(_2\) and Ar\(_2\)), heteronuclear dimers (NeAr), and a small fraction of larger clusters. The cluster beam was directed vertically and crossed the incident radiation at right angles.

Our momentum-resolved electron–ion multicoincidence \[16,25\] is equivalent to cold-target recoil-ion momentum spectroscopy or reaction microscope \[26\] and is based on recording times of flight (TOFs) for electrons and ions with two position and time sensitive multihit-capable detectors (Roentdek HEX120 for electrons and HEX80 for ions). Knowledge of 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 \[25\]. 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. Results and discussions

3.1. Ion-ion coincidence map

Fig. 2 depicts the ion-ion coincidence TOF spectra. The horizontal and vertical coordinates correspond to the TOFs of the first and the second ions of the coincidence pair. Pairs of Ne and/or Ar atomic ions satisfying the momentum conservation laws within the plane perpendicular to the TOF axis are shown in the figure. There are correlation lines of ion pairs indicating that the sum of momenta of two ions parallel to the TOF axis are zero. Finding these correlation lines excludes existence of the third atom which can take some momentum and thus evidences that ion pairs are released from dimers. Coincidence events originating from the \(^{22}\)Ne isotopes are also seen in Fig. 2 but are not included in the following analysis. Although some correlation lines due to NeAr are overlapped with those of Ne\(_2\) or Ar\(_2\), those can be easily distinguished by the fact that ratio of velocities of Ne and Ar released from NeAr must be 2:1 whereas that of Ne and Ne or Ar and Ar must be 1:1 to satisfy the momentum conservation law.

The ion pairs Ne\(^-\)-Ne\(^+\), Ar\(^-\)-Ar\(^+\) and Ne\(^-\)-Ar\(^+\) are formed mostly as a result of radiative and/or non-adiabatic charge transfer after Auger decay \[27–29\]. The ion pairs Ne\(^{2-}\)-Ne\(^+\), Ar\(^{2-}\)-Ar\(^+\), Ne\(^{2-}\)-Ar\(^+\) and Ne\(^-\)-Ar\(^{2+}\) are formed mostly as a result of ICD after triple ionization of Ar\(_2\), respectively \[12\].

Below, we will discuss in detail the ion pair formation channels via ICD and ETMD from triply ionized states, after double Auger decay following Ne 1s photoionization, using electron and ion energy distributions in the Ne\(^{3-}\)-Ne\(^+\), Ne\(^{2-}\)-Ne\(^+\) and Ne\(^{3-}\)-Ar\(^+\) formation channels found in Fig. 2.

3.2. Ne\(^{3-}\)-Ne\(^+\) and Ne\(^{2-}\)-Ne\(^+\) coincident channels

Fig. 3(a) depicts the energy distribution of electrons recorded in coincidence with Ne\(^{3-}\)-Ne\(^+\) ion pairs. The peak that appears at \(\sim 19\) eV corresponds to the Ne 1s photoelectron. There are another structures at the lower energy region which are considered to correspond to the ICD electron emission as we discuss below. Fig. 3(b) depicts KER for the two dissociating ions Ne\(^{2+}\) and Ne\(^-\) recorded in coincidence. For describing fragmentation of a multiply charged van der Waals dimer, it is a very good approximation to take only the Coulomb repulsion between two ions \[3\]. Using this commonly used approximation, we find that the measured KER peak of 14 eV corresponds to an internuclear distance of 3.1 \(\AA\). This value agrees with the equilibrium distance 3.09 \(\AA\) \[32\] of the neutral ground state of Ne\(_2\).
Fig. 3. (a) Kinetic energy distribution of electrons detected in coincidence with Ne3+–Ne– pairs. (b) Kinetic energy release (KER) for Ne3+–Ne+fragmentation channel. (c) Correlation map between emitted electron energy and KER.

Fig. 4. Energy distributions for the sum of the emitted electron energy and the KER in (a) Ne3+–Ne– and (b) Ne3+–Ne+.

energy differences between possible candidates of initial and final states, we can identify the transitions as given below:

\[ \gamma: \text{Ne}^{2+}(2s^2p^2d^2S)-\text{Ne} \rightarrow \text{Ne}^{2+}(2p^64S)-\text{Ne}^{2+}(2p^64S) + e_{\text{ETMD}}, \]
\[ \delta: \text{Ne}^{2+}(2s^2p^2d^2S)-\text{Ne} \rightarrow \text{Ne}^{2+}(2p^64P)-\text{Ne}^{2+}(2p^64P) + e_{\text{ETMD}}, \]
\[ \epsilon: \text{Ne}^{2+}(2s^2p^2d^2D)-\text{Ne} \rightarrow \text{Ne}^{2+}(2p^65D)-\text{Ne}^{2+}(2p^65D) + e_{\text{ETMD}}, \]
\[ \zeta: \text{Ne}^{2+}(2s^2p^2d^2D)-\text{Ne} \rightarrow \text{Ne}^{2+}(2p^65P)-\text{Ne}^{2+}(2p^65P) + e_{\text{ETMD}}. \]

The energy differences of these initial and final states for the transitions \( \gamma, \delta, \epsilon \) and \( \zeta \) are 20.5, 23.7, 29.2 and 32.4 eV, respectively [24], in good agreement with the measurements. Those energies are shown in Fig. 4(b) as broken lines.

Fig. 5 is a schematic energy diagram for the initial and final states of ICD and ETMD. Energies of the initial states Ne3+–Ne– (labeled by arabic numbers 1–4) are approximated by the horizontal lines given by the relevant atomic energies [24]. Energies of the final states Ne3+–Ne2+ (labeled by alphabets A–G) and Ne3+–Ne– (H–J) are approximated by the sum of the atomic energies [24] and Coulomb repulsion energies. Let us focus on Ne3+(2s2p2d2S)-Ne– (line 1) and Ne3+(2s2p2d2D)-Ne– (line 2). Because these states are below the ICD final states Ne3+–Ne– (H–J) in the Franck–Condon region (~3.09 Å), these states are not subject to ICD but can decay to the states Ne3+–Ne2+ below them via ETMD. The measured KER for Ne3+–Ne2+ peaked at ~28 eV corresponds to internuclear distance of ~2.1 Å assuming the Coulomb repulsion. This internuclear distance likely corresponds to the inner repulsive wall of the van der Waals potential. Because only Ne3+(2s2p2d2S)-Ne– (line 2) can decay to Ne3+(2p64S)-Ne2+(2p64P) (line A) or Ne3+(2p64P)-Ne2+(2p64P) (line B) around internuclear distance of 2.1 Å, those ETMD channels (\( \epsilon \) and \( \zeta \)) are observed when Ne3+(2s2p2d2S)-Ne– (line 2) is populated. In the case Ne3+(2s2p2d2P)-Ne– (line 1) is populated, again only decays to Ne3+(2p64P)-Ne2+(2p64P) (line A) or Ne3+(2p62P)-Ne2+(2p62P) (line B) are energetically possible. Thus, those ETMD channels (\( \gamma \) and \( \delta \)) are also observed. The internuclear distances where the ETMD occurs are, however, likely close to the crossing points of the potential energy curves.
of the ETMD initial and final states, i.e., the shortest possible distances but longer than 2.1 Å.

3.3. Ne$^3^+$/Ar$^+$ coincident channels

Let us discuss the ICD channels for the hetero dimers NeAr. Fig. 6(a) is the energy distribution for the sum of the electron kinetic energy and the KER in Ne$^3^+$/Ar$^+$. The broad structure around 30 eV is due to coincidences with Ne 1s photoelectrons; KER peaked at 11.8 eV corresponds to NeAr equilibrium internuclear distance $\sim$3.48 Å [33]. Based on the energy scheme in Fig. 6(b), we can expect that ICD transitions may take place from Ne$^3^+$(2$s^1$2$p^2$2$D$), (2$s^1$2$p^2$2$D$)-Ar to Ne$^3^+$(2$p^3$4$s^1$2$D$2$P$)-Ar$^+(3$p^1$2$P$). The energy differences for the initial and final states of these transitions are in the range between 10.6 and 23.9 eV, as illustrated in Fig. 6(a) by the vertical blue bars.

4. Conclusion

We have carried out electron–ion-ion coincidence spectroscopy on homonuclear dimers Ne$_2$ and heteronuclear dimers NeAr. Measuring energy of electrons and the kinetic energy release between the two fragment atomic ions in coincidence, we could identify, without any ambiguity, the ICD processes leading to fragmentation of Ne$^3^+$-Ne into Ne$^3^+$-Ne$^+$ and Ne$^3^+$-Ar into Ne$^3^+$-Ar$^+$, and ETMD processes leading to fragmentation of Ne$^3^+$-Ne into Ne$^3^+$-Ne$^+$. ETMD processes are usually much slower than ICD processes. However, for the lower energy states for which ICD is energetically forbidden, ETMD becomes dominant decay processes. The present study illustrates that ETMD is not an unusual process but can be commonly seen for loosely bound systems as ICD does.

Acknowledgments

The experiments were performed at SPring-8 with the approval of JASRI. We are grateful to L.S. Cederbaum and A.I. Kuleff for helpful discussion. The work was supported by Grant-in-Aid (21244062) from JSPS, by the Management Expenses Grants for National Universities Corporations from MEXT, and by IMRAM project funding.

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