Asymmetry in Multiple-Electron Capture Revealed by Radiative Charge Transfer in Ar Dimers

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We measured kinetic energies of the fragment ions of argon dimers multiply ionized by low-energy Ar^{9+} collisions. For $(Ar_2)^{4+}$ dissociation, the asymmetric channel $(Ar^{3+} + Ar^+)$ yield is found unexpectedly higher than the symmetric channel $(Ar^{2+} + Ar^{2+})$ yield in contrast with previous observation for covalent molecules or clusters. For the dissociation channel $(Ar_2)^{2+} \rightarrow Ar^+ + Ar^+$, two well-separated peaks were observed, clearly evidencing that the direct Coulombic dissociation and the radiative charge transfer followed by ionic dissociation alternatively occur for the dicationic dimers. The respective intensity of these two peaks provides a direct mean to unravel the respective proportion of one-site and two-site double-electron capture, which are found equal for this collision system.

Rare-gas dimers are characterized by large internuclear distances and behave as if each moiety is nearly independent. Very recently, rare-gas dimers have attracted much attention due to the fact that they allow us to study a pure situation of two neighbor atoms. In particular, recent experiments [1,2] have confirmed the theoretical predictions of Cederbaum *et al.* [3] that new deexcitation channels open up for an ion when located in the vicinity of another atom. Such atomic edifices have never been used as targets in highly charged ion (HCI) collisions. If one site of the dimer is multiply ionized, would near isolation of the individual atoms lead to slow charge rearrangement in the dimer? This might be expected for rare-gas dimers, mainly because only few potential energy curve crossings between different ionic arrangements exist. This unique feature may allow us to investigate how the electrons are captured at the instant of the collision and to study electron dynamics in charge transfer collisions with HCIs. The answer to this fundamental question has been hidden up to now by the fast intramolecular charge rearrangement in covalent molecules.

Indeed, diatomic molecule multiple ionization leads usually to dissociation into equally charged fragments. Charge asymmetric channels have been found to be much weaker than the charge symmetric sharing among the fragments. Most of those studied so far (N_2, CO) present a strong covalent character, for which the valence electronic orbitals are delocalized over the whole molecule [4–6]. Rare-gas dimers offer an interesting alternative for which the ground state valence orbitals are well localized on each atomic center and may behave differently as far as the electronic arrangement around the fragments is concerned.

Several methods allow the investigation of highly charged molecular ion production. The literature concerning single photon multiple ionization is abundant [7]. In this case, the one-electron dipole operator associated to the electromagnetic field can barely produce directly multiple ionization. Such a process is associated to the electronic correlation and is usually quite small with respect to Auger processes. The latter results from inner-shell ionization, leaving the system in an Ar^{+*}-Ar configuration, which decays by Auger cascades.

The HCI collision-induced production of multiply charged molecular ions is quite different as it does not rely on correlation effects between the molecular electrons. For relatively slow highly charged ionic projectiles, the intensity of the Coulomb field of the incoming ion is large enough to lead to multiple processes with a high probability. In other words, the perturbation expansion of the wave function is slowly convergent and high order terms associated to multiple electronic processes need to be taken into account. A similar effect is observed for high-intensity photon fields, for which many electrons can be emitted simultaneously from the molecule. One distinct advantage of slow highly charged ionic projectiles over photons is to produce a multiply ionized target with a very limited degree of excitation [8]. In the case of Ar, capture occurs mainly in the outer $3p$ shell, and thus, the deexcitation of a multiply charged transient dimer by Auger cascade following single ionization is negligible. As such, it offers the possibility to produce a multiply charged dimer by removing electrons either from one of the atoms or from both of them. For a total number n of removed electrons, several final arrangements $Ar^{q+} + Ar^{p+}(p + q = n)$ can be observed, for which the multiply charged fragments are mainly in their ground state. In the particular case $n = 2$, the dimer dication is left in one of its lowest-energy states correlating asymptotically with the $Ar^{2+} + Ar^0$ or $Ar^+ + Ar^+$ dissociation limits. If two electrons are

captured from both sites, the resultant [Ar$^+$-Ar$^+$] directly dissociates along the nearly Coulombic (Coulomb explosion, CE) potential energy curve toward the Ar$^+$ + Ar$^+$ dissociation limit. Otherwise, if the electrons are ejected from one single site, the only way open for the upper state [Ar^{2+}-Ar^0] to deexcite to the dissociative ground state of the dimer dication is through the radiative charge transfer (RCT) process. The RCT process has been first invoked and observed for charge transfer collisions between neutral and doubly charged rare-gas atoms at thermal energies [9,10]. For homonuclear rare-gas collisions, no curve crossings exist between the states correlating with the Ar^{2+} + Ar^0 and Ar$^+$ + Ar$^+$ dissociation limits. Thus, charge transfer requires photon emission [11,12]. Recently, inner-shell photoionization experiment reported dimer deexcitation either by a one-center Auger effect followed by RCT [13] or by a two-center Auger effect, i.e., by interatomic Coulombic decay (ICD) [1].

The two processes, CE and RCT, related to the capture site location are schematically shown in Fig. 1. Since the equilibrium internuclear distance of the neutral dimer is much longer than that in the [Ar^{2+}-Ar^0] states, vibrationally excited states are generated by the vertical transition

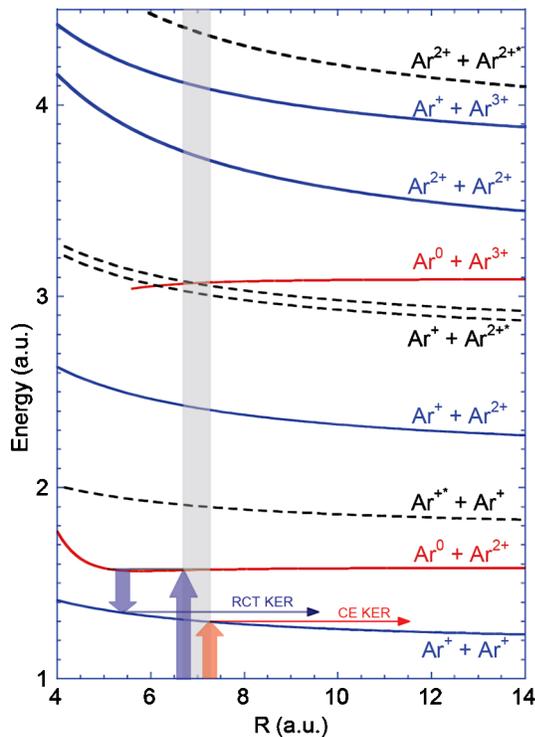FIG. 1 (color online).   Calculated potential energy curves for different fragmentation channels of (Ar$_2$)$^{2+}$ and (Ar$_2$)$^{3+}$ obtained by asymptotic limits, Coulombic and polarization energies. Solid (dashed) lines correspond to channels with fragments in their ground (first excited) states. The light and dark gray arrows represent the Coulomb explosion (CE) and radiative charge transfer (RCT) processes, respectively. The gray band shows the position of the Franck-Condon region.

associated to the capture process. The radiative lifetime in the ns range is much longer than the period of the vibrational motion and RCT occurs preferentially at the classical turning points of the upper (one-site) states. As can be seen in Fig. 1, the RCT process is expected to give a kinetic energy release (KER) peak at higher energy than that for the direct CE process, allowing a clear separation of these two processes. That is to say, RCT and direct dissociation correspond to dimer implosion and explosion, respectively.

In the present study, we have observed the reaction Ar$_2$ + Ar^{9+} → (Ar$_2$)$^{n+}$ + ... → Ar^{p+} + Ar^{q+} + ..., where $n = p + q = 2, 3, 4$. The KER distribution and the branching ratios for charge sharing were measured. The aim is to elucidate the dynamics of electron capture and subsequent ionic dissociation, focusing attention onto the asymmetry in the electron capture leading to the RCT process. For the highest number of captured electrons, and contrary to previously observed diatomic molecules, we observe for the first time a strong asymmetry in the fragment charge states highlighting an unexpected electron dynamics. In this Letter, we show how the low electron mobility across van der Waals dimers is revealed through the fragmentation process dynamics.

The experiments were performed on the ARIBE beam line at the GANIL facility (Caen, France). The Ar^{9+} ions were extracted from an electron-cyclotron-resonance (ECR) source at an energy of 152 keV, while the argon dimers were produced by an Ar supersonic expansion at a stagnation pressure of 4 bars through a 75 μm nozzle at room temperature. The crossed beam configuration allows us to neglect collisional quenching of the upper states. The ratio of the dimer to the monomer in the target jet is of the order of 10^{-3}. After collision, the momenta of the correlated fragments from the dimer ion were measured in coincidence using a COLTRIM spectrometer in a 3D focusing mode for high momentum resolution measurement [14]. The event-by-event position and time data recorded in a list mode were examined in detail by an offline analysis. The double-hit events were sorted to exclude the monomer events, and momentum conservation restriction was imposed to eliminate larger clusters and random coincidences contributions. More details of the experiments will be given elsewhere [15].

The observed dimer dissociation channels are the following:

I: (Ar$_2$)$^{2+}$ → Ar$^+$ + Ar$^+$,
II: (Ar$_2$)$^{3+}$ → Ar^{2+} + Ar$^+$,
IIIa: (Ar$_2$)$^{4+}$ → Ar^{3+} + Ar$^+$, and
IIIb: (Ar$_2$)$^{4+}$ → Ar^{2+} + Ar^{2+},

with branching ratios of 0.42, 0.30, 0.19, and 0.09, respectively. The most striking result is easily visible on these ratios. The preference for the asymmetric IIIa channel instead of the energetically more favorable symmetric IIIb channel is quite unusual, in sharp contrast with the case of covalent diatomic molecules, for which the

symmetric charge sharing is by far dominant [4,5,16]. The ratio of asymmetric to symmetric channel yields is about 2, which is 1 order of magnitude higher than those reported for diatomic molecules. As an example ratios between 0.2 and 0.3 have been measured for CO molecules [4,17]. These channels reflect directly on which target center the electrons were captured since the corresponding potential energy curves do not cross each other (Fig. 1). Thus, memory of the initial process is kept while for molecules, it is lost due to the high number of curve crossings experienced by the system during its dissociation. To the best of our knowledge, this is the first experimental observation of such reverse order of the priority in the charge sharing for the homonuclear diatomic systems. It should be noted that $(C_{60})_2$, a quasi homonuclear van der Waals dimer, prefers symmetric charge sharing upon dissociation (monomerization) [18].

The KER distribution obtained for channels II, IIIa and IIIb show a single peak at the expected Coulombic values (7.6, 11.4, and 15.2 eV, respectively) [15]. The ground state potential energy curves of these channels are purely repulsive so no charge transfer is expected during the dissociation process. For the most asymmetric dissociation channels, $(Ar^{3+} + Ar^0)$ and $(Ar^{4+} + Ar^0)$, curve crossings exist with more symmetric channels excited states, close to the equilibrium internuclear distance (3.8 Å) of the neutral dimer Ar_2 (Fig. 1). Thus, a fast charge transfer may occur at these crossings and a Coulombic value is expected for the KER. This process prevents separation of the highly asymmetric channels. Nevertheless, such a process reduces the observed asymmetry and for a total degree of ionization $n = 4$, the ratio between asymmetric ($p = 3$, $q = 1$) and symmetric ($P = 2$, $q = 2$) channels is a lower boundary to the initial asymmetry ratio.

On the contrary, for the dimer dication, there is no curve crossing leading to predissociation of the states correlating with the $Ar^{2+} + Ar^0$ asymptote. Our experimental setup allows us in this case to identify the initial arrangement produced by the electron capture process, using the KER spectrum analysis. Two distinct peaks are clearly observed in the KER distribution for the fragmentation channel I $(Ar^+ + Ar^+)$ shown in Fig. 2. The energy of the first peak well agrees with the value expected for pure Coulombic dissociation (3.8 eV) at the internuclear distance of the neutral dimers (3.8 Å), or evaluated by theoretical calculations (3.8–4.0 eV) [13]. This peak is assigned to the direct process in which the dicationic dimer with a hole in each center is directly formed during the HCI-dimer collision. The energy of the second peak is close to that reported for the inner-shell ionization experiment (5.3 eV) in which the RCT process was invoked. The KER distribution reported for photoionization shows a narrow band around 5 eV with a tail toward the lower KER side down to 3 eV and agrees well with the RCT peak shape observed in the present study. This confirms for the first time that direct
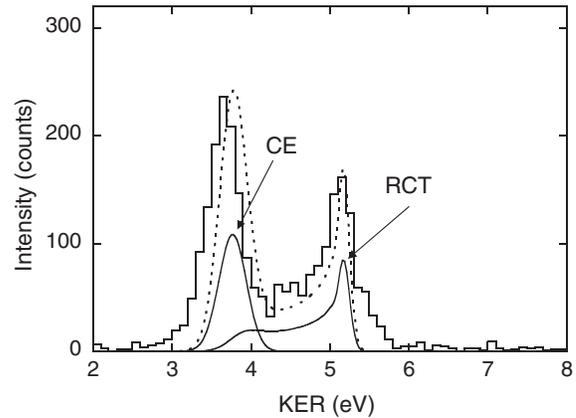

FIG. 2.   KER distributions of the fragment pair $Ar^+ + Ar^+$. The curves CE and RCT are theoretically obtained distributions. The weighted sum is depicted in the dotted curve.

Coulombic dissociation and RCT process followed by ionic dissociation alternatively occur during the double capture collisions. They correspond, respectively, to one-site and two-site double-electron capture.

A widely accepted idea is that the transitions to the near Coulombic repulsive potential lead the KER distribution to be a reflection of the probability function of internuclear distances in the initial state. The photoionization study of helium dimer shows that the stationary wave function of transient He_2^+ gives fair agreement with the observation [2,19], while the ICD lifetimes (20 fs 50 ps) are sometimes shorter than the vibration period of He_2^+ (about 300 fs). The RCT process is much slower than the ICD process, and thus, the RCT band shape in KER spectrum will be a closer fingerprint of the stationary wave function. Although the statistics is not sufficient to discuss the fine structure of the RCT band, the peak on the higher energy side with a low-energy tail is consistent with the qualitative prediction that the amplitude of the wave function near the classical turning point is larger.

To better sign the underlying processes, we performed a simulation of the direct (CE) and RCT processes. In both cases, the double capture mechanism from the neutral ground state of Ar_2 is assumed to be independent of the dimer bond length. For both CE and RCT processes the dissociation takes place on one of the 12 repulsive states correlating with the $Ar^+(^2P) + Ar^+(^2P)$ asymptote [12]. The corresponding potential energy curves are all nearly Coulombic and for the sake of simplicity, we assume that dissociation takes place on one single, purely Coulombic, potential energy curve. The CE KER distribution is obtained from the transformation of the vibrational ground state probability density of neutral Ar_2 by means of the reflection principle. For the RCT process, a transient electronic bound state correlated with one of the $Ar(^1S) + Ar^{2+}(^{2S+1}L)$ asymptote is produced [12]. Their radiative lifetimes are much longer than the typical vibrational period, so that the system can explore the whole potential

well of this transient state. The RCT KER distribution is obtained by projecting the ground vibrational state of neutral Ar_2 onto all vibrational states $\varphi_v(R)$ associated with one of the electronic bound states of Ar_2^{2+}. After weighting the bond length distributions $R^2\varphi_v(R)^2$ by the transition dipole, which depends on R, each vibrational state produces its own KER distribution obtained again by means of the reflection principle. All contributions are then summed to produce the complete KER spectrum associated with one electronic transient dication state. All these states are rather similar, with a well depth distributed between 4500 and 3200 cm^{-1}, and a minimum located between 3.0 and 3.2 Å. The KER distribution obtained for the $^3\Sigma_g^-$ transient state is depicted in Fig. 2. It presents a main peak at high energy corresponding to the inner turning point of the $^3\Sigma_g^-$ well, where all vibrational states $\varphi_v(R)$ have a large amplitude. The other transient states produce a similar KER distribution, with a position of the maximum distributed between 5.2 and 5.8 eV. Approximately 20 vibrational states contribute effectively to the KER spectrum in our case. This is of course much more than for a light molecule like He_2 for which some structures associated to the oscillatory behavior of the vibrational states have been observed [2,19]. This RCT contribution corresponds to the photo-ionization case as observed experimentally [13]. In the case of ion impact, we need to add the CE process contribution, which is also plotted in Fig. 2. The CE peak is slightly shifted toward higher energy with respect to experimental value because of our assumption of the pure Coulombic curve. Finally, we have plotted a weighted sum of the two contributions to fit the experimental results which allows us to establish unambiguously the origin the KER distribution. Our analysis shows that the contribution of double-electron capture by 152 keV Ar^{9+} on one single center can be clearly separated and is equal to that on each of the Ar atoms.

In this Letter, we present the first evidence of large charge asymmetry in the dissociation of Ar dimer following multiple-electron capture. For the dimer dication, such an effect might be observable in any system if the asymptotic energies for ($X^0 \rightarrow X^{2+}$) are lower than the energy for ($2X^0 \rightarrow X^+ + X^{+*}$). Since the potential energy curve (PEC) for the two-center channel is repulsive while the PEC for the one-center channel is attractive at long range, the crossing between the different charge arrangements is unlikely allowing the RCT process to take place. For double-electron capture, unambiguous separation between two-site and one-site capture was possible from the KER spectrum analysis. Our results show that these two processes have equal cross sections in the collision regime investigated here. Similarly, if the energy for the asymmetric ionization ($2X^0 \rightarrow X^{(n-1)+} + X^{(n+1)+}$) is lower than that for symmetric ionization to form one of them in the first excited state ($2X^0 \rightarrow X^{n+} + X^{n+*}$), potential energy curves do not cross since the potential curve for the

symmetric channel should be steeper. This leads to a novel approach to investigate electron capture from diatomic systems, which allows us to study preference in symmetric and asymmetric capture processes at the instant of the collision.

Detailed analysis of the correlation between the recoil ions and projectile, as for instance the role played by the orientation of the dimer with respect to the projectile beam axis, will allow us to deepen the understanding of the collision process. Finally, the analysis of double-electron capture on He_2 dimers would be an excellent test case for the study of the RCT process since the number of electronic states reduces to only two transient states ($^1\Sigma_u$ and $^1\Sigma_g$) correlating asymptotically to $He(^1S) + He^{2+}$ and one single singlet repulsive state $^1\Sigma_g$ correlating asymptotically to $He^+(^2S) + He^+(^2S)$.

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