Observation of resonant Auger decay driving intermolecular Coulombic decay in molecular dimers

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During the last years it was shown that an atomic process termed "Intermolecular Coulombic Decay" (ICD) [1] typically yields low energy electrons as a decay product as (for example) the decay of small water droplets was examined in great detail [2,3]. Low energy electrons are known to effectively cause DNA double strand breakups by attaching to and fragmenting the constituents of DNA [4,5]. Thus, the occurrence of radiation damage in biological systems due to ICD was suggested and more recently the high effectiveness of creation of low energy electrons due to ICD after irradiating a well-defined model system with alpha particles was revealed [6]. ICD occurs if an excited particle is placed in a loosely bound chemical environment such as hydrogen or Van der Waals bonded systems. In that case the excitation energy is transferred to an atomic or molecular neighbor causing that neighbor to emit an electron. A wealth of studies [7-11] following the experimental proof of ICD [12–14] suggests that it is actually a very common phenomenon. The group of L. Cederbaum recently suggested [15] that ICD can be triggered efficiently and site-selectively by resonant excitation of molecules. Here we show experimentally that resonant Auger induced ICD can indeed be observed in small molecular model systems. Furthermore we prove the efficiency of ICD: the decay occurs before the individual molecule is able to undergo dissociation, i.e. on a time scale < 20 fs. As it has been proposed to use resonant excitation instead of broadband irradiation to locally deposit energy at malignant cells tagged with high-Z elements in an approach termed "X-ray resonant theranostics" [16,17] our findings might give new impulses to the fairly mature field of Auger electron driven cancer therapy.

In the present letter we show experimentally that ICD can be initiated by resonant excitation of a *K*-shell electron to a bound state followed by Auger decay (see Fig. 1 for a sketch) just as proposed in [15]. In this case an electron is resonantly excited as in [7,8], but the state undergoing ICD is created after the system partly de-excited in a *local* Auger decay. The Auger decay of this excited molecule can lead to the ground state of the molecular ion in a so-called "participator Auger decay". In many cases, however, the excited electron will act just as a "spectator" to an Auger decay in which an electron from the valence or inner valence shell fills the core hole and a second electron from the valence shell is emitted. This scheme produces ionic states which are high enough in excitation energy to allow for ICD. In carbon monoxide molecules for example approx. 75 % of core-excited molecules decay on that "spectator" pathway [18]. Our approach to investigate the overall scenario uses two simple model systems that (in turn) allow for an investigation in great detail. By using smallest clusters of just two carbon monoxide or nitrogen molecules the Auger decay occurring after resonant excitation into the lowest unoccupied molecular orbital (LUMO) and the subsequent ICD are examined:

$$h\nu + N_2/N_2 \rightarrow N_2^* \ (1s^{-1}\Pi^*)/N_2 \ \text{(local, resonant excitation)} \qquad (1)$$

$$N_2^* \ (1s^{-1}\Pi^*)/N_2 \rightarrow N_2^{+*}/N_2 + e_{Auger} \ \text{(spectator Auger decay)} \qquad (2)$$

$$N_2^{+*}/N_2 \rightarrow N_2^+ + N_2^+ + e_{ICD} \ \text{(ICD + two-site Coulomb explosion)} \qquad (3)$$
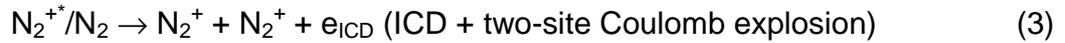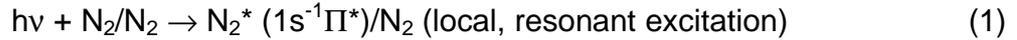
The correlation between the kinetic energy release (KER) of the two molecular ions and the kinetic energy of the electrons measured in coincidence is shown in Figure 2(a) and (b). Contrary to similar plots for ICD in rare gas dimers [13] no discrete structures are observed in Figure 2. This is a direct consequence of the repulsive nature of the intermediate state populated by the resonant Auger decay and of the vibrational and rotational degrees of freedom of the ionic fragments. The resonant Auger decay onto a repulsive state of the molecule leads to a continuum of Auger energies and hence to a continuum of excitation energies of the intermediate N_2^{+*}/N_2 (CO^{+*}/CO) state. On one hand, Figs. 2(a) and (b) reveal the terminal step of ICD, i.e. the Coulomb explosion of the molecular dimer, as two singly charged molecular ions are detected. On the other hand, the KERs measured support the picture of ICD being the underlying process, as the values of KERs measured for both target systems are consistent with those found in the literature: the maximum of the KER distribution observed is 3.1 eV for $(N_2)_2$ and 3.7 eV for $(CO)_2$. This KER can be compared to the kinetic energy of two singly charged point particles starting a Coulomb explosion at the typical mean intermolecular distance of CO and N_2 dimers. Assuming a simple Coulomb potential, which is a good approximation for Van der Waals bound systems, the kinetic energy (in atomic units) is given by $KER=1/R$ where R is the distance between the two charges. For $(N_2)_2$ a distance of 4.03 Å has been reported [19] which corresponds to a KER of 3.5 eV matching the value observed in our experiment. For the CO dimer a mean value of 3.9 Å has been reported [20,21]. This corresponds to a KER of 3.7 eV thus being consistent to our observation, as well. All these findings support the scenario of an intermolecular decay mechanism such as ICD. Still, one alternative mechanism is imaginable that would lead to two singly charged molecular ions being launched at the mean intermolecular distance of the dimer in its groundstate, namely an intermolecular *knock-out*, as recently observed in He_2 [22]. If the fast Auger electron is emitted in the direction of the neighboring molecule it can knock out an electron. Thus, the neighboring molecule is ionized yielding the two molecular ions observed, an Auger electron of reduced energy and a low energy electron. However, as demonstrated in [22] this process can only happen if the neighboring molecule is located in the direction of emission of the Auger electron. The orientation of the dimer in space at the instant of Coulomb explosion is known from our coincidence momentum measurement. The direction of the fast Auger electron is measured in our setup for every event via its recoil on the center of mass of the two Coulomb-exploding molecular ions. The Auger angular emission pattern with respect to the molecular axis of the dimer is plotted in Fig. 2(c). It

is nearly isotropic. This eliminates the intermolecular knock-out scenario which would lead to an emission pattern strongly directed along the molecular axis.

Our present experimental study reveals ICD to be a prominent decay channel for excited N_2 and CO dimers. The effect of ICD on the fate of an excited molecular ion, however, is substantial and yet only poorly studied. Excited molecular ions are rarely stable and would dissociate as isolated species but they might survive as stable entities in solution or in any other chemical environment where ICD can occur. As the energy relaxation by dissociation without release of an electron is a competing channel to (3):

$$N_2^{+*}/N_2 \rightarrow N^+ + N + N_2 \text{ (one-site dissociation)} \tag{4}$$
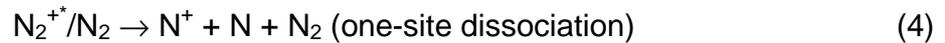
ICD can effectively prohibit dissociation if it occurs fast enough. Alternatively also the inverse might be true: ICD in a molecular system [channel (3)] might become a rare phenomenon as one-site dissociation [channel (4)] is known to be a very fast competing channel. The potential energy curves of the CO^{+*} which lie above the single ionization potential of CO are all steeply repulsive [23]. The fact that we observe ICD and a breakup of the molecular dimer into CO^+/CO^+ hence shows that ICD outpaces dissociation. Furthermore, we can use the molecular dissociation as a clock to obtain an estimate of time scale on which ICD occurs in the present case. The typical slopes of the potential curves involved are 10 eV/Angstrom. From this and the fact that we observe only ICD events where the CO^+ does not fragment one can estimate the maximum time which can have elapsed before the molecular ion has to relax via ICD. For a repulsive state the potential energy of the system decreases as the molecule dissociates. Therefore, for a given potential energy surface one can calculate how long it will take before an internuclear distance has been reached at which the potential energy has dropped below the threshold for ICD. For the case of the molecules and states populated here, this time is < 20 fs. Accordingly ICD must occur on a time scale shorter than 20 fs.

Still ongoing research in biomedical physics explored the interaction of X-rays with high-Z elements [16], as it was suggested to use molecular markers consisting of at least one atom of high atomic number to tag malignant cells. While today usually broadband irradiation of biological tissue is used to destroy cancerous cells, the use of resonant excitation of these high-Z marker atoms localizing the damage to a specific site inside a biological system is investigated in an approach termed "X-ray resonant theranostics" [16]. The advantages are obvious: by using energetically well-defined radiation only distinct atoms or molecules are excited resonantly while the surrounding tissue remains mostly unaffected. The use of high-Z elements allows for the use of photons in the X-ray regime to excite a core electron. These photons penetrate deeply into biological tissue. The width in energy of these resonances is typically in the range of a few 10 meV. A resonant excitation of the kind described here is typically ten times stronger compared

to non-resonant ionization used by broadband irradiation. Therefore the overall radiation dose can be minimized using monochromatized X-rays tuned to this resonance. This irradiation is expected to create genotoxic low energy electrons from high energetic primary electrons after multiple scattering inside the biological system. With ICD a mechanism is present that directly creates low energy electrons after irradiating a system with photons of a suitable energy. For larger systems consisting of many atoms or molecules, the atom to be excited can be addressed selectively using a matching resonant photon energy. Thus, with the scheme described here the exact site in a larger system at which ICD and the emission of a low energy electron is triggered can be selected. This was suggested by Gokhberg and coworkers [15]. Our experimental work confirms: as ICD occurs efficiently after resonant excitation and Auger decay, it will add a low energy electron (< 15 eV) as a final reaction product to the other advantages of resonant theranostics using high-Z markers.

Note added: during the peer-review two other groups confirmed nicely the existence of RA-ICD in raregas clusters [24] and further showed that the ICD electron energy may be selected by changing the initial excitation energy [25,26].

METHODS SUMMARY

In our experiment we employ COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS) [27,28] to measure all charged particles that are created in a single reaction in coincidence. The details on the spectrometer can be found in [29]. In brief, a time focusing approach was used on the electron arm and time and spatial focusing was set up on the ion arm of the COLTRIMS analyzer. The electric and magnetic fields applied allowed for a full solid angle coincident detection [30] of ions up to a kinetic energy of 5 eV and electrons up to an energy of 15 eV. Particles of higher energy were detected with reduced solid angle of emission. The N_2 and CO dimers were produced using a precooled supersonic jet. The experiment has been performed at beam line 11.0.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory.

METHODS

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dimer production. The supersonic beam was collimated by a set of two skimmers and then crossed with the photon beam inside a COLTRIMS spectrometer. The details on the spectrometer can be found in [29]. An electric field of 7.4 V/cm and a parallel magnetic field of 7.0 Gauss guided electrons and ions to two position sensitive micro channel plate detectors with delay line readout [30]. The fields were adjusted such that electrons of up to 15 eV kinetic energy could be collected with 4π solid angle. Due to the long ion drift arm the spectrometer accepted only N_2^+ or CO^+ (in case their kinetic energy is higher than 5 eV), which were emitted within 10° with respect to the spectrometer axis. The light polarization was circular in the case of N_2. The data were recorded in list mode. For each ionization event we recorded the positions of impact and times-of-flight of all registered particles. This allowed us to extract the very weak dimer signal from our data, as the dimer fraction in our beam was only 0.1 % - 1 %. Thus most recorded ions and electrons resulted from ionization of the monomer. We can identify the ICD channel by selecting only events in which two N_2^+ (CO^+) ions with equal and opposite momentum occur. This back-to-back emission is a unique signature of the final step of Coulomb explosion following ICD, i.e. equation 3.

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[30] see http://www.roentdek.com for details on the detectors.

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AUTHOR CONTRIBUTIONS

All authors contributed to the experiment. F.T. and T.J. performed the data analysis. All authors contributed to the manuscript.

AUTHOR INFORMATION

Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to F.T. (trinter@atom.uni-frankfurt.de) or T.J. (jahnke@atom.uni-frankfurt.de).

Fig. 1: Cascade mechanism: Series of events of Resonant Auger driven ICD (see Equations 1-3). (a) One molecule of the molecular dimer is core excited. (b) The core excited state decays by a spectator Auger decay to a highly excited state of the molecular ion. (c) ICD transfers the excitation energy to the molecular neighbor where a low energy ICD electron is emitted.

a)
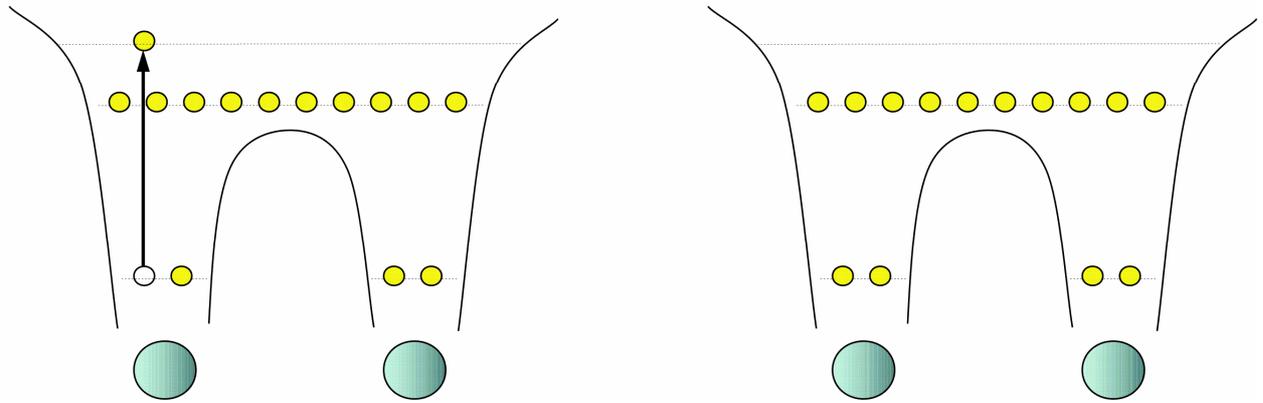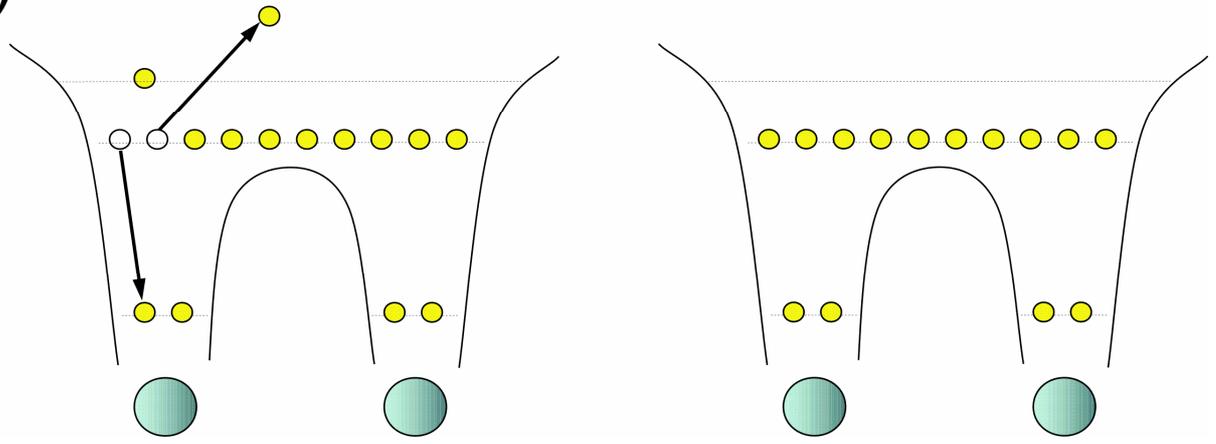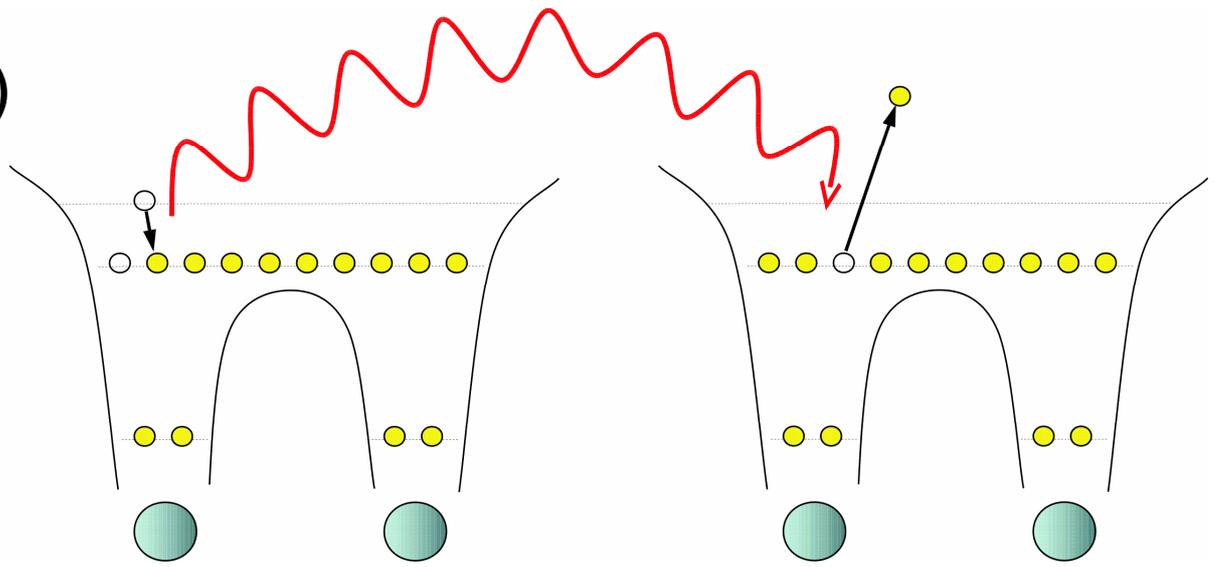
FIG. 2: Results: (a) Kinetic energy release of $(CO)_2$ versus energy of one of the two electrons created by ICD after resonant excitation and subsequent Auger decay at a photon energy of 287.4 eV (Π^* excitation of CO). (b) Same plot for $(N_2)_2$ recorded at a photon energy of 401.9 eV (Π^* excitation of N_2). (c) Emission direction of the Auger electron with respect to the molecular axis of the N_2 dimer (with statistical error bars). The dimer is oriented horizontally as depicted by the icon. The grey circle is a line to guide the eye corresponding to isotropic emission.

c)