Interatomic Electronic Decay Driven by Nuclear Motion

Nicolas Sisourat,1,* Hendrik Sann,2 Nikolai V. Kryzhevoi,1 Přemysl Kolorenc,3 Tilo Havermeier,2 Felix Sturm,2 Till Jahnke,2 Hong-Keun Kim,2 Reinhard Dörner,2 and Lorenz S. Cederbaum1
1Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg
2Institut für Kernphysik, Universität Frankfurt, Max-von-Laue-Str. 1, D-60438 Frankfurt am Main, Germany
3Institute of Theoretical Physics, Faculty of Mathematics and Physics, Charles University in Prague,
V Holešovičkách 2, 180 00 Prague, Czech Republic
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The interatomic electronic decay after inner-valence ionization of a neon atom by a single photon in a neon-helium dimer is investigated. The excited neon atom relaxes via interatomic Coulombic decay and the excess energy is transferred to the helium atom and ionizes it. We show that the decay process is only possible if the dimer’s bond stretches up to 6.2 Å, i.e., to more than twice the equilibrium interatomic distance of the neutral dimer. Thus, it is demonstrated that the electronic decay, taking place at such long distances, is driven by the nuclear motion.

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Nuclear motion in molecules is controlled and driven by electrons constituting the bonds. In photochemistry, photons are used to drive electronic transitions, the changes in the electronic wave function then induce rearrangement of the molecular geometry. In the present Letter, we demonstrate the reverse: nuclear motion can also drive electronic transitions. We show that after inner-valence ionization of a neon atom within a neon-helium dimer (NeHe), the system can deexcite via interatomic Coulombic decay (ICD) only when the two atoms are at more than 6.2 Å apart, more than twice the equilibrium distance of the NeHe of about 3.0 Å. The dimer must stretch significantly before ICD becomes open. Thus, the electronic decay is controlled by the nuclear motion. We also demonstrate that ICD channels open at shorter and shorter interatomic distances upon excitation to higher electronic states above the Ne+(2s−1) threshold. The influence of the nuclear motion on the ICD process is investigated for the Ne+(2s−1) − He state and the 3 first excited states above this latter, as shown in Fig. 1.

ICD is an ultrafast nonradiative decay process for excited atoms embedded in a chemical environment. The excited atom relaxes and the excess energy is used to ionize a neighboring atom or molecule. ICD was predicted theoretically in 1997 [1] and observed for the first time after inner-valence ionization of neon in large neon clusters [2] and shortly after in neon dimers [3]. Since the pioneering works on neon clusters, ICD was demonstrated in many other systems [4–8]. Recently, it was demonstrated to happen in water clusters [9,10] which is of particular interest for biological and chemical processes.

Until now, the ICD process was observed in clusters where this channel is open at the equilibrium geometry of the system. For those systems, no nuclear dynamics is necessary to initiate ICD. Nevertheless, nuclear dynamics during the ICD process has a substantial impact on the shape of the ICD electron spectrum as shown for the case of the neon dimer [11] and helium dimer [12,13]. Furthermore, driving nuclear motion can be used to actively modify the ICD electron spectrum [14].

FIG. 1 (color online). Ab initio data for the NeHe dimer. Upper panel: Total ICD widths as functions of the interatomic distances for 2Σ+[Ne+(2s−1) − He(1s2), state 1], 2Σ− and 2Π [Ne+(2p−23s) − He(1s2), states 2a and 2b] and 2Σ+[Ne+(2p−23s) − He(1s2), state 3]. Middle panel: Potential energy curves (PECs) for the decaying Ne+ − He states (presented in the upper panel) and for the Ne+(2p−1) − He+(1s−1) final states (dashed lines) of the ICD. Lower panel: PEC of the electronic ground state of NeHe. The probability density for finding the two atoms at given interatomic distances in this electronic state is shown in yellow.
In this combined experimental-theoretical study, the neon atom is ionized to \( \text{Ne}^+ (2s^{-1}) \) and \( \text{Ne}^+ (2p^{-2}3s) \) and the ICD leading to \( \text{Ne}^+ (2p^{-1}) + \text{He}^+ (1s^{-1}) + e_{\text{ICD}} \) is investigated, where \( e_{\text{ICD}} \) is the ICD electron. The experiment has been performed at BLU125-2/SGM at the BESSY synchrotron radiation facility using the COLTRIMS technique \[15,16\]. A supersonic beam of a He Ne gas mixture expanded through a cooled nozzle was intersected with a linearly polarized photon beam of an energy of 55.8 eV. The ions and electrons were guided by homogeneous electric and magnetic fields towards two position and time sensitive detectors with delay line readout \[17\]. From the time-of-flight and position of the impacts we obtained the momentum vectors and thus the energy of all particles in coincidence. The two singly charged ions from the dimer from the huge background of charged ions in the final state are emitted back-to-back.

Afterudo et al. \[17\] investigated, where see that ICD opens at 6.2 Å for state 1, at 4.5 Å for states 2a and 2b and at about 2.5 Å for state 3. The corresponding ICD widths summed over all final states are shown in the top panel of Fig. 1. Obviously, they are equal to zero at distances where ICD is energetically forbidden. They are maximal just after the crossing point and then decrease like \( 1/R^6 \) (as predicted by the virtual photon mechanism \[21\]) at larger interatomic distances. The radiative decay width of \( \text{Ne}^+ (2s^{-1}) \) is of about 3.8 \( \mu \text{eV} \). Thus, when ICD is open it dominates the radiative decay for interatomic distances below 10 Å (not shown).

We first turn our attention to the decay process after ionization of neon leaving the system in state 1. As seen in Fig. 1, after vertical ionization of the dimer at its equilibrium geometry, the system cannot relax via ICD. Because of nuclear dynamics in the electronic ground state, the dimer explores a larger range of interatomic distances. After photoionization, we see that only a small fraction of the distribution of the two atoms within the dimer, shown in yellow in Fig. 1, is at interatomic distances where ICD is open. As the PEC is attractive, the two atoms move towards shorter interatomic distances and thus might close the ICD process. In this case and if the nuclear wave packet never returns to this region, it is expected that the emission of an ICD electron from this excited state is very weak and that the system decays mainly by emitting a photon. For states 2a and 2b, ICD is also closed at the equilibrium interatomic distance of NeHe but we see that ICD opens for a larger range of interatomic distances. Thus, we expect that ICD process is more probable than for state 1. In the experiment however, states 2a and 2b are populated by the shake-up process and are therefore weaker populated by the initial photoionization process \[22\]. Finally, in the case of state 3 ICD is open for all relevant interatomic distances. As ICD width for state 3 is much larger than that of the radiative decay, the system in this state decays essentially via ICD.

The computed potential energy curves (PECs) are shown in Fig. 1. The ground state exhibits a shallow minimum around 3 Å. The probability density for finding the two atoms at given interatomic distances is shown in yellow in the same figure. The density is maximal at around 3.5 Å and has a long tail up to about 8 Å. The PECs of the decaying states are shown in the middle panel of Fig. 1. In the order of increasing energy, there are first a \( ^3\Sigma^- \) molecular state which corresponds to \( \text{Ne}^+ (2s^{-1}) - \text{He}(1s^2) \) at infinite interatomic distance, two states \( ^2\Sigma^- \) and \( ^2\Pi \) at about 49 eV corresponding to \( \text{Ne}^+ (2p^{-2}3s) - \text{He}(1s^2) \) asymptotically and finally one \( ^2\Sigma^+ \) state representative for the manifold of states \( \text{Ne}^+ (2p^{-2}3s) - \text{He}(1s^2) \) at energy around 52 eV. We label these 4 states, as 1, 2a, 2b, and 3, respectively. The PECs of the \( \text{Ne}^+ (2p^{-1}) - \text{He}^+ (1s^{-1}) \) final states of the ICD are shown in the same figure. They all behave like \( 1/R \) over the relevant interatomic distance range. They cross the PECs of the decaying states at different interatomic distances. ICD is energetically allowed at distances larger than the crossing point. We see that ICD opens at 6.2 Å for state 1, at 4.5 Å for states 2a and 2b and at about 2.5 Å for state 3. The corresponding ICD widths summed over all final states are shown in the top panel of Fig. 1. Obviously, they are equal to zero at distances where ICD is energetically forbidden. They are maximal just after the crossing point and then decrease like \( 1/R^6 \) (as predicted by the virtual photon mechanism \[21\]) at larger interatomic distances. The radiative decay width of \( \text{Ne}^+ (2s^{-1}) \) is of about 3.8 \( \mu \text{eV} \). Thus, when ICD is open it dominates the radiative decay for interatomic distances below 10 Å (not shown).

The experimental and the theoretical (ab initio) calculations have been performed at BLU125-2/SGM at the BESSY synchrotron radiation facility using the COLTRIMS technique \[15,16\]. A supersonic beam of a He Ne gas mixture expanded through a cooled nozzle was intersected with a linearly polarized photon beam of an energy of 55.8 eV. The ions and electrons were guided by homogeneous electric and magnetic fields towards two position and time sensitive detectors with delay line readout \[17\]. From the time-of-flight and position of the impacts we obtained the momentum vectors and thus the energy of all particles in coincidence. The two singly charged ions from the dimer are emitted back-to-back.

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observed, which demonstrates that ICD happens at interatomic distances larger than 6.2 Å, i.e., at more than twice the equilibrium interatomic distance of the neutral dimer.

In order to understand how the dimer can decay at such large interatomic distances, we follow the nuclear dynamics on the decaying electronic state. We show in Fig. 3 the probability for finding the two atoms at a given interatomic distance as function of time for state 1. In the upper part of the figure, we show the density right after the photoionization process. The vertical lines show the position where ICD opens for each decaying state. In the lower panel of Fig. 3, we show only the tail of the density between $R = 5.8$ Å and 7 Å, which is relevant for the ICD process of state 1. In this panel, we see that the nuclear wave packet on the PEC of the decaying state leaves this region and comes back to it periodically. The period of these oscillations is of about 1.5 ps. Initially ($t = 0$), a small part of the density is at interatomic distances where ICD is open. Then, the dimer starts to contract and after about 750 fs the density in this same region is almost zero. After 1.5 ps, the nuclear wave packet returns, allowing the dimer to again decay via ICD. Therefore, the dimer stretching and shrinking back and forth in the electronic excited state must drive the electronic decay. We can follow the decay in time by looking at the time derivative of the norm of the wave packet in the decaying state. This gives us an instantaneous total (ICD plus radiative decay) rate as a function of time, which we normalized by the radiative decay rate. The normalized instantaneous rate (Fig. 4) shows how much faster ICD is in comparison to radiative decay at time $t$. If the system deexcites exclusively by radiative decay, the normalized instantaneous rate is equal to one after the photoionization and then decreases like $e^{-\Gamma_{R}\Delta t}$, where $\Gamma_{R}$ is the radiative decay rate. In the case of state 1, we see that it is between 2 and 3. This shows that even at 6.2 Å apart, the energy transfer between the excited neon ion and the helium is faster than the radiative decay of the former. The instantaneous rate exhibits oscillations with a period of 1.5 ps. It is evident that these oscillations are due to the stretching of the molecule, with the same period as mentioned above.

FIG. 2 (color online). Measured (top panel) and computed (lower panel) kinetic energy release of the $\text{Ne}^+ - \text{He}^+$ fragments versus the energy of one of the two electrons from the photoionization of $\text{NeHe}$ dimer at photon energies of 55.8 eV. Several intermediate electronic states are populated by photoionization. Each of them gives a different signal (see text). The calculated spectra were convoluted with the experimental resolution function.

FIG. 3 (color online). Upper panel: Density of probability for finding the two atoms at given interatomic distances just after photoionization. The vertical lines show the position where ICD opens for state 1 (black line), states 2a and 2b (red line) and state 3 (green line). Lower panel: Same density as function of time for the electronic state 1.

FIG. 4 (color online). Normalized instantaneous total rate (i.e., time derivative of the norm of the wave packet in the decaying state divided by the radiative decay rate) as a function of time for states 1, 2a, 2b, and 3. It shows how much faster ICD is in comparison to radiative decay at time $t$ for each of the states.
This is a clear evidence that ICD is driven by the nuclear motion. Therefore, following the ICD process in time gives us a clock for the vibrational motion of the dimer in the excited state.

We discuss now the instantaneous rate of the states 2a, 2b, and 3. In the case of states 2a and 2b, ICD is about 10 times faster than for state 1 and about 20–30 times faster than the radiative decay. The instantaneous rate also oscillates but with a different period of 1 ps. This corresponds to the vibrational period of the second and last vibrational state of states 2a and 2b. Thus, the electronic decay is also controlled by the vibrational motion. Finally, we see that state 3 decays much faster than the three other states. The instantaneous rate exhibits some structures due again to the motion of the wave packet along the PEC. However, those structures are not periodic as in the case of the other states. That is because in the case of state 3, ICD is completely open for all its vibrational levels whereas only one vibrational level is involved for each of the states 1, 2a, and 2b. The several vibrational levels of state 3 have different vibrational periods, wiping off periodic structures in the normalized instantaneous rate. The instantaneous rate of state 3 drops to a value close to 1 after 20 ps because most of the wave packet has already decayed via ICD to the final states. The rest of the wave packet then decays equally by photon emission.

With NeHe, nature provides a particularly interesting example for studying interatomic decay processes as the decay opens at smaller internuclear distances by exciting higher excited states above the Ne 2s ionization threshold. In this simple model system thus totally different situations can be investigated: ICD is quasi-closed, partially closed, and totally open. For the most populated state by photoionization studied here, we show that ICD happens even if it is by far not energetically allowed at the equilibrium geometry ($R = 3 \text{ Å}$) of the neutral system. The electronic decay is driven by the nuclear motion and the dimer has to stretch up to 6.2 Å before ICD can become operative. Following the ICD process in time gives us a clock for the vibrational motion of the decaying ionized NeHe dimer.

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*Nicolas.Sisourat@pci.uni-heidelberg.de