Interatomic Electronic Decay Driven by Nuclear Motion

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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.

Nuclear motion in molecules is controlled and driven by
electrons constituting the bonds. In photochemistry, pho-
tons 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 demon-
strate 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 theo-
retically 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].
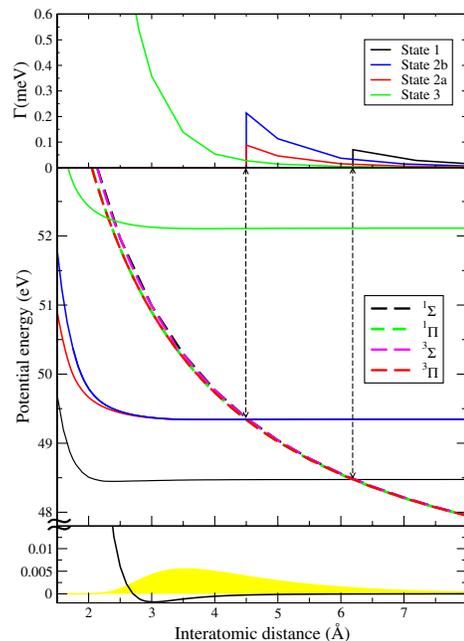
FIG. 1 (color online).　*Ab initio* data for the NeHe dimer. Upper
panel: Total ICD widths as functions of the interatomic distances
for $^2\Sigma^+$ [$Ne^+(2s^{-1}) - He(1s^2)$, state 1], $^2\Sigma^-$ and $^2\Pi$
[$Ne^+(2p^{-2}3s) - He(1s^2)$, states 2a and 2b] and $^2\Sigma^+$
($Ne^+(2p^{-2}3s) - He(1s^2)$, state 3). Middle panel: Potential en-
ergy curves (PECs) for the decaying $Ne^{+*} - He$ states (pre-
sented 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 $Ne^+(2s^{-1})$ and $Ne^+(2p^{-2}3s)$ and the ICD leading to $Ne^+(2p^{-1}) + He^+(1s^{-1}) + e^-_{ICD}$ is investigated, where e^-_{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 in the final state are emitted back-to-back with equal momentum. This signature allows us to distinguish the ions from the dimer from the huge background of monomer ions. This coincidence was also essential to distinguish the HeNe dimer breakup from that of the Ne_2 dimers which are also created in our expansion. We have performed *ab initio* calculations to follow the nuclear dynamics during the ICD process. The coincidence spectrum has been computed from the nuclear dynamics simulation. The potential energy curves of the involved electronic states were computed using configuration interaction with all single, double and triple substitutions. The Dunning's cc-pVDZ and cc-pVTZ basis set were used for the helium and neon atoms, respectively. In addition, a set of continuumlike Gaussian functions of Kaufmann-Baumeister-Jungen type [18] were centered on neon. The decay widths as functions of interatomic distance (R) were obtained for each of the decaying states by the Fano-Green's functions-Stieltjes technique [19]. The potential energy curves and the ICD widths were used as input data for computing the coincidence spectrum using the approach developed by Moiseyev *et al.* [20].

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. Note that the density is small for interatomic distances above 6 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 $^2\Sigma^+$ molecular state which corresponds to $Ne^+(2s^{-1}) - He(1s^2)$ at infinite interatomic distance, two states $^2\Sigma^-$ and $^2\Pi$ at around 49 eV corresponding to $Ne^+(2p^{-2}3s) - He(1s^2)$ asymptotically and finally one $^2\Sigma^+$ state representative for the manifold of states $Ne^+(2p^{-2}3s) - He(1s^2)$ at energy around 52 eV. We label these 4 states, as 1, 2a, 2b, and 3, respectively. The PECs of the $Ne^+(2p^{-1}) - He(1s^{-1})$ 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 $Ne^+(2s^{-1})$ is of about 3.8 μeV. 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 and measured coincidence spectra after photoionization with photon energy of 55.8 eV are shown in Fig. 2. The agreement between the two spectra is very good. We see one signal at a kinetic energy release (KER) = 2 eV and an ICD electron energy (E_e) = 0.2 eV which corresponds to the ICD process of state 1. The signal at KER = 3 eV and E_e = 0.2 eV is the signature of ICD of states 2a and 2b. Finally, the most intense signal extending from KER = 2.8 eV to 4.5 eV and E_e between 1 and 3 eV corresponds to ICD of state 3. The computed coincidence spectrum for each of these states were scaled with respect to the relative photoionization cross sections of the neon atom as measured by [22] and thus they are directly comparable to the measured data. As expected, the contribution of state 3 is dominant. Nevertheless, ICD of state 1 is clearly
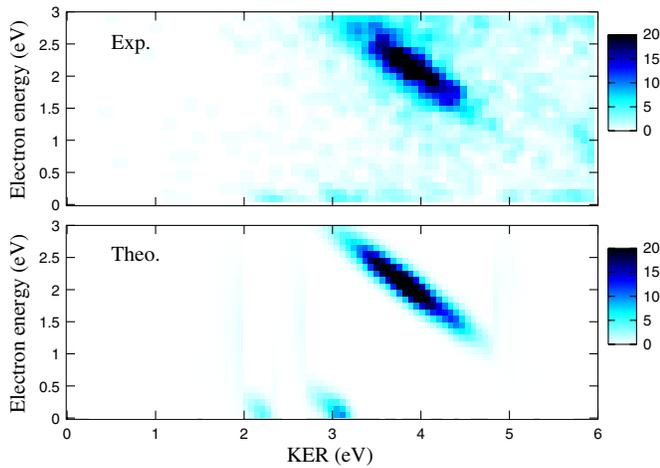
FIG. 2 (color online). Measured (top panel) and computed
(lower panel) kinetic energy release of the $Ne^+ - He^+$ fragments
versus the energy of one of the two electrons from the photo-
ionization of NeHe dimer at photon energies of 55.8 eV. Several
intermediate electronic states are populated by photoionization.
Each of them gives a different signal (see text). The calculated
spectra were convoluted with the experimental resolution function.

observed, which demonstrates that ICD happens at inter-
atomic 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 dynam-
ics 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 photoioniza-
tion process. The vertical lines show the interatomic dis-
tance where ICD becomes energetically allowed 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 dis-
tances where ICD is open. Then, the dimer starts to con-
tract 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 elec-
tronic 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
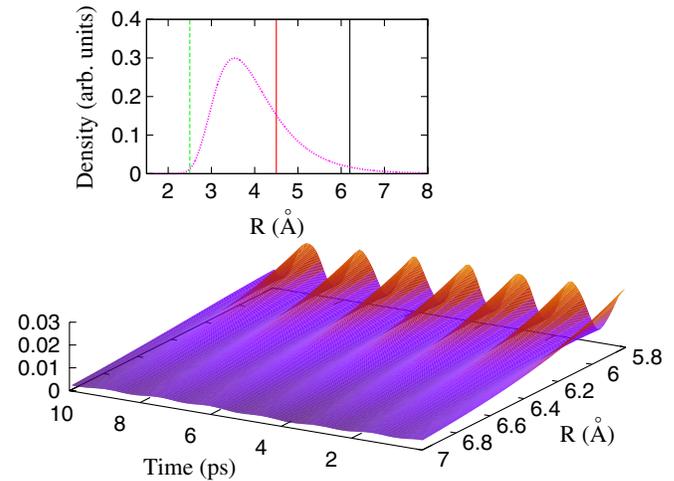
FIG. 3 (color online). Upper panel: Density of probability for
finding the two atoms at given interatomic distances just after
photoionization. The vertical lines show the position where ICD
opens for state 1 (black line), states 2a and 2b (red line) and state
3 (green line). Lower panel: Same density as function of time for
the electronic state 1.

and then decreases like $e^{-\Gamma_{RD}t}$, where Γ_{RD} 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 instanta-
neous 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.
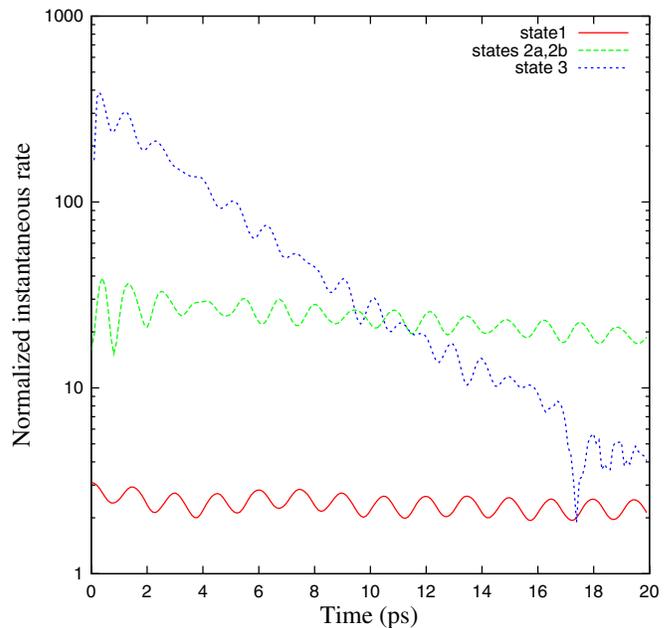
FIG. 4 (color online). Normalized instantaneous total rate (i.e.,
time derivative of the norm of the wave packet in the decaying
state divided by the radiative decay rate) as a function of time for
states 1, 2a, 2b, and 3. It shows how much faster ICD is in
comparison to radiative decay at time t for 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 ($R = 3$ 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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