Giant Interatomic Coulombic Decay

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Abstract. On the example of the giant helium dimer, we present an efficient electronic decay process for excited atoms or molecules embedded in a chemical environment, called Interatomic (intermolecular) Coulombic decay (ICD). After simultaneous ionization and excitation of a helium atom within a helium dimer, the excited ion relaxes by ICD to He+ (1s) and the neighbor neutral helium is ionized to He+ (1s) as well and emits a secondary electron. A short review on ab initio methods developed during the last 10 years to accurately describe ICD is reported. Finally, the main striking results on the helium dimer obtained experimentally and theoretically are summarized.

1. Introduction
Interatomic (Intermolecular) Coulombic decay (ICD) is an ultrafast non-radiative electronic decay process for excited atoms or molecules embedded in a chemical environment. Via ICD, the excited system can get rid of the excess energy and this excess energy is transferred to one of the neighbors and ionizes it. As an example, after inner-valence ionization of an atom in a cluster, this atom can relax by ionizing another unit of the cluster. For the example case of neon dimer, this can be summarize as follows:

\[
\text{Ne} - \text{Ne} \xrightarrow{\text{hv}} \text{Ne}^{+*} (2s^{-1}) \rightarrow \text{Ne} + e^{-}_{ph} \xrightarrow{\text{ICD}} \text{Ne}^{+} + \text{Ne}^{+} + e^{-}_{ph} + e^{-}_{\text{ICD}}
\] (1)

It should be stressed that whereas the same excited atom when isolated relaxes only by emitting a photon in a time range of picoseconds to nanoseconds, ICD takes place in the femtosecond range. Thus, ICD is generally the most favorable decay process.

ICD was predicted in 1997 by L.S. Cederbaum and coworkers on the example of small clusters of water and hydrogen fluoride molecules [1] and since then was observed experimentally in van der Waals clusters [2, 3, 4, 5] as well as in hydrogen bonded systems [6, 7, 8]. Recently, ICD after ionization of a water molecule in water clusters [7, 8] was observed. As water is the most abundant solvent in nature, ICD in water clusters is relevant for chemical and biological processes. It should also be mentioned that ICD was demonstrated in various bimolecular systems that contain an oxygen atom as a proton donor or as a proton acceptor and that represent the most common types of hydrogen bonding between water and biochemically relevant molecules [9]. Furthermore, the typical energy of the emitted ICD electron is of about few electron-Volts and it was demonstrated that low kinetic energy electrons induce significant
Figure 1. After simultaneous ionization and excitation of one helium atom by a single photon (see (a)), this atom relaxes via ICD by transferring its excess energy to the other helium atom which is then ionized and emits the ICD electron (see (b)). The resulting two He$^+$ in their ground state undergo a Coulomb explosion (see (c)).

damage to DNA [10, 11]. Thus, ICD as a direct source of low kinetic energy electrons must be taken into account in future radiation damage studies. For example, it was demonstrated that ICD may happen after ion impact [12] which is relevant in cancer therapy.

Through ICD, the energy transfer between the two atoms or molecules can take place over large distances, even much beyond distances where the overlap of the wavefunctions involved becomes negligible. The giant helium dimer is a perfect candidate to investigate how far can atoms or molecules transfer their excess energy to a neighbor via ICD. The existence of helium dimer had been discussed for decades before being observed experimentally [13]. It is the most weakly bound system in nature, with a binding energy of only about $10^{-7}$ eV ($\approx 1.1$ mK) and a very large average bond length of around 52 Å! [14]. After simultaneous ionization and excitation of one helium atom within the dimer, the energy stored by this excited ion suffices to ionize the neighboring neutral helium atom. It should be mentioned that the excess energy of the excited ion is at least 40 eV which is enough to ionize any neutral molecules in nature. The excited ion relaxes by ICD to He$^+$(1s) and the neutral helium is ionized to He$^+$ as well and emits the ICD electron. The resulting two He$^+$(1s) then undergo a Coulomb explosion and fly apart (see Fig. 1). In short:

$$\text{He} - \text{He} \xrightarrow{\hbar \nu} \text{He}^{++} - \text{He} + e_{\text{ph}}^{-} \xrightarrow{\text{ICD}} \text{He}^+ + \text{He}^+ + e_{\text{ph}}^{-} + e_{\text{ICD}}^{-}$$

(2)
2. Methods
ICD is an electronic decay process taking place on the same time scale of typical vibrational motion. It is therefore necessary to take the nuclear dynamics during the decay process into account. Furthermore, ICD leads to emission of an electron (called the ICD electron) and to the fragmentation of the system into at least two charged subsystems. The distribution of the kinetic energy of the ICD electron and of the two charged fragments (usually called kinetic energy release spectrum or KER spectrum) contain therefore all the informations on the dynamics of the ICD process. We will only discuss the KER spectra in the present manuscript. Classically, they are the mirror image of the ICD electron spectra.

There are two main ab initio approaches to compute a KER spectrum taking explicitly into account the vibrational motion during the decay process: a time-dependent and a time-independent approach [15]. The former one (also called wavepacket propagation method) consists of propagating the initial vibrational wavepacket onto the potential energy surfaces of the coupled decaying and final states. The nuclear wave packets propagating on the final potential energy surfaces contain all the spectroscopic information required for the computation of the KER spectrum. The latter is given, for example, by the flux going through a complex absorbing potential introduced in the Hamiltonian [15]. The second approach (time-independent) resides in computing the following quantity:

$$\sigma(KER = E_f) = \int dE_e \left| \sum_{j=1}^{n_d} \frac{\langle F_f | \hat{W} | D_j \rangle (D_j | I \rangle)}{E_e + E_f - \epsilon_j + i\Gamma_j/2} \right|^2$$

where $E_e$, $E_f$ and $\epsilon_j + i\Gamma_j/2$ are the energy of the ICD electron, of the final state $|F_f\rangle$ and of the decaying state $|D_j\rangle$, respectively. It should be noted that the decay width $\Gamma_j$ include both the ICD contribution and the radiative decay. The states $|I\rangle$ and $|F_f\rangle$ are the nuclear eigenstates of the neutral and the final electronic states, respectively. The states $|D_j\rangle$ are the right-hand eigenstates of the complex Hamiltonian $\hat{H}_d$ of the electronic decaying state. The operator $\hat{W}$ is equal to $\sqrt{2\pi\gamma_D}$, where $\gamma_D$ is the partial ICD rate. Both approaches are, in principle, similar: they contain the same informations and should lead to the same results. For practical reasons depending on the system considered, one or the other method is preferable. For example, for systems with multiple nuclear degrees of freedom the time-dependent method is more suitable because it avoids the computations of many excited multi-dimensional vibrational states [16].

Whatever the chosen method, ab initio electronic structure data are needed. The potential energy surfaces of the electronic states involved as well as the decay rates of the decaying electronic states are essential. One important aspects of ICD is that it involves decaying highly excited states. Accurate computations of the potential energy surfaces of these states are not straightforward but can be obtained by difficult excited-states methods. Furthermore, an accurate theoretical prediction of ICD rates is a challenging problem which combines scattering and many-body aspects. The first method applied for quantitative evaluation of ICD rates was the Complex Absorbing Potential (CAP) method in conjunction with Configuration Interaction (CI) wave functions (CAP-CI) [17]. However, this technique is inherently inapplicable to polyatomic systems since it is based on CI method which is known to converge very slowly and to be not size-consistent. Recently, the group of L. S. Cederbaum has developed the so-called CAP-ADC method [18] which is size-consistent and allows for an accurate treatment of relatively large systems. In the above abbreviation ADC stands for algebraic diagrammatic construction scheme (a way of computing Green’s functions and propagators). CAP-ADC is very promising for treating ICD in large systems.

Another approach to calculate interatomic decay widths is based on the picture of those metastable states as bound states embedded and interacting with the continuum. The coupling between an initial bound excited state and the ionization continuum of the environment is governed by interatomic electron correlation. The resulting decay width can be obtained from the corresponding golden-rule like expression [19]. The initial and final states of the decay may be constructed by a variety of techniques. For example, the description of the initial and the final states of the decay may be based on the restricted
He states
He+(2p)–He states
He+(2s)–He states
Figure 2. Potential energy curves of the decaying electronic states corresponding to He+(n=2)-He asymptotically. There are 6 decaying states that can be sorted in two classes. The first kind is related to He+(2p) - He (full blue line: $^2\Pi_g$, green line: $^2\Pi_u$, red line: $^2\Sigma^+_u$ and black line: $^2\Sigma^+_g$) states and the second kind is related to He+(2s) - He states (dashed black line: $^2\Sigma^+_g$ and red line: $^2\Sigma^+_u$).

Hartree-Fock solution for the neutral cluster such as in Wigner-Weisskopf method [19]. As a result, such important effects as relaxation, intra-atomic (intramolecular) correlation, and channel coupling are completely neglected and the calculated decay rates represent only rough estimations of the true ones. It was demonstrated that the initial and the final states may be produced using ADC [19]. In this way, the relaxation and the correlation effects in the initial state of the decay, as well as the intra- and interchannel couplings in the final state of the process can be taken into account, making the method fully quantitative and clearly superior to the Wigner-Weisskopf approach. The main disadvantage of these methods is the use of continuum electron wave functions whose asymptotic behavior and correct normalization cannot be reproduced by $L^2$ basis sets. This difficulty has been overcome [19] by combining these methods with the Stieltjes imaging technique. The decay widths can then be evaluated using $L^2$ basis sets.

3. Results on the helium dimer
As mentioned above, the distribution of the kinetic energy of the two He$^+$ ions after ICD (the KER spectrum) is the signature of the decay process. We computed fully ab initio the KER spectrum from which we could show that the two helium atoms exchange energy over distances of about 14 Å (45 times the atomic radius of a helium atom). It should be noted that the typical interatomic distances within a molecule is around 1 Å and of 3 Å within van der Waals clusters. ICD was previously observed to happen within 2 to 4 Å. It is the first time that such ultralong range energy transfer between two atoms was unambiguously demonstrated. We also showed that the KER spectrum exhibits structures and we demonstrated that they reflect the nodal structures of the vibrational states involved in the ICD process. These results have been presented in several papers [20, 21, 22]. We summarize here the most important points of these studies.

We consider here a photon energy range in which only He$^+$ (n) up to n=2 can be reached. Higher lying excited states have been considered experimentally in [23]. The potential energy curves and the
Figure 3. ICD rates as function of the interatomic distance (same color notation as in Fig. 2 is used). The horizontal lines indicate the values of the radiative decay rates for He\(^+\)(2s) (red) and for He\(^+\)(2p) (black). ICD is the dominant decay channel at distances below 10 Å for all the decaying electronic states.

The correspondence decay rates for He\(^+\)(n=2)-He states as a function of the interatomic distance are shown in Fig. 2 and in Fig. 3, respectively. The methods used to compute these ab initio data and a discussion of the results are presented in details in [22].

There are 6 decaying states that can be sorted in two classes. The first kind is related to He\(^+\)(2p)-He states (2 doubly degenerate \(2\Pi\) states and 2 \(2\Sigma^+_g,u\) states) whose the potential energy curves exhibit minima around 2 Å. The second kind is related to He\(^+\)(2s)-He states (2 \(2\Sigma^+_g,u\) states) and the corresponding potential energy curves possess shallower minima centered around 5 Å. Together with the molecular electronic terms nomenclature, we also use a notation where electronic states are distinguished according to the orbital to which an electron is excited: 2p or 2s. All the respective electronic states can decay to He\(^+\)-He\(^+\) singlet as well as triplet final states (not shown). Their ICD rates (Fig. 3) must be compared to their corresponding radiative decay rates. According to the atomic spectroscopic data [24, 25], the radiative lifetime of the He\(^+\)(2p) states is about 100 ps and that of the He\(^+\)(2s) state is 2 ms. The radiative decay is an atomic property and the extremely weak He-He interaction within the dimer has little influence on it. Therefore, the radiative decay rate is assumed to be constant over the relevant internuclear distances. As seen in Fig. 3, ICD is the dominant decay channel at distances below 10 Å for all the decaying electronic states. At larger distances, photon emission starts to be competitive and is largely dominant at interatomic distances above 20 Å.

We show in Fig. 4 the computed KER spectra of the two He\(^+\) ions after ICD. The spectra exhibit a series of peaks in the energy range of 1 to 9 eV whose intensities increase with increasing energy. The series of peaks are the signature of the vibrational motion during the ICD process. After the photoionization process the total nuclear wavefunction of the system in the electronic state under consideration is a linear combination of the vibrational levels of this state. The lifetime of each involved vibrational level for all electronic states varies between 20 fs and 50 ps. Since the characteristic vibration period of He\(^+_2\) is about 300 fs, the dimer can make up to 100 vibrational cycles before it decays completely, having time to span several times the entire internuclear distance populated by these states.
vibrational levels. It was demonstrated that the KER spectrum is determined by the projection of the vibrational levels onto the repulsive (He$^+$-He$^+$) final curve weighted by the ICD rates. This makes clear that ICD can be used to map the vibrational wavefunctions of the helium dimer.

The total KER spectrum have been measured by the group of R. Dörner using COLTRIMS [23]. The measured KER spectrum is the sum of all partial spectra shown in Fig.4. The calculated total KER spectrum is compared with that measured in Fig 5. All partial spectra are shown in the figure as well. The agreement between the computed and measured KER distributions is surprisingly good for such complex quantum system. The total KER spectrum exhibits an intense peak at about 8.5 eV and a series of smaller peaks at lower KER. These peaks are due to the survival of the structures showing up in the

**Figure 4.** Partial KER spectra of the two He$^+$ ions after ICD for the different He$^+$(n=2)-He electronic states decaying into singlet (dashed-lines) and triplet (full lines) He$^+$-He$^+$ states.
individual partial spectra and these in turn are images of the vibrational wavefunctions participating in the ICD process.

From the KER spectra, we can determine the internuclear distance distribution over which ICD takes place. The intense peak at 8.5 eV corresponds to interatomic separation of around 2 Å. Signals at smaller KER correspond to larger internuclear distances. One can see in the inset of Fig. 4 that the last observable low KER signal is at about 1 eV, which corresponds to internuclear distance around 14 Å. At larger interatomic distances radiative decay becomes the main channel and this limits the observability of ICD at larger internuclear distances.

4. Conclusions
In conclusion, ICD is a general decay process for excited atoms or molecules embedded in a chemical environment. ICD has been observed after inner-valence photoionization, simultaneous photoionization-excitation and after ion impact and it certainly takes place after many other ionization or excitation processes (electron impact, chemical ionization). Rare gas clusters as well as chemically and biologically relevant clusters have been investigated and it was shown that ICD is always among the dominant decay channels.

We have presented a short review on the methods developed for the ab initio description of ICD. It is clear that accurate calculations of the ICD rates are the bottleneck of all theoretical ICD studies and ICD rates are known only for few small clusters. CAP-ADC is the most promising method to obtain ICD rates for larger systems.

Finally, on the example of helium dimer we demonstrated that ICD can take place at enormous interatomic separations. We also identified the nodal structures of the vibrational wavefunctions of the helium dimer in the KER spectra. In addition to its fundamental importance, our study showed the applicability of ICD to investigate the environment of a system over large distances, making ICD spectroscopy a powerful tool for probing matter.
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