The interatomic Coulombic decay in Ne$_2$

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Abstract. The Interatomic Coulomb Decay (ICD) is a radiationless decay mechanism occurring via electron emission in inner valence ionized weakly bound clusters. In this article the theoretical description of the ICD in the inner valence ionized Ne dimer is presented, using a time-dependent formalism based on nuclear wave packet propagation. The theoretical predictions are compared with the first experimental results, and a very good agreement is found.

1. Introduction

The Interatomic Coulomb Decay (ICD) [1] is a fast decay process occurring via electron emission in loosely bound inner valence ionized atomic or molecular clusters. The mechanism at the basis of the ICD is an efficient energy transfer between neighboring monomers: The inner valence hole localized on one of the monomers is filled by an outer valence electron of the same monomer; the energy gained in this transition is transferred to a neighboring monomer, which uses it to emit one of its outer valence electrons (see figure 1).

![Figure 1](image-url) Figure 1. (color online) A) The inner valence (iv) hole is localized on monomer 1; B) Electronic transition in monomer 1 associated with energy transfer between neighboring monomers and emission of an outer valence (ov) electron from monomer 2. C) The final system is a doubly ionized cluster with two outer valence holes localized on two different but neighboring monomers. The resulting cluster eventually undergoes fragmentation due to the Coulomb repulsion between the two positive charges. The core electrons (c) are not participating in the process.

Energetically the occurrence of the ICD is made possible by the lowering of the double ionization potential which takes place when the two positive charges are distributed over two or more monomers, a fact which reduces the Coulomb repulsion between them. The efficiency of the energy transfer mechanism on which the ICD is based is strongly dependent on the nuclear distance between monomers, so that basically only neighboring monomers are involved in the process. In particular, if the monomers are very close the double ionization potential is too high and the ICD is energetically forbidden; if they are too far apart the energy transfer mechanism is not effective. This is reflected in a marked coordinate
dependence of the IC decay rate, which represents one of the peculiar characteristics of the mechanism. The lifetime of the inner valence ionized state is typically on the order of a few to one hundred fs. Consequently, nuclear dynamics and electronic decay can occur on comparable time scales and interplay significantly.

The ICD process with its underlying dynamics has been theoretically predicted a few years ago [1]. Very recently its occurrence has been experimentally confirmed in large Ne clusters [2] as well as in Ne₂ [3]. In the following the ICD in the Ne dimer is described, together with the fragmentation process following the decay.

2. Theoretical framework

The ICD in the Ne dimer proceeds according to the following steps:

\[
\hbar \omega + \text{Ne}_2 \rightarrow \text{Ne}_2^+(\text{i.v.}) + e^- \\
\rightarrow \text{Ne}_2^{2+} (\text{o.v.}) + e^- + \varepsilon_{\text{ICD}} \\
\rightarrow \text{Ne}^+ + \text{Ne}^+ + e^- + \varepsilon_{\text{ICD}}
\]

that is, initial inner valence ionization caused e.g. by incident radiation, successive decay to a doubly outer valence ionized state and final Coulomb explosion of the doubly ionized system into two outer valence ionized Ne⁺ fragments.

In the present work the ICD of Ne₂ is described in the framework of a time-dependent formalism based on nuclear wave packet propagation [4]. This requires the solution of the following system of coupled time-dependent Schrödinger equations for the nuclear wave packets \( \Psi_{i, dn, fm} \) associated to the initial (i), decaying (d) and final (f) electronic states (the indices \( n \) and \( m \) number the different intermediate and final states, respectively):

\[
\begin{align*}
\text{i} | \Psi_i(t) \rangle &= \hat{H}_i | \Psi_i(t) \rangle \\
\text{i} | \Psi_{dn}(t) \rangle &= \hat{F}_d(t) | \Psi_i(t) \rangle + \hat{H}_{dn} | \Psi_{dn}(t) \rangle \\
\text{i} | \Psi_{fm}(E,t) \rangle &= \hat{W}_{nm}(E) | \Psi_{dn}(t) \rangle + (\hat{H}_{fm} + E \hat{1}) | \Psi_{fm}(E,t) \rangle.
\end{align*}
\]

In coordinate representation the nuclear wave packets depend on the internuclear distance between the Ne atomic nuclei as well as on time. The final wave packets have an additional dependence on \( E \), the kinetic energy of the emitted ICD electron. The nuclear dynamics in the initial and final electronic states is governed by the Hamilton operators \( \hat{H}_i, \hat{H}_{fm} \), the one in the intermediate electronic states by the effective Hamilton operator \( \hat{H}_{dn} \), defined by

\[
\hat{H}_{dn} = \hat{H}_{dn} - i\hat{\Gamma}_{dn}/2 \quad \text{where} \quad \hat{H}_{dn} = \hat{T}_N + \hat{V}_{i, fm}.
\]

\( \hat{\Gamma}_{dn} \) is the total decay width of the \( n^{\text{th}} \) intermediate state and is obtained as the sum of the partial decay widths \( \hat{\Gamma}_{nm} \) to the different final states (\( \hat{\Gamma}_{dn} = \sum_m \hat{\Gamma}_{nm} \)). The coupling operators \( \hat{F}_n \) and \( \hat{W}_{nm} \) describe the excitation from the initial to the \( n^{\text{th}} \) intermediate electronic state and the coupling of the latter to the \( m^{\text{th}} \) final state, respectively. In the present case an instantaneous, vertical excitation is considered, and therefore \( \hat{F}_n \) is coordinate independent and simply a \( \delta \) function in time; \( \hat{W}_{nm} \) is defined via the partial decay widths as \( \hat{W}_{nm} = \sqrt{\hat{\Gamma}_{nm} \hat{\Gamma}_{nm}} \).

From the knowledge of the nuclear wave packets all the spectroscopic information of interest can be derived. In particular, the ICD spectrum as a function of the kinetic energy \( E \) of the emitted ICD electron can be obtained from the final wave packets as

\[
\sigma(E) = \lim_{t \to \infty} \sum_m \sigma_m(E, t) = \lim_{t \to \infty} \sum_m \langle \Psi_{fm}(E, t) | \Psi_{fm}(E, t) \rangle
\]

(3)
3. Input quantities

The electronic states involved in the ICD of Ne₂ are the initial electronic state (the electronic ground state of Ne₂), the two inner valence ionized \(2^2 \Sigma^+\) and \(2^2 \Sigma_u^+\) states of Ne²⁺, as well as the lowest 9 singlet and 9 triplet states of the outer valence ionized Ne⁷⁺. The required input quantities are the potential energy surfaces (PES) \(\hat{V}_{id}\) associated to each electronic state as well as the partial decay widths of the intermediate electronic states. The PES for the initial electronic state has been taken from [5] and is the result of very accurate ab-initio calculations. The ab-initio PES for the intermediate and final electronic states have been computed via the Algebraic Diagrammatic Construction (ADC) method [6] using the ADC(3) and ADC(2) schemes, respectively. The employed PES, used already in [7], are shown in figure 2, where for simplicity only one final PES has been plotted, all the other ones being very similar to it.

The computation of the decay widths for this process is a very complicated task, so that up to this moment only the total decay width \(\Gamma_{id}\) of each intermediate state could be calculated (figure 2). This was done in [8] using the CAP/CI method. Due to this limitation, for this work it has been assumed that all the partial decay widths are equal and given by \(\frac{1}{18} \Gamma_{id}\).

Concerning the initial conditions, the initial wave packet at the time \(t_0\), \(\Psi_i(t_0)\), has been taken to coincide with the lowest vibrational eigenfunction of the electronic ground state; since a vertical and instantaneous excitation is considered, the initial condition for the intermediate wave packets is \(\Psi_{id}(t_0) = \Psi_i(t_0)\), while of course \(\Psi_{fm}(t_0) = 0\) for all the final wave packets.

4. Numerical methods

A discrete spatial representation on a uniformly spaced grid has been employed for all the wave packets and PES. The time propagation is performed by the Lanczos-Arnoldi [9] algorithm, which is a generalization of the short iterative Lanczos method to the case of non-hermitian operators.

In order to avoid artificial reflections at the end of the grid a Complex Absorbing Potential (CAP) [10] has been adopted for the propagation of the final wave packets along the repulsive final state PES. In this way the Hamilton operators \(\hat{H}_{fm}\) have been replaced by non-hermitian Hamilton operators \(\hat{H}_{fm} = \hat{A}_{fm} - i\hat{C}\), where \(\hat{C}\) is the CAP operator defined as:

\[
\hat{C} = \eta \cdot (R - R_0)^3 \theta(R - R_0).
\]

The parameter \(\eta\) determines the CAP strength, while \(R_0\) is the internuclear distance at which the CAP
begins to act. \( R_0 \) has to be chosen outside the region where the decay takes place. Since the non-hermiticity of \( \hat{H}_{fm} \) implies the non conservation of the norm of the final wave packets \( \Psi_{fm}(E,t) \), the partial decay spectra \( \sigma_m(E,t) \) in (3) have to be replaced by:

\[
\sigma_m(E,t) = \langle \Psi_{fm}(E,t) | \Psi_{fm}(E,t) \rangle + F_m(E,t). \tag{5}
\]

The function \( F_m(E,t) \), defined as:

\[
F_m(E,t) = 2 \int_{t_0}^{t} dt' \langle \Psi_{fm}(E,t) | \hat{C} | \Psi_{fm}(E,t) \rangle \tag{6}
\]

represents the flux going through the CAP and accounts for the reduction of the norm of \( \Psi_{fm}(E,t) \) due to the CAP absorption in the time interval \((t_0,t)\).

The CAP turns out to be not only a very convenient numerical tool: It can indeed be further exploited for the computation of the Kinetic Energy Release (KER) of the Ne\(^+\) fragments [11]. For a fixed kinetic energy \( E \) of the emitted ICD electron the latter is given by:

\[
\sigma_{KER}^{m,E}(E') = \frac{2}{\pi} \text{Re} \int_{t_0}^{\infty} d\tau \int_{t_0}^{\infty} dt \langle \Psi_{fm}(E,t) | \hat{C} | \Psi_{fm}(E,t+\tau) \rangle e^{iE'\tau}, \tag{7}
\]

where \( E' \) is the total energy \( E' = E_{fr} + E + V_{as} \), where \( E_{fr} \) is the energy of the two emitted Ne\(^+\) fragments, \( E \) the energy of the ICD electron and \( V_{as} \) is the asymptotic value of \( V_f \). Since the two Ne\(^+\) fragments are emitted back to back with equal speed they have the same energy and \( E_{fr} = 2E_{Ne^+} \).

The KER spectrum as a function of the total kinetic energy of the two fragments is then obtained as:

\[
\sigma_{KER}(E_{fr}) = \sum_m \int dE \sigma_{m,E}^{KER}(E_{fr}) \tag{8}
\]

5. Results

Shown in figure 3 are the partial decay spectra obtained from the decay of the \( 2^2\Sigma_u^+ \) and \( 2^2\Sigma_g^+ \) states to the multitude of final electronic states. The shape of the spectral distributions can be understood in terms of the characteristics of the potential energy curves and of the decay widths of the electronic states involved as it reflects the structure of the intermediate wave packets in their spatial representation [4]. Indeed, as the final PES are purely repulsive Coulomb-like curves, the characteristics of the intermediate wave packets is practically mapped onto the kinetic energy spectrum of the ICD electron, except for being partially distorted by the shape of the decay widths governing the decay. The differences in the two spectra originate from the different vibrational structure of the decaying states (\( 2^2\Sigma_u^+ \) and \( 2^2\Sigma_g^+ \) support 11 and 1 bound vibrational states, respectively), from the position of their minimum (2.1 Å for \( 2^2\Sigma_u^+ \) and 3.1 Å for \( 2^2\Sigma_g^+ \)) as well as from the slightly different shape of the associated decay widths (see

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**Figure 3.** Partial ICD electron spectra resulting from the decay of the \( 2^2\Sigma_u^+ \) (left) and \( 2^2\Sigma_g^+ \) (right) electronic state to the multitude of final states.
While the Gaussian-like shape of the decay spectrum associated to the $2^2\Sigma^+_g$ state was expected in view of the absence of bound vibrational excited levels, the relatively simple structure of the spectrum associated to the $2^2\Sigma^+_u$ might at first surprise. This structure can nevertheless be very easily understood (compare [4, 7]): The decay can take place only at relatively large internuclear distances ($R > 2.6\,\text{Å}$) and hence only the most external and mainly structureless part of the intermediate nuclear wave packets can decay, resulting in a relatively unstructured spectrum.

For the computation of the total ICD electron spectrum an equal population of the two intermediate states during the excitation process has been assumed. Consequently the total ICD electron spectrum has been obtained as the sum of the two partial decay spectra illustrated in figure 4. The KER spectrum for the Ne$^+$ fragments has been computed using (8). As can be seen, the two spectra are complementary since the total kinetic energy shared by the ICD electron and the Ne$^+$ fragments is approximately constant and equal to 5.37 eV, the asymptotic energy difference between the intermediate and final electronic states.

The agreement between the calculated spectra and the experimental results [3] is very satisfactory, as shown in figure 4.

6. Conclusions

The theoretical description of the ICD in Ne$_2$ has been presented. The calculated spectra, obtained using a time-dependent formalism for nuclear wave packets propagation, show a very good agreement with recent experimental results. This work, together with the successful experiment reported in [3], represent the first quantitative proof of the existence of this novel decay process, namely ICD, and confirm the nature of its underlying mechanism, which was proposed theoretically a few years ago, before any experimental evidence was available.

Acknowledgments

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