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Interatomic electronic decay processes in singly and multiply ionized clusters

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ABSTRACT

Since their theoretical prediction in 1997, interatomic (intermolecular) Coulombic decay (ICD) and related processes have been in the focus of intensive theoretical and experimental research. The spectacular progress in this direction has been stimulated both by the fundamental importance of the discovered electronic decay phenomena and by the exciting possibility of their practical application, for example in spectroscopy of interfaces. Interatomic decay phenomena take place in inner-shell-ionized clusters due to electronic correlation between two or more cluster constituents. These processes lead to the decay of inner-shell vacancies by electron emission and often also to disintegration of the resulting multiply ionized cluster. Here we review the recent progress in the study of interatomic decay phenomena in singly and multiply ionized clusters.

1. Introduction

The present day knowledge of interatomic (intermolecular) decay mechanisms in clusters encompasses a diversity of distinct physical phenomena, all stemming from interatomic (intermolecular) electronic interaction. In this section we give an overview of the predicted and observed interatomic decay processes induced by inner-shell ionization.

1.1. Interatomic (intermolecular) Coulombic decay

Core vacancy states of atoms and molecules represent very highly excited states of the corresponding atomic or molecular ions, typically lying above the double or even multiple ionization thresholds. As a result, these states decay by electron emission in a specific type of autoionization process named after its discoverer, Auger [1]. Kinetic energies of the electrons emitted in the course of Auger decay are given by the differences between the bound states of singly and doubly charged species and thus are quantized. This property explains the great spectroscopic value of the Auger electron spectroscopy (AES) [2], as well as its importance for numerous analytical applications, e.g. in surface science (see, for example, Ref. [3]). Auger decay is typically an intraatomic process, only modestly affected by the environment. Usually, such an effect is manifested in the so-called chemical shift of the Auger electron lines (see, for example, Ref. [4]).

In 1997, the authors of the theoretical work [5] took a pioneering approach to the issue of the environment effects on the decay of vacancy states [5]. The question posed by the authors was:

> Can a vacancy decay non-radiatively *only* due to the effect of the environment?

Surprisingly, it turned out that such an environment-mediated decay is not only possible, but is also a general phenomenon, typical of relatively low-energy inner-shell vacancies. In particular, clusters of various types prove to be the ideal objects to study this kind of decay phenomenon [5]. In order to get an idea of the new decay process discovered by Cederbaum and co-workers, one can consider the decay of 2*s* vacancy of neon, once in an isolated ion and once in a cluster, e.g. in Ne_n. The $2s^{-1}$ state of the isolated Ne^+ lies below the double ionization threshold of Ne and thus cannot decay by Auger mechanism. As a result, $(2s^{-1})$ Ne^+ decays radiatively on a nanosecond time scale. However, if $(2s^{-1})$ Ne^+ is allowed to interact with an environment, e.g. with other Ne atoms, the situation changes dramatically. Indeed, as shown schematically in Fig. 1 for neon dimer, in a Ne_n cluster, one can consider not only the high-energy $Ne^{2+}Ne_{n-1}$ doubly ionized states, but also the ones of the

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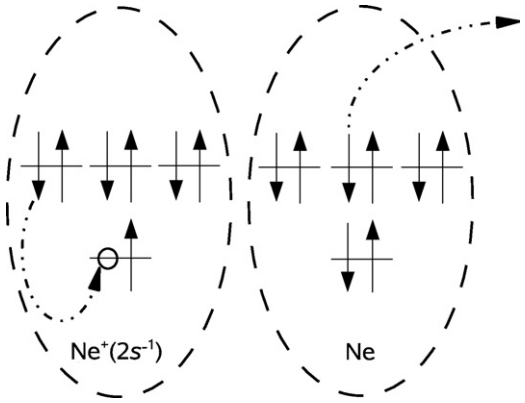

Fig. 1. A schematic representation of the ICD process in Ne dimer. 2*p* electron of the inner-valence-ionized Ne recombines into the 2*s* vacancy while a 2*p* electron of another Ne is ejected into continuum. The resulting doubly charged cluster decomposes by Coulomb explosion mechanism.

type $(Ne^+)_2Ne_{n-2}$. The latter states are relatively low in energy due to the separation of the positive charge between two neon atoms. In fact, the charge-separated states lie several electron-volts lower than $(2s^{-1})\ Ne^+Ne_{n-1}$. This leads to a very interesting *interatomic* decay process in which 2*p* electron of the ionized Ne fills the 2*s* vacancy, while 2*p* electron of another Ne atom is ejected into continuum. Since such a process is enabled by the Coulombic interaction between the electrons of the two Ne atoms, it has been called interatomic Coulombic decay (ICD). In a small loosely bound cluster, such as neon dimer, the repulsion between the two charges created by ICD leads to Coulomb explosion of the system [6] (see Ref. [7] for an exception). Under such conditions, the excess energy of the initial vacancy state is partitioned between the outgoing electron and the separating positively charged fragments. Thus, while Auger decay leads to quantized Auger electron energies, ICD in small clusters makes the total of the electron and the cluster fragment energies to be quantized. The kinetic energy of the relative motion of the fragments is often called kinetic energy release (KER).

The last several years have witnessed a series of remarkable advances in the experimental study of ICD. Hergenhahn, Möller and co-workers have presented the first experimental evidence of ICD by clearly identifying the new process in neon clusters [8]. Dörner, Jahnke and co-workers have conducted a detailed study of ICD in neon dimer [9] using the cold target recoil ion momentum spectroscopy (COLTRIMS) [10]. They have been able to measure in coincidence both the ICD electrons and the neon ions generated by the Coulomb explosion of $(Ne^+)_2$. The coincidences detected by Frankfurt group were found to be arranged along the energy conservation line corresponding to the sum of the electron energy and the KER being about 5 eV. Thus, the experiment of Dörner and co-workers constitutes the most detailed direct proof of the ICD. The electron kinetic energy and the KER spectra of Frankfurt group were later confirmed by theoretical calculations [11]. Going back to larger neon clusters, Örwall et al. have estimated the dependence of the ICD lifetime on the neon cluster size by distinguishing between the "bulk" and the "surface" peaks in the ICD electron spectra [12]. These experimental findings were found it to be in a reasonable agreement with earlier theoretical predictions of Santra et al. [13] (see also the more recent theoretical work of Vaval and Cederbaum [14]).

Both theoretical and experimental investigations have established ICD as a highly general and a very efficient decay process. Indeed, ICD is characteristic of vacancy states of van der Waals clusters (see, e.g. Refs. [5,8]), hydrogen bonded clusters (see, e.g. Refs. [16,15]), and even endohedral fullerenes [17]. The ICD lifetimes were found to belong to the range of 1–100 fs [13,12,17], many orders of magnitude shorter than those of the competing photon emission process. Thus, ICD is the main decay mode of moderate-energy (Auger-inactive) inner shell vacancies in clusters. Further studies of ICD are motivated, however, not only by the generality and efficiency of this new physical process, but also by the perspectives of its practical use, for example in spectroscopy. The very first step in this highly promising direction has been already done by Hergenhahn and co-workers who have shown that ICD electron spectra can be used in order to identify the Ne/Ar interface [18].

1.2. Beyond ICD of singly ionized states

1.2.1. Interatomic decay in inner-shell excitations

Recently, Barth et al. [19] have addressed the question, whether interatomic decay can occur not only in the inner-valence-ionized, but also in the inner-valence-excited states of clusters. They have created Ne $(2s^{-1}3p)$ excitations in Ne_n clusters (n being 70 on average) and detected the electrons emitted due to the $(2s^{-1}3p)NeNe_{n-1} \rightarrow (2p^{-1}3p)Ne(2p^{-1})Ne^+Ne_{n-2} + e^-$ process. Aoto et al. [20] studied in detail a similar decay phenomenon in neon dimer. This process is related to ICD exactly in the same way in which the resonant Auger effect [21,22] is related to the regular Auger effect [1,2]. Consequently, it has been called resonant interatomic Coulombic decay (RICD) [19].

RICD physics is richer and more involved that the ICD physics due to several reasons. First, the interatomic decay of inner-shell-excited states is accompanied by the intraatomic autoionization, e.g. $(2s^{-1}3p)Ne \rightarrow (2p^{-1})Ne + e^-$. Whereas ICD competes only with slow radiative decay, RICD has to compete with a fast non-radiative process. Nevertheless, both experimental [19,20] and theoretical [23] evidence show that this competition does not lead to a suppression of RICD. Another important difference between ICD and RICD comes from the fact that the inner-valence-excited electron can participate in RICD process. Exactly as the resonant Auger decay [21,22], RICD can occur either by *spectator* (*s*RICD) or by *participator* (*p* RICD) mechanism. While the *s* RICD process has been observed experimentally, *p*RICD has yet to be identified in the RICD electron spectra.

Yet another distinction between ICD and RICD has its origin in the higher energy accumulated in the inner-valence-excited states relative to the one of the inner-valence-ionized states. For example, $(2s^{-1}3p)Ne$ lies about 45.5 eV above the Ne ground state, whereas $(2s^{-1})\ Ne^+$ lies only about 26.9 eV above the Ne^+ ground state. As a result, decay of inner-valence-excited states can be accompanied by double ionization of the cluster. This can happen according to a variety of mechanisms which have been discussed qualitatively in Ref. [23]. The predicted double ionization interatomic processes still await their detailed quantitative study. The essential question is whether the double ionization processes are fast enough to compete with autoionization and *s* RICD. The subject of RICD will not be described in detail in this short review that will instead focus on the inter-atomic decay processes triggered by ionization.

1.2.2. Auger-ICD cascade

It is well known that Auger decay of core vacancies often results in highly excited states of the corresponding doubly ionized species. Sometimes, this brings about another stage (or even several stages) of Auger decay, forming what is usually called a decay cascade. Often, however, the excited doubly ionized states created by Auger process are not energetic enough to decay by an intraatomic mechanism. Under such conditions, formation of decay cascade is impossible in isolated species, but can occur in clusters with the second step of the cascade being of the ICD, rather than of the Auger type. The Auger-ICD cascade has been first predicted by Santra and Cederbaum [24] in 1*s*-ionized neon dimer and has