



## Interatomic and intermolecular coulombic decay: The early years

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### ABSTRACT

Autoionization is an important pathway for the relaxation of electronically excited states. In weakly bonded matter, efficient autoionization channels have been found, in which not only the initially excited state, but also neighbouring atoms or molecules take part. Since their theoretical prediction in 1997 these processes are known as interatomic or intermolecular coulombic decay (ICD). The author summarizes the experimental research on ICD up to the present. Experiments on inner valence ICD in rare gas clusters, on cascade ICD after Auger decay and on ICD of satellite states are explicitly discussed. First experiments on water clusters and on solutes will be reviewed. An outlook on other non-local autoionization processes and on future directions of ICD research closes the article.

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### 1. Introduction

A vacancy site in an isolated atom or molecule can relax by fluorescence, dissociation or—if energy permits—by autoionization. If we, instead of the isolated situation, consider a vacancy in a cluster of identical atoms or molecules, one may ask if and how the environment influences the relaxation process. In the case of a strong covalent bonding, such as in metal clusters, the electronic structure changes completely and any comparison would be difficult. In the case of weak bonding, e.g. by hydrogen bridges or dispersion forces, it is possible to discuss the electronic structure in terms of the one of the isolated system. It is this case which we will discuss here. Considering autoionization in particular, this can take place if the ionization energy used to produce the initial vacancy is above the double ionization threshold of the system. It has long been known that the double ionization threshold of clusters is lower with respect to the monomer [1]. This is natural, as in a cluster two hole states can have the vacancies located at different sites, resulting in a Coulomb repulsion energy which is lower than in the isolated system. But will these states play any role in autoionization, is it possible that a single vacancy in a weakly bonded cluster undergoes a direct transition into a state consisting of positive charges at two different sites and a continuum electron? In the last thirteen years it has been found that such autoionization channels indeed exist, that often they are far more effective than any other mode of relaxation and that they exhibit so many qual-

itative differences from other autoionization transitions that it is meaningful to designate them by a new name: intermolecular or interatomic coulombic decay (ICD), respectively [2], depending on whether we discuss a system composed of atomic or molecular entities.

This article intends to give a mini-review about the first years of research on ICD from an experimentalists perspective. The plan of the work is as follows: a simple example will be used as an introduction into the topic in the next subsection, followed by some essential points from the theory of ICD. A number of experiments will be reviewed next, separated into sections on noble gas clusters and on other systems. A variant of ICD taking place after resonant excitation, instead of non-resonant ionization, will be described after that. I will close with some remarks about the perspectives of the field, and will use Appendix A to discuss relations between ICD and numerous other processes.

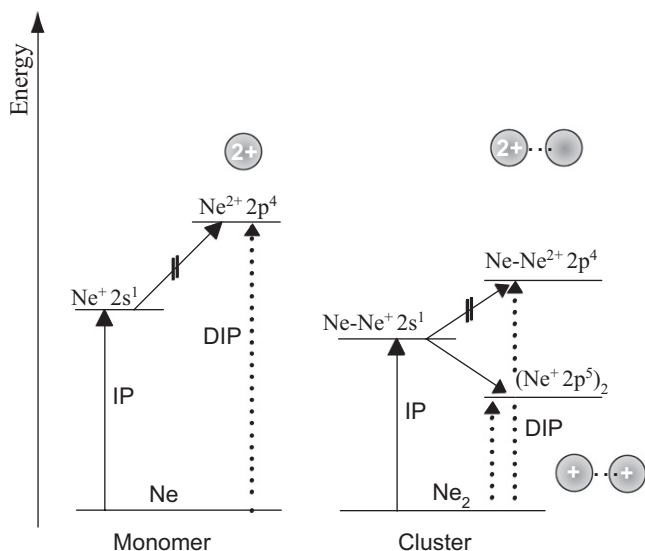
Due to the limited space available it is not possible to give a complete review of the field here, and I apologize to all whose important works are not cited here. Two useful reviews on the theory of ICD have appeared [3,4].

#### 1.1. An example—the Ne dimer

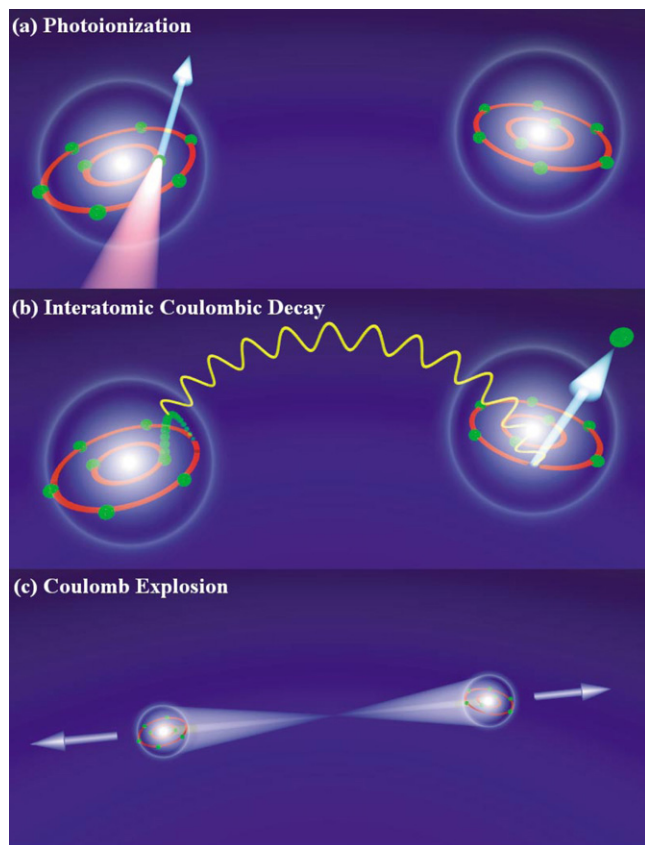
It is instructive to review an example. Fig. 1 shows an energy diagram of Ne clusters in comparison to atomic Ne. Clearly, the Ne 2s level in atomic Ne cannot autoionize, and will decay by fluorescence on a ps time scale [5,6]. In a Ne dimer (or any larger Ne cluster) instead, a decay into a  $(\text{Ne}^+ 2p^{-1})_2$  two hole state is energetically viable. The first successful experiments on ICD in 2003 [7] and 2004 [8,9] confirmed that the expected autoionization process indeed takes place. Fig. 2 gives a sketch of the three steps involved in

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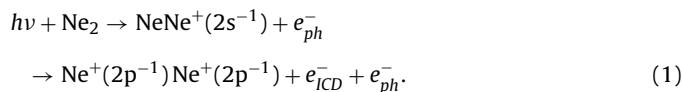


**Fig. 1.** Sketch of the energy levels relevant for inner valence ICD in a Ne atom (panel a) compared to Ne clusters (panel b). In a cluster, the  $2s^{-1}$  inner valence vacancy can autoionize into states with two vacancies at two different, preferentially neighbouring sites (arrow pointing downward). Exact ionization energies depend on the cluster size and—in larger clusters—on the ionized site (see text). For an atom, only atomic doubly ionized states are available for autoionization, which are located at higher energies however. Autoionization transitions from inner valence singly ionized states into the former are therefore energetically not possible (arrows pointing upward).



**Fig. 2.** Sketch of interatomic coulombic decay in a Ne dimer. (a) The  $2s$  valence level is ionized by a photon. (b) A  $2p$  electron relaxes into the vacancy. The energy released by that is transferred to the neighbouring atom via a virtual photon (see text). Theoretical work shows that these two processes indeed occur at the same time. (c) Two atomic ions with outer valence vacancies have been formed. As the system has been bonded very weakly, their potential curve is plainly repulsive. A Coulomb explosion follows. From [8], Copyright: American Physical Society.

ICD of the Ne dimer initiated by photon impact: (1) photoionization of an inner valence level, (2) autoionization (the actual ICD), and (3) Coulomb explosion of the final state, as the two vacancies produced repel each other. The reaction equation in this system reads



( $e_{ph}^-$  and  $e_{ICD}^-$  denote the photoelectron and the ICD electron, respectively). The signature of ICD has been seen in all three steps described above: a lifetime broadening of the photoelectron line resulting from the instability of the Ne  $2s$  level was demonstrated [9], the electrons resulting from ICD have been directly detected [7,8] and the ion pair with opposite momenta of equal magnitude, created in the Coulomb explosion of the ICD final state, was seen using different variants of ion spectroscopy [8,10].

## 1.2. Theoretical considerations

Like all autoionization processes, ICD is driven by the Coulomb interaction between the electrons involved in the transition. The matrix element of the process can thus be written as

$$\langle iv, \hat{\mathbf{k}}\varepsilon | V | ov, ov' \rangle, \quad (2)$$

where  $V$  is the Coulomb operator,  $|iv\rangle$  is an inner valence electron,  $|\hat{\mathbf{k}}\varepsilon\rangle$  the continuum orbital with momentum  $\hat{\mathbf{k}}$  and energy  $\varepsilon$ , and  $|ov\rangle$  and  $|ov'\rangle$  are the outer valence orbitals located at one and the other site respectively. It is important that for most cases the energy difference leading to IC decays is small.  $|\hat{\mathbf{k}}\varepsilon\rangle$  describes an electron of low kinetic energy, that is of large wavelength. It is for this reason that the matrix element (2) may connect the two orbitals  $|ov\rangle$ ,  $|ov'\rangle$  at different sites effectively. For a more detailed discussion of the matrix element I refer to the literature [3,11]. Some results are mentioned here:

- The matrix element (2) factorizes into a direct and an exchange term, the former being associated with energy transfer between the two sites and the latter with charge transfer. It turns out that energy transfer in most systems dominates by far. Non-local autoionization going along with charge transfer will be discussed in Section 5.
- The ICD rate depends strongly on the spatial distance  $R$  between the two entities involved. Without considering overlap between the orbitals  $|ov\rangle$ ,  $|ov'\rangle$  the rate drops  $\sim R^{-6}$ , characteristic of a dipole–dipole coupling. This is a remarkable property of ICD, as most energy and charge transfer processes known today have an exponential dependence on distance. In realistic cases however, finite overlap between the orbitals strongly modifies the ICD rate. That is saying, when  $R$  is decreased from asymptotically large distances the rate increases much faster than  $R^{-6}$  as overlap sets in [11]. The asymptotic case might be reached for the Ne dimer, but for most other systems discussed here it is probable that orbital overlap does have an influence on the rate of the decay.
- The  $R^{-6}$  dependence of ICD is reminiscent of Förster Resonant Energy Transfer (RET) [12], another process driven by a dipole–dipole coupling. Intermolecular coulombic decay however is not a resonant process, and therefore is far more general as RET. As a dipole–dipole coupling in quantum electrodynamics is mediated by photon exchange, the exchange of a virtual photon has been used as a rationalization for the energy transfer going on in ICD. At least in this context there is no rigorous definition of the notion of a virtual photon. One may say it is shorthand for a certain matrix element resulting from coulombic interactions.
- Interatomic coulombic decay depends strongly on the number of nearest neighbours. The more neighbours, the faster ICD pro-

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