Journal of Electron Spectroscopy and Related Phenomena xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Time-resolved studies of interatomic Coulombic decay

U. Frühling[a,b], F. Trinter[c], F. Karimi[a,b], J.B. Williams[c], T. Jahnke[c,*]

[a] Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany
[b] Center for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany
[c] Institut für Kernphysik, Goethe Universität, Max-von-Laue-Str.1, 60438 Frankfurt, Germany

ARTICLE INFO

Article history:
Available online xxx

Keywords:
Coulombic decay
Electronic decay mechanism
Time-resolved experiments

ABSTRACT

Interatomic Coulombic decay (ICD) is a decay mechanism occurring in loosely bound matter, e.g. in systems bound by van der Waals-forces or hydrogen bonds. In many such cases the decay time is similar to the time scale of nuclear motion during the decay. As the efficiency of ICD strongly depends on the internuclear distance of the atoms or molecules involved in the decay, an overall non-trivial temporal decay behavior arises. The progress of examining the time-domain aspects of interatomic Coulombic decay is summarized in this short topical review with a special emphasis on experiments that are now feasible due to the developments of free-electron lasers.

1. Introduction

Time-resolved studies typically have a particularly intriguing appeal, as they give in many cases intuitive and comprehensive insight into to the dynamics of atomic or molecular processes. Many techniques to access the time domain of the microscopic, atomic level have been employed during the last decades. While high resolution energy spectroscopy is often used to identify atomic or molecular states, it unveils (in many cases) information from the time domain, as well. The energy width of a decaying state is, for example, directly connected to its lifetime. Since the late 1980s laser pump-probe experiments explored the temporal evolution of the energy surfaces of bound molecular states on the femtosecond time scale [1]. Time-resolved electron diffraction enables observation of geometrical changes with subpicosecond resolution [2] and time-resolved X-ray diffraction is the key rationale for X-ray free-electron lasers being built around the world. The shortest time scales down to the attosecond regime are typically accessed not by pump-probe measurements, but by using the concept of streaking. Just as in the case of a classic streak camera, a time dependent electric field is used to add momentum to an electron [3]: the electron momentum is then measured, enabling the time evolution of an atomic process to be determined. In a pioneering experiment of this type an attosecond VUV-pulse, created by high harmonic generation (HHG) by employing an 800 nm laser pulse, was used to eject a core-electron from Krypton atoms[4]. The 800 nm laser pulse was furthermore used to streak the subsequently emitted Auger electrons. Different versions of this technique were used in ground breaking experiments, which for example studied in a time-resolved manner the photoelectric effect in atoms [5], obtained information about tunneling times [6,7], and monitored electron emission from surfaces [8].

Being finally able to *directly* examine an Auger decay in a time-resolving experiment demonstrated incredible skills and progress in experimental techniques [4]. The de facto gain of atomic physics knowledge due to these impressive experiments was, however, limited, as the decay function of an Auger decay is strictly exponential and the corresponding decay width was already known for a long time from spectroscopy experiments. A decay phenomenon that has a more complex decay behavior, as compared e.g. to an Auger decay, is interatomic (or intermolecular) Coulombic decay (ICD). ICD was predicted in 1997 by Cederbaum and coworkers [9] as a decay mechanism that occurs if an excited atom or molecule is embedded in a chemical environment. Typical scenarios where ICD takes place consist of loosely bound matter as van der Waals-Clusters or systems bound by hydrogen bonds. In such systems, an excitation energy can be transferred from an excited atom or molecule to a neighboring particle causing an emission of an electron from the particle receiving the energy. This electron is called an *ICD electron* and is typically of low kinetic energy. A sketch of ICD in a neon dimer is shown in Fig. 1 (taken from [10]). A photoionization of an inner-valence electron of the left atom of the dimer creates an excited state that will undergo ICD (Fig. 1a). As ICD occurs the right atom is ionized (Fig. 1b), finally causing the doubly charged dimer to fragment in a Coulomb-explosion (Fig. 1c). In the case of ICD, the decay probability depends strongly on the internuclear

* Corresponding author. Tel.: +49 6979847025.
E-mail address: jahnke@atom.uni-frankfurt.de (T. Jahnke).

http://dx.doi.org/10.1016/j.elspec.2015.06.012
0368-2048/

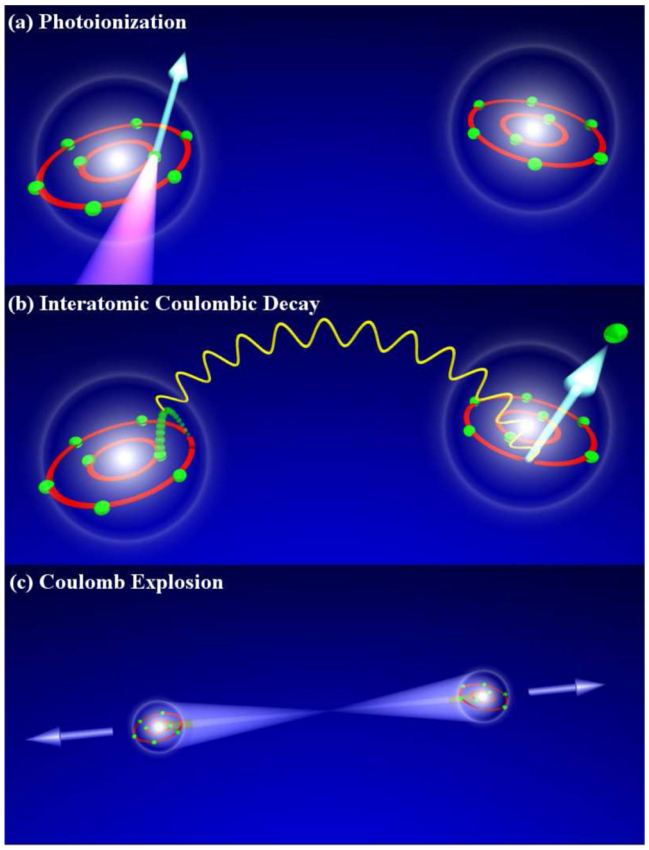

Fig. 1. Interatomic Coulombic decay in a neon dimer: (a) A 2*s*-electron is removed from the left atom of a neon dimer. (b) As the vacancy is filled by a 2*p*-electron the energy gained is transferred to the right atom of the dimer. (c) Two singly charged neon ions are facing each other after the decay, thus causing the dimer to fragment in a Coulomb explosion.
The figure was taken from [10].

distance R between the excited particle and the atom or molecule that emits the ICD electrons [11–15]. For large internuclear distances, for example, the main contribution to ICD scales with $1/R^6$ [16]. Already early theoretical investigations on ICD in neon dimers examined in high detail the dependence of the decay width Γ on the internuclear distance as shown in Fig. 2 [11]. The key ingredient to a complex decay behavior is the typical time scale of ICD: the decay occurs on the same time scale as that of nuclear motion. When photoionization occurs nuclear motion is initiated, since in a typical scenario the excited state consists of a slightly attractive potential energy surface (i.e. the dimer starts to shrink). Therefore the dependence of the decay width on the internuclear distance has a large impact already on elementary features, such as the ICD electron energy spectrum or the kinetic energy release (KER) of the emitted ions. Additionally, it is obvious, that ICD became a prime candidate for a time-resolved examination: already the decay function was expected to show a distinct non-exponential behavior and as the vibrational wave packet of the decaying state evolves during the decay, observing its temporal evolution seemed intriguing.

1.1. Early theoretical and experimental work

Already one of the three pioneering publications that demonstrated in an experiment that ICD exists [17,10,18] investigated temporal aspects of the decay. Öhrwall et al. determined the lifetime of a 2*s* vacancy in neon clusters [18]. They found that in contrast to neon monomers, where the 2*s* vacancy has a lifetime of 150 picoseconds [19], the lifetime reduces to a few femtoseconds

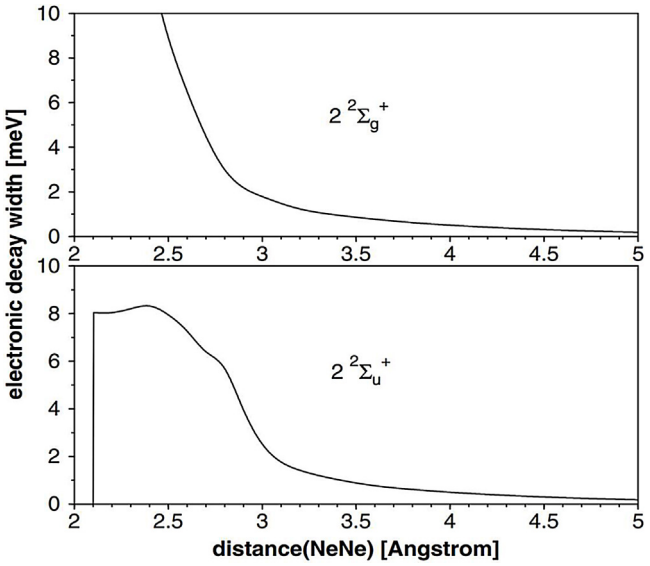

Fig. 2. The decay width of the two inner-valence states of the neon dimer as a function of the internuclear distance.
The figure was taken from [11].

in the case of neon clusters. The experimental results are shown in Fig. 3. The contribution from non-condensed neon atoms is located at a relative binding energy of 0 eV. It occurs as a Gaussian line shape with a spectral width of 30 meV, which is due to the instrumental broadening. The features that were attributed to bulk and surface atoms of the clusters, however, show a substantial lifetime broadening. Employing a Voigt-fit, the 2*s* hole lifetime for bulk atoms was found to be 6 ± 1 fs, while atoms being located at the surface of the cluster decay on average after times longer than 30 fs.

These findings were in line with earlier predictions by Santra et al. [20] that elucidated the effect of increasing the number of nearest neighbors to an inner-valence ionized neon monomer. It was found that the lifetime of the vacancy decreases with increasing size of the cluster due to the increasing number of open decay channels (i.e. "decay partners"). While a 2*s* vacancy in a neon dimer decays within 85 fs, the lifetime of a 2*s* hole in larger clusters of size $n = 13$ goes down to approx. 3 fs. Fig. 4 shows the calculated decay width for clusters Ne_n of different size n. More recent theory work on this issue has been published, e.g. in [21,22].

A similar approach to that of Öhrwall et al. [18] was recently chosen by Trinter and coworkers [23]. In their experimental work they investigated ICD after resonant excitation of a HeNe mixed cluster [24–31]: a resonant excitation of the He atom caused the Ne atom to be ionized after ICD. The amount of resulting $HeNe^+$ was measured while scanning the photon energy of the exciting synchrotron beam from below to slightly above the threshold of the He-resonance. This absorption measurement yielded vibrationally resolved decay widths of ICD of the different vibrational states of the HeNe dimer. The lifetimes obtained depend on the exact vibrational state populated and are in the range of 100 fs to 1 ps. A detailed theoretical description can be found in [32].

Theoretical investigations of ICD in NeAr dimers after KLL Auger decay of the Ne atom suggested another potential possibility to measure the decay time in an experiment [33]. Detailed analysis of the possible decay pathways identified a decay from $Ne^{2+}(2s^{-1}2p^{-1})^3PAr$ into the manifold of $Ne^{2+}(2p^{-2})^3P\text{-}Ar^{1+}(3p^{-1})$ final states. As the decay of the triplet state is comparably slow (estimations of 80 fs were given), the decay time is for these states again in the same range as typical times of nuclear dynamics. The computed ICD electron spectra showed a broadened, asymmetric distribution with a shoulder on the low energy side, which was

Please cite this article in press as: U. Frühling, et al., Time-resolved studies of interatomic Coulombic decay, J. Electron Spectrosc. Relat. Phenom. (2015), http://dx.doi.org/10.1016/j.elspec.2015.06.012