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# Reprint of Measuring the efficiency of interatomic coulombic decay in Ne clusters

M. Förstel[a,*], T. Arion[b,1], U. Hergenhahn[a,**]

[a] Max-Planck-Institut für Plasmaphysik, EURATOM Association, Wendelsteinstr. 1, 17491 Greifswald, Germany
[b] Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmanstr. 2, 85748 Garching, Germany

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ABSTRACT

The efficiency of interatomic coulombic decay (ICD) in Neon clusters with a mean size of $\langle N \rangle = 480$ is measured directly. By detecting the photoelectrons and the ICD electrons in coincidence and normalizing their ratio using the detection probability of the respective electrons we show that the relaxation of Ne 2*s* vacancies in Ne clusters by ICD has an efficiency of unity.



## 1. Introduction

Core holes in atoms, molecules and bulk matter are known to decay almost exclusively by autoionization, called 'Auger decay' when autoionization of a positively charged state is considered. For more shallow inner valence holes Auger decay is energetically forbidden. In an aggregate they can nevertheless autoionize, when the chemical environment of the initial vacancy assists by delocalizing the final state charge over the atom in question and the environment. The direct autoionization of an inner valence hole into a delocalized final state has been termed interatomic coulombic decay (ICD) [1]. After its first experimental demonstration [2] this process has attracted considerable interest in the last decade (see e.g. the review papers [3,4]). As ICD has been shown to proceed on a femtosecond timescale [5–10], it seems highly plausible that it forecloses other relaxation channels, such as fluorescence or nuclear dynamics [11]. Often, it is tacitly assumed that such channels are completely quenched. It thus may seem surprising that few experiments have been documented, in which the efficiency of ICD was determined quantitatively and taking into account the branching ratios also into conceivable, non-autoionizing relaxation pathways. In our earlier work, we have shown for Ne clusters that the intensity of the 2*s* photoelectron line, creating the initial state of ICD, equals the intensity of ICD electrons over a wide interval of cluster sizes [12]. We are not aware of other studies of this type however. This might be explicable because, despite its conceptual simplicity, performing an actual experiment on the competition of ICD with other mechanisms faces some difficulties. Thus there is a clear need for an experimental method to determine the efficiency of ICD in a quantitative and general way. Despite the fact that numerous studies have shown that ICD is a very important channel of electronic relaxation, its effectiveness has never been quantified.

In this contribution we demonstrate that analysis of photoelectron-ICD electron coincidence spectra can yield an accurate figure for the branching ratio of the ICD channel. By *branching ratio* we mean the percentage of Ne 2*s* vacancies which decay via ICD. We show that relaxation of 2*s* vacancies in Ne clusters by ICD has an efficiency of unity. Different than the study of Barth et al. [12], our experiment does not rely on a comparison between two features which are measured independently in the same spectrometer, but probes the electron pairs, which are causally correlated by ICD.

Why has no other experiment addressed this topic earlier? A technique which has been widely used to detect the signature of ICD is cold target recoil ion momentum spectroscopy (COLTRIMS, see [13]). While COLTRIMS is extremely powerful as it detects the occurrence of ICD from the back-to-back Coulomb explosion of the final state (see e.g. [14] and examples cited in [4]), the same fact makes it 'blind' against other, non-autoionizing channels, in which no second positively charged fragment is produced. For the case of

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* Corresponding author. Tel.: +49 30 8062 1 3122; fax: +49 30 8062 1 2990.
** Corresponding author. Tel.: +49 30 8062 1 3124; fax: +49 30 8062 1 2990.
*E-mail addresses:* marko.foerstel@ipp.mpg.de (M. Förstel), uwe.hergenhahn@ipp.mpg.de (U. Hergenhahn).
[1] Present address: University of Hamburg, CFEL, Luruper Chaussee 149, 22761 Hamburg, Germany.

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Ne clusters, we show here that such channels are below the 10% level, which is the sensitivity of our experiment.

We note that the situation is different for the ICD-like decay of core-excited or core-ionized states [15]. Here, the main competing channel is Auger decay (decay into local two-hole final states), and a direct comparison between ICD and Auger final states is often possible, as they can be separated spectroscopically [19]. If Auger decay and ICD are both energetically allowed, as a rule of thumb Auger decay is the more important channel.

## 2. Experimental

Interatomic or intermolecular coulombic decay can be initiated by different excitation mechanisms. For the sake of its study, photoionization by synchrotron radiation offers the advantage of a controlled energy deposition in the initial state, which then decays. Creation of the ICD initial state can be monitored by detection of a photoelectron with a binding energy in the inner-valence range. (Core level ICD is not considered in this work.) We have shown earlier that photoelectron-ICD electron coincidence spectroscopy is a powerful technique to detect ICD of clusters larger than the dimer [16,17,4]. Details of the experiment reported here are as follows: our cluster source uses expansion of Ne gas through a cryogenically cooled, conical nozzle made from copper [18]. The expansion pressure was set to 1.21 bar, the nozzle had a diameter of 80 μm, half an opening angle of 15° and was cooled down to 48 K. Applying an empirical scaling law [20], an expectation value for the cluster size of $\langle N \rangle = 480$ follows. For further details of the apparatus see [17]. Electrons are detected by a highly efficient magnetic bottle spectrometer, the properties of which have been described [21]. Details of the design of this instrument can be found in [22]. Here, the most important property of the instrument is its high, and predictable detection efficiency of around 60% (see below). The experiment has been carried out at the undulator beamline UE112-PGM-1 of Helmholtz–Zentrum Berlin using the single bunch mode. In this mode of operation, synchrotron radiation arrives in flashes of few tens of ps length, with a separation in time of $\tau \approx 800$ ns. Using a small accelerating voltage into the drift tube of our spectrometer, the maximum flight time of electrons stayed below $\tau$. The decay time of ICD is in the fs range, and has no influence on the detection process.

## 3. Measured data and data analysis

Fig. 1 shows the electron, electron coincidence spectrum of Ne clusters. Each pixel of the color-coded map displays the number of electron pairs detected, with energy $e_1$ of the electron arriving first ('fast electron') plotted against the vertical axis, and energy $e_2$ of the second electron ('slow electron') plotted against the horizontal. A (small) background of random coincidences was determined by measuring the amount of $e_1$ electrons from the $n$th synchrotron radiation bunch arriving in coincidence with $e_2$ electrons from the $(n+1)$th bunch, and was subtracted. Raw spectra recorded as time-of-flight maps were converted to kinetic energy using measured energies of atomic photolines. Data were recorded in list mode, and coincidence spectra were assembled by searching for events, in which two electrons were detected within the same bunch period.

For a given photon energy, the kinetic energy $e_{2s}$ of photoelectrons pertaining to 2$s$ photoionization can be easily calculated (binding energy approx. 48.2 eV, see [5]). Inspecting the coincidence map in Fig. 1, the coincidences with ICD electrons of low kinetic energy $e_{ICD}$ can easily be found, in agreement with earlier results [2,4]. For unit efficiency of ICD, and recorded with an ideal detector, the intensity (events/time) of such coincidences would equal the intensity of primary 2$s$ photoelectrons, determined

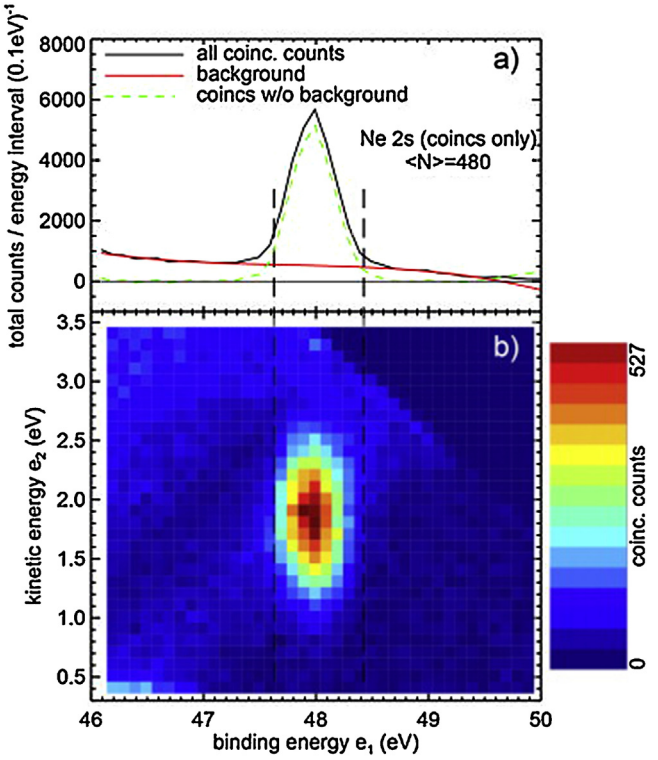


**Fig. 1.** Electron–electron coincidence spectrum of Ne clusters recorded with a photon energy of $h\nu = 52$ eV. Panel (a) energy distribution of the 'fast' electron on a binding energy scale (horizontal axis). Panel (b) color coded map of the number of events, in which a fast electron with kinetic energy $h\nu - e_1$ (horizontal axis) and a slow electron with energy $e_2$ (vertical axis) have been detected. Events in (b) are per pixel of 100 meV × 100 meV size, the color scale is linear. Panel (a) is derived from (b) by summation of all events along lines of constant $e_1$. By their binding energy, the fast electrons can be identified as Ne 2$s$ photoelectrons. The energy distribution of slow electrons agrees with earlier measurements of Ne ICD in larger clusters [9]. A background of inelastically scattered electrons is shown in panel (a).

without discrimination for the occurrence of a coincident partner electron. In a realistic experiment, already due to the not perfect solid angle acceptance of the spectrometer and the finite efficiency of its microchannel plate detector, for some of the primary photoelectrons the ICD electron is lost. We call the latter events 'singles', as opposed to 'doubles', in which two electrons were detected. The main idea laid out in this paper consists in a careful calibration of all apparative factors that may influence the singles/doubles ratio. Any deviation of this ratio from unity after correction for these factors would signal the presence of relaxation channels, which do not proceed via emission of an ICD electron.

We now formalize this idea: let us write the count rate in the photoline (singles) as

$$p(e_{ph}) = \gamma(e_{ph}) r_{ph} \tag{1}$$

and the coincident count rate for photoelectron-autoionization electron coincidences (doubles) as

$$P(e_{ph}, e_{au}) = p(e_{ph})\,\gamma(e_{au})\alpha_{au} = \gamma(e_{ph}) r_{ph}\,\gamma(e_{au})\alpha_{au} \tag{2}$$

Here, $p$ is measured photoelectron count rate, independent of whether a second electron was coincident with the photoelectron or not, $P$ is the measured coincidence event rate, $\gamma$ is the detection probability (which might depend on kinetic energy $e_{ph}$ or $e_{au}$, resp.), $r_{ph}$ is the rate of photoelectrons created (dependent on numerous factors that are difficult to quantify, such as photon flux, sample density, ionization cross section), $\alpha_{au}$ is the summed branching ratio into all autoionization channels. This is the quantity to be determined. We use the fact that the MCP detector and the