

Measuring the Efficiency of Interatomic Coulombic Decay in Ne Clusters

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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 2s vacancies in Ne clusters by ICD has an efficiency of unity.

Keywords: Interatomic Coulombic Decay, ICD, Clusters, Autoionization, Electron-Electron-Coincidence

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 nev-

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6 ertheless autoionize, when the chemical environment of the initial vacancy
7 assists by delocalizing the final state charge. The direct autoionization of an
8 inner valence hole into a delocalized final state has been termed Interatomic
9 Coulombic Decay (ICD) [1]. After its first experimental demonstration [2]
10 this process has attracted considerable interest in the last decade (see e.g.
11 the review papers [3, 4]). As ICD has been shown to proceed on a fem-
12 tosecond timescale [5–10], it seems highly plausible that it forecloses other
13 relaxation channels, such as fluorescence or nuclear dynamics[11]. Often, it
14 is tacitly assumed that such channels are completely quenched. It thus may
15 seem surprising that few experiments have been documented, in which the
16 efficiency of ICD was determined quantitatively and taking into account the
17 branching ratios also into conceivable, non-autoionizing relaxation pathways.
18 In our earlier work, we have shown for Ne clusters that the intensity of the
19 $2s$ photoelectron line, creating the initial state of ICD, equals the intensity of
20 ICD electrons over a wide interval of cluster sizes [12]. We are not aware of
21 other studies of this type however. This might be explicable because, despite
22 its conceptual simplicity, performing an actual experiment on the competi-
23 tion of ICD with other mechanisms faces some difficulties. Thus there is a
24 clear need for an experimental method to determine the efficiency of ICD
25 in a quantitative and general way. Despite the fact that numerous studies
26 have shown that ICD is a very important channel of electronic relaxation, its
27 effectiveness has never been quantified.

28 In this contribution we demonstrate that analysis of photoelectron-ICD
29 electron coincidence spectra can yield an accurate figure for the branching
30 ratio of the ICD channel. By *branching ratio* we mean the percentage of Ne $2s$

31 vacancies which decay via ICD. We show that relaxation of $2s$ vacancies in
32 Ne clusters by ICD has an efficiency of unity. Different than the study of
33 Barth *et al.* [12], our experiment does not rely on a comparison between two
34 features which are measured independently in the same spectrometer, but
35 probes the electron pairs, which are causally correlated by ICD.

36 Why has no other experiment addressed this topic earlier? A technique
37 which has been widely used to detect the signature of ICD is cold target recoil
38 ion momentum spectroscopy (COLTRIMS, see [13]). While COLTRIMS is
39 extremely powerful as it detects the occurrence of ICD from the back-to-back
40 Coulomb explosion of the final state (see e.g. [14] and examples cited in [4]),
41 the same fact makes it ‘blind’ against other, non-autoionizing channels, in
42 which no second positively charged fragment is produced. For the case of Ne
43 clusters, we show here that such channels are below the 10% level, which is
44 the sensitivity of our experiment.

45 We note that the situation is different for the ICD-like decay of core-
46 excited or core-ionized states [15]. Here, the main competing channel is
47 Auger decay (decay into local two-hole final states), and a direct comparison
48 between ICD and Auger final states is often possible, as they can be separated
49 spectroscopically [16]. If Auger decay and ICD are both energetically allowed,
50 as a rule of thumb Auger decay is the more important channel.

51 **2. Experimental**

52 Interatomic or Intermolecular Coulombic Decay can be initiated by dif-
53 ferent excitation mechanisms. For the sake of its study, photoionization by
54 synchrotron radiation offers the advantage of a controlled energy deposition

55 in the initial state, which then decays. Creation of the ICD initial state can
56 be monitored by detection of a photoelectron with a binding energy in the
57 inner-valence range. (Core level ICD is not considered in this work.) We have
58 shown earlier that photoelectron-ICD electron coincidence spectroscopy is a
59 powerful technique to detect ICD of clusters larger than the dimer [4, 17, 18].
60 Details of the experiment reported here are as follows: Our cluster source
61 uses expansion of Ne gas through a cryogenically cooled, conical nozzle made
62 from copper [19]. The expansion pressure was set to 1.21 bar, the nozzle had
63 a diameter of 80 μm , half an opening angle of 15° and was cooled down to
64 48 K. Applying an empirical scaling law [20], an expectation value for the
65 cluster size of $\langle N \rangle = 480$ follows. For further details of the apparatus see [18].
66 Electrons are detected by a highly efficient magnetic bottle spectrometer, the
67 properties of which have been described [21]. Details of the design of this
68 instrument can be found in [22]. Here, the most important property of the
69 instrument is its high, and predictable detection efficiency of around 60 %
70 (see below). The experiment has been carried out at the undulator beamline
71 UE112-PGM-1 of Helmholtz-Zentrum Berlin using the single bunch mode.
72 In this mode of operation, synchrotron radiation arrives in flashes of few tens
73 of ps length, with a separation in time of $\tau \approx 800$ ns. Using a small accel-
74 erating voltage into the drift tube of our spectrometer, the maximum flight
75 time of electrons stayed below τ . The decay time of ICD is in the fs range,
76 and has no influence on the detection process.

77 3. Measured data and data analysis

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

90 For a given photon energy, the kinetic energy e_{2s} of photoelectrons per-
91 taining to $2s$ photoionization can be easily calculated (binding energy approx.
92 48.2 eV, see [6]). Inspecting the coincidence map in figure 1, the coincidences
93 with ICD electrons of low kinetic energy e_{ICD} can easily be found, in agree-
94 ment with earlier results [2, 4]. For unit efficiency of ICD, and recorded with
95 an ideal detector, the intensity (events/time) of such coincidences would
96 equal the intensity of primary $2s$ photoelectrons, determined without dis-
97 crimination for the occurrence of a coincident partner electron. In a realistic
98 experiment, already due to the not perfect solid angle acceptance of the
99 spectrometer and the finite efficiency of its microchannel plate detector, for
100 some of the primary photoelectrons the ICD electron is lost. We call the
101 latter events ‘singles’, as opposed to ‘doubles’, in which two electrons were

102 detected. The main idea laid out in this paper consists in a careful cali-
 103 bration of all apparative factors that may influence the singles/doubles ratio.
 104 Any deviation of this ratio from unity after correction for these factors would
 105 signal the presence of relaxation channels, which do not proceed via emission
 106 of an ICD electron.

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

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

109 and the coincident count rate for photoelectron-autoionization electron coin-
 110 cidences (doubles) as

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

111 Here, p is measured photoelectron count rate, independent of whether a sec-
 112 ond electron was coincident with the photoelectron or not, P is the measured
 113 coincidence event rate, γ is the detection probability (which might depend
 114 on kinetic energy e_{ph} or e_{au} , resp.), r_{ph} is the rate of photoelectrons created
 115 (dependent on numerous factors that are difficult to quantify, such as photon
 116 flux, sample density, ionization cross section), α_{au} is the summed branching
 117 ratio into all autoionization channels. This is the quantity to be determined.
 118 We use the fact that the MCP detector and the acquisition electronics are
 119 multi-hit capable (able to record several events within one period of length
 120 τ) as long as the electrons have some difference in kinetic energy.

121 From an experiment, α_{au} can be determined as

$$\frac{P(e_{ph}, e_{au})}{p(e_{ph})} \frac{1}{\gamma(e_{au})} = \alpha_{au}. \quad (3)$$

122 p, P are measured quantities, the apparatus factor $\gamma(e_{au})$ remains to be
123 determined.

124 The experimental value of P can be determined from the data shown in 1.
125 The photoelectron data which lead to the value of the total count rate p are
126 shown in Fig. 2. Due to the worse energy resolution of the magnetic bottle
127 spectrometer compared to an electrostatic analyser, the monomer component
128 of the $2s$ line, and the bulk-surface splitting within the cluster photoelectron
129 line [6, 12] cannot be resolved. A flank at the high binding energy side of the
130 peak is nevertheless visible in the total photoelectron signal, in particular
131 when the peak shape is compared to the line profile derived from the coin-
132 cident data (top panel of Fig. 1 or bottom trace in Fig. 2). Another reason
133 why the monomer feature is less apparent than in earlier data [12] is a higher
134 degree of condensation, which can be achieved with the expansion chamber
135 layout used in the current experiment. The value of p has been determined
136 from the background-subtracted spectrum shown in Fig. 2 by integration
137 between the vertical dashed lines.

138 The detection probability or transmission function γ basically is the prod-
139 uct of accepted solid angle (as a fraction of 4π) times probability to register
140 a charged particle on the detector. It can be determined by comparing mea-
141 sured count rates for photoelectron, Auger electron coincidences from a rare
142 gas. Here, we have used coincidences of Xe $4d$ photoelectrons followed by Xe
143 $N_{4,5}OO$ Auger decay, similar as described in [21]. The detection efficiency
144 of our magnetic bottle has been measured for kinetic energies between 0 and
145 5 eV and was found constant if the guiding magnetic field is chosen not too
146 low [21]. We therefore neglect an energy dependence of γ .

Table 1: Results of the experiment. The error of the ICD efficiency is calculated using error propagation assuming a 5% uncertainty in the detection efficiency and a 5% error in p due to non-perfect separation against atomic photoelectrons.

all events	coinc. events	detection efficiency	ICD efficiency
$p * 30$ s	$P * 30$ s	γ	α_{au}
397881	244091	0.62 ± 0.05	0.99 ± 0.11

147 4. Results and Discussion

148 The main result of our study is given in Tab. 1. Experimentally, we
 149 find unit efficiency of the ICD process in $\langle N \rangle = 480$ Ne clusters within the
 150 sensitivity limit of our experiment. This is in line with an earlier experiment
 151 [12].

152 We have so far discarded the influence of inelastic scattering. In the
 153 current data set, this process seems to be unimportant. This can be explained
 154 with the low kinetic energy of both photoelectron and ICD electron. In [12],
 155 measured at 60.5 eV, the results suggested a few % intensity loss from the
 156 photoelectron line. Coincident data measured over a range of photon energies
 157 exist and will be presented in a forthcoming publication.

158 In summary, we have presented a case study of the efficiency of Inter-
 159 atomic Coulombic Decay by a method, which will be applicable to numerous
 160 systems. While our earlier work on the same topic [12] relied on the separate,
 161 spectroscopic identification of the photoelectron and the ICD electron peak,
 162 the method presented here directly measures the correlated electron pairs.
 163 We therefore expect that it will still be useable when the identification of the

164 respective peaks in a conventional electron spectrum is difficult because of
165 congestion by scattered electrons, or overlapping signal from monomers.

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225 **Figure Captions**

226 Figure 1: Electron-electron coincidence spectrum of Ne clusters recorded
227 with a photon energy of $h\nu = 52$ eV. Panel a) Energy distribution of the
228 ‘fast’ electron on a binding energy scale (horizontal axis). Panel b) Colour
229 coded map of the number of events, in which a fast electron with kinetic
230 energy $h\nu - e_1$ (horizontal axis) and a slow electron with energy e_2 (vertical
231 axis) have been detected. Events in b) are per pixel of 100×100 meV size,
232 the colour scale is linear. Panel a) is derived from b) by summation of all
233 events along lines of constant e_1 . By their binding energy, the fast electrons
234 can be identified as Ne $2s$ photoelectrons. The energy distribution of slow
235 electrons agrees with earlier measurements of Ne ICD in larger clusters [12].
236 A background of inelastically scattered electrons is shown in panel a).

237

238 Figure 2: Ne $2s$ photoelectron spectrum of Ne clusters recorded with a
239 photon energy of $h\nu = 52$ eV, vs. binding energy e_1 . Black, solid trace: All
240 events (sum of singles and doubles). Red trace: Background of inelastically
241 scattered electrons. Upper dashed trace (blue): All events, background sub-
242 tracted. Lower dashed trace (green): Coincident events only. The latter is
243 identical to the green, dashed spectrum in panel a) of Fig. 1. Intensity is
244 expressed as events/eV.

245

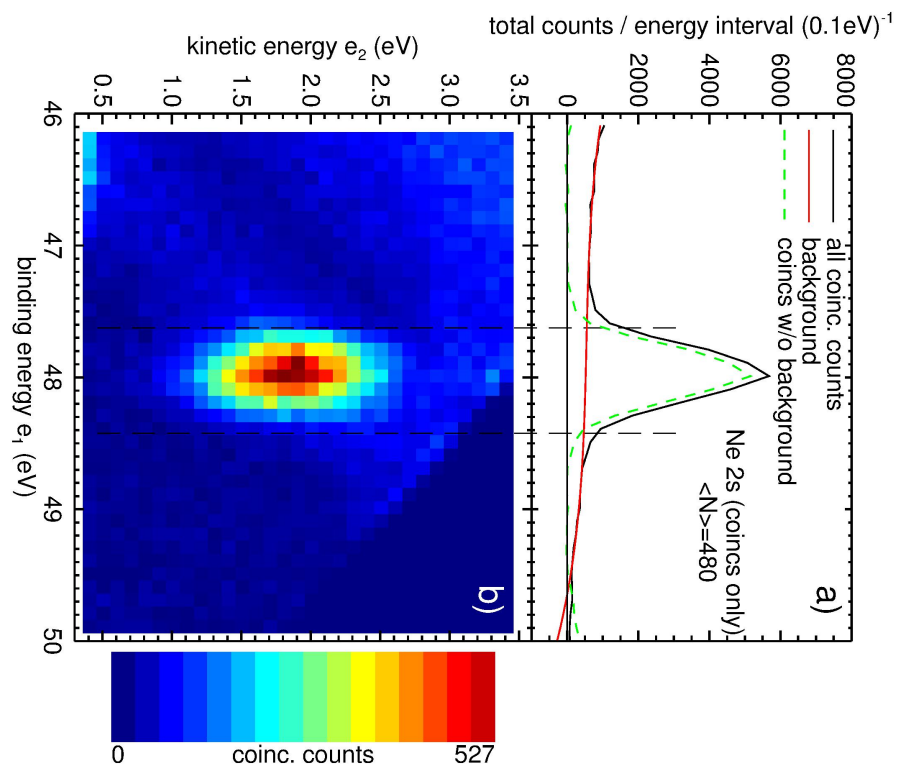


Figure 1:

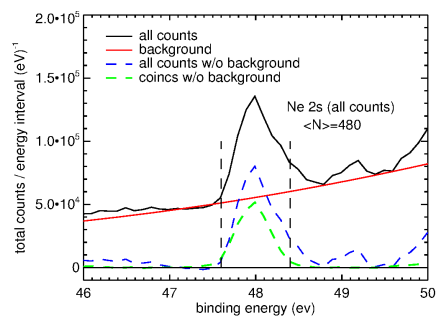


Figure 2: