

Femtosecond Interatomic Coulombic Decay in Free Neon Clusters: Large Lifetime Differences between Surface and Bulk

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A quantitative determination of $2s$ vacancy lifetimes in surface and bulk atoms of free Ne clusters has been made. While for free atoms the $2s$ inner-valence hole has a ps lifetime, it reduces to 6 ± 1 fs for cluster bulk atoms. For surface atoms, the lifetime is on average longer than 30 fs. The lifetime estimate was obtained from fits of high-resolution photoelectron spectra of Ne clusters. The shortening of the lifetime is attributed to the coordination dependent interatomic Coulombic decay, which is extremely sensitive to internuclear distances.

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It is well established that the binding energy of a core electron is dependent on its chemical surrounding. This is the basis of ESCA (electron spectroscopy for chemical analysis) [1], which today is a standard technique for surface analysis. Whether there is a dependence of the core-hole lifetime on the chemical surrounding is less well studied. Experimental attempts to find variations of the core-hole lifetime predicted in some calculations [2,3] did not have conclusive results [2,4,5], thus corroborating the picture of Auger decay as a local process. The only known exception to this seems to be molecules with strongly ionic (fluorine) ligands, in which some works found an influence of the number of ligands on other centers [6,7].

Recently, however, Cederbaum and co-workers have suggested a novel type of electronic decay mechanism, which should quite generally prevail in weakly bound complexes and which is *only* possible due to the presence of the chemical surroundings. In this process a vacancy in an inner-valence shell is filled by an outer-valence electron, while a valence electron from a neighboring site in the complex is emitted into the continuum. It has been known that in a cluster or a solid, a delocalized two-hole state may well have a lower energy than an inner-valence hole, and a transition of this type is thus energetically possible, but it has not until now been realized that this mechanism will be the dominant relaxation pathway in many cases of inner-valence photoionization. According to investigations by Cederbaum and co-workers, vacancy lifetimes including this decay channel can be of the order tens to hundreds of femtoseconds, i.e., much shorter than the radiative decay, which has a lifetime in the order of hundreds of picoseconds. The first system they investigated was F $2s$ holes in the hydrogen bonded molecular cluster (HF)₃ [8], but also, in van der Waals bonded systems like Ne clusters, $2s$ vacancies are expected to

show the same behavior [9,10]. A direct experimental proof for the existence of this type of decay was recently reported by Marburger *et al.* [11], where the low kinetic energy electrons emitted in the decay of $2s^{-1}$ states in Ne clusters were observed.

There is a central difference between this decay mechanism and Auger decay: The Auger process is essentially an *intra-atomic* mechanism, whereas this new decay process is *interatomic*. Hence, it has been named interatomic or intermolecular Coulombic decay (ICD). The participation of neighboring sites in this process makes the lifetime of an inner-valence hole which decays by ICD much more sensitive to the environment than what has been observed for Auger decay. This again is backed by theoretical investigations of Cederbaum and co-workers, who predict that the Ne $2s$ lifetime strongly decreases with an increasing number of neighbors in Ne clusters. For the central atom in a Ne₁₃ cluster, the Ne $2s$ lifetime was estimated as 3 fs, compared to about 85 fs for the Ne dimer. The surface atoms in the Ne₁₃ cluster were predicted to have an ICD lifetime on the order of 10 fs [10]. These findings are all related to a strong dependence of the interatomic decay rate on the number and distance of neighboring atoms [9,10].

A lifetime of 3 fs corresponds to a Lorentzian spectral width of more than 200 meV. This width would be easy to resolve in conventional photoelectron spectroscopy, where much higher resolutions can be achieved. In this Letter we present photoelectron spectroscopy results for Ne clusters with an experimental resolution of 30 meV, in which we observe a lifetime broadening consistent with predictions including the ICD process. Furthermore, we report a lifetime difference between surface and bulk features, as predicted by Cederbaum and co-workers.

The experiments were performed at beam line I411 at the synchrotron facility MAX-lab in Lund, Sweden [12].

I411 is a high-flux, high-resolution soft-x-ray beam line, using radiation from an undulator. It has an end station equipped with a Scienta SES-200 electron spectrometer [13]. The spectrometer lens axis was positioned at the magic angle, at 54.7° to the plane of polarization of the radiation. The spectrometer broadening contributions to the experimental spectral line shapes were 20 or 40 meV, and the photon bandwidth varied between 20 and 30 meV. The cluster source used is based on an adiabatic expansion of gases, and is similar to the setup presented in Ref. [14]. The expansion creates clusters with a distribution of sizes around a mean value, $\langle N \rangle$, which can be controlled by varying the stagnation pressure and nozzle temperature. The average size $\langle N \rangle$ of the Ne clusters was determined from the expansion conditions using the scaling parameter Γ^* formalism, and the recommendations in Ref. [15]. The uncertainty in this method of size determination can be estimated by a factor of 2, and the ratio of surface to bulk areas obtained from fitting our spectra suggests somewhat larger cluster sizes. The vacuum level of the cluster features can be calibrated accurately against features from uncondensed Ne atoms. A value of 48.48 eV [16] for the IP of the atomic Ne 2s level has been used. From this line, we have also determined the apparatus resolution.

In Fig. 1 we show our main result. It presents a photoelectron spectrum of the Ne 2s level of clusters with $\langle N \rangle \approx 900$. In the main part of the figure, the experimental spectrum is plotted together with a fit using symmetric Voigt functions, with free Lorentzian and Gaussian widths, to describe the cluster features. In the inset of the figure, the experimental spectrum is presented together with a fit using pure Gaussian line shapes for the cluster

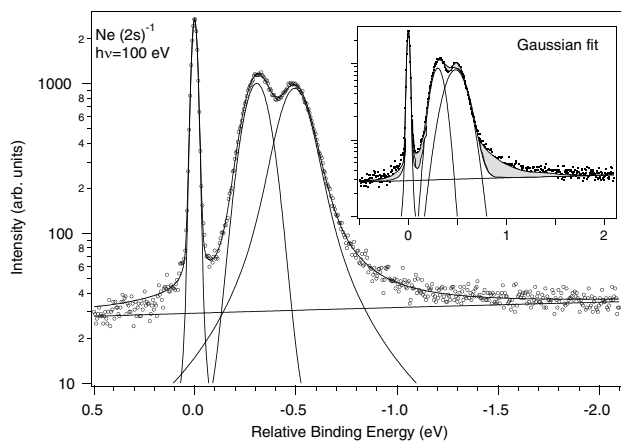


FIG. 1. Photoelectron spectrum of the Ne 2s level of cluster with $\langle N \rangle \approx 900$. The spectrum is presented on a logarithmic intensity scale to emphasize the tails of the features. In the main part, a fit using a Voigt line profile is presented, and in the inset a Gaussian line profile is used. The regions which are not well described by the Gaussian line profile are shaded in the inset. The full width at half maximum of the atomic line, at 0 eV relative binding energy, is 30 meV, which is determined by the instrumental broadening.

features. An identical linear background has been subtracted in both cases. The spectra are presented on a logarithmic intensity scale to emphasize the tails of the cluster feature. Note that on a logarithmic scale, a Gaussian curve is a parabola, as can be seen in the inset. The Ne 2s level is a deep inner-valence level, and we do not expect it to show any appreciable effects of band broadening. We therefore use the same model as has successfully been used for core levels of other rare gas clusters, with Voigt line profiles where the Lorentzian part corresponds to the lifetime broadening and the Gaussian part to other cluster inherent or experimental broadenings. The atomic peak, which has a full width at half maximum of 30 meV, has a Gaussian line shape due to instrumental broadening. Since there are more free parameters in the fit using a Voigt profile, it does model the experimental spectrum better, as can be expected. However, the best fit using a pure Gaussian shape has some notable shortcomings; for instance, the tail towards lower binding energy cannot be modeled at all. The best fit using Voigt line profiles has some interesting features: The cluster feature at higher binding energy is more or less defined by the shoulder towards higher binding energy, and is best fit with a line profile which is close to a pure Gaussian, whereas the feature at lower binding energy is best fit using a considerable Lorentzian width to model the tail towards lower binding energy. In contrast, for the 3s inner-valence state in Ar clusters (see Fig. 2), we have observed that a pure Gaussian line shape for both cluster features gives a very satisfactory fit. For a more thorough discussion of inner-valence photoelectron spectroscopy of rare gas clusters, see Ref. [17].

We can compare again to Ar clusters for an identification of the two cluster features we have observed. For the Ar 2p core levels [18–20] and the 3s level [17], we have established that ionization of interior atoms corresponds

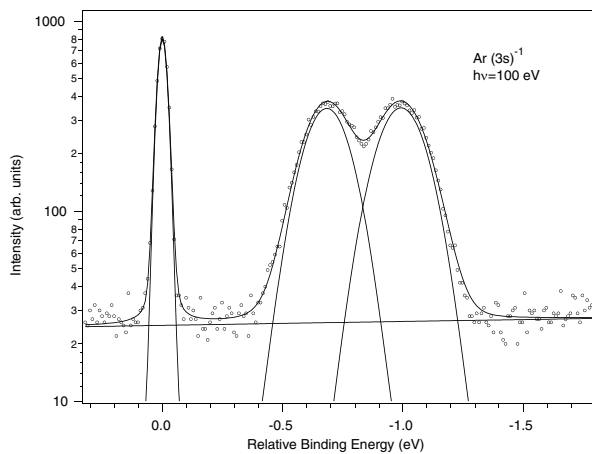


FIG. 2. Photoelectron spectrum of the Ar 3s level for clusters of size $\langle N \rangle \approx 2000$. The spectrum is presented on a logarithmic intensity scale. The sharp peak at 0 eV relative binding energy comes from uncondensed atoms. The line shape of the cluster features is almost perfectly Gaussian, in contrast to Ne 2s.

to the cluster feature at lower binding energy and ionization of surface atoms to higher binding energy.

In solid neon, it has been suggested that the ordering is the reverse for surface and bulk peaks in the photoelectron spectrum, both for Ne $2s$ [21] and Ne $1s$ [22]. In addition, the binding energies of surface and bulk atoms were claimed to be lower and higher, respectively, than the vacuum level. However, the only cluster features observed in the vicinity of the Ne $2s$ ionization threshold lie at a lower binding energy relative to the atomic peak. Furthermore, the splitting between the two cluster features is less than 0.2 eV. Wiethoff *et al.* deduced a Ne $2s$ ionization potential for surface atoms of 47.9 and 49.1 eV for bulk atoms [21]. This surface-bulk splitting of 1.2 eV and the order of states in this study is in great contrast to our findings, and cannot be explained by differences due to size. For comparison, in argon clusters, it has been found that the difference between surface and bulk binding energy, the so-called surface shift, has almost reached the same value as in the solid for clusters of hundreds of atoms, and does not depend strongly on size [18].

To investigate this further, we have performed a size-dependence study (see Fig. 3). In Table I, some of the more important parameters determined from curve fitting the spectra in Figs. 1 and 3 are collected. Note that the uncertainty of the Lorentzian widths for the cluster feature at the higher binding energy reported in Table I is large. A Lorentzian broadening of less than 20 meV has limited significance compared to the Gaussian contribution which typically is about 150 meV. The cluster feature lying lower in binding energy grows in relative intensity when the size is increased, and this behavior identifies this feature as resulting from the ionization of bulk atoms. We thus find that the Ne $2s$ cluster features behave in a

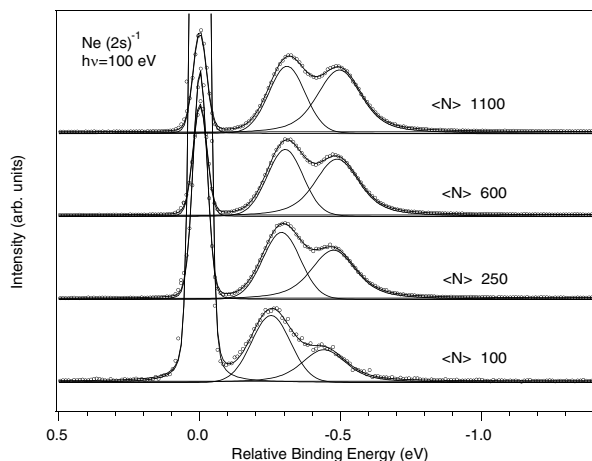


FIG. 3. Photoelectron spectra of the Ne $2s$ level for clusters of varying sizes, recorded with an experimental resolution of 50 meV. The spectra have been normalized to give the cluster feature at higher binding energy the same intensity. The lower binding energy peak increases with increasing size, indicating that it originates from interior atoms. The cluster features also shift to lower binding energy with increasing size.

manner similar to core levels in heavier rare gas clusters: the energy ordering of surface and bulk peaks in the cluster photoelectron spectrum is the same; the atom-to-cluster splitting increases with size; and the surface shift is almost constant [18,20]. In addition, we have performed a binding energy calculation for Ne₁₄₇ similar to that for argon clusters in Ref. [19], using the polarizability of atomic neon, the internuclear distance in solid neon and assuming a cuboctahedral structure of the cluster. From this, an atom-to-surface splitting of close to 0.3 eV and a surface shift of 0.2 eV was obtained, in good agreement with the measurements.

Thus, the bulk feature in Fig. 1 is best described by a Voigt line profile with a substantial Lorentzian contribution, and the surface peak has close to a Gaussian line shape. The spectrum contains contributions from a distribution of cluster sizes, which causes broadening of the features in the spectrum. There are differences in screening as a function of size [18,19], and hence the binding energy of the cluster features varies. If the cluster features were lifetime broadened, as the theoretical investigations of Cederbaum and co-workers suggest, we should expect to observe a sum of features with a Voigt profile, which may be slightly shifted in energy with respect to each other. The observed line shape depends on the size distribution in a complex way, but since the binding energy shifts due to size are small, the overall line shape should still be close to a Voigt profile. One important point to stress is that there is a tail of the bulk feature stretching towards lower binding energies (i.e., higher kinetic energy), and such a tail cannot be explained by the size distribution or inelastic scattering. Note also that, as already stated, in the case of Ar $3s$, the cluster specific broadening mechanisms add up to a line profile very close to a pure Gaussian.

We thus find that the bulk $2s$ photoelectron line of Ne clusters has a substantial lifetime width. The intrinsic broadening that occurs for clusters makes it difficult to accurately determine the Lorentzian width, but it is close to 100 meV. The Lorentzian width of the surface $2s$ peak is, however, considerably smaller. Santra *et al.* calculated that the lifetime of a Ne $2s$ hole will be strongly and

TABLE I. Parameters obtained from fitting the spectra presented in Figs. 1 and 3. ΔE_{as} is the atom-to-surface shift, ΔE_{sb} is the surface-to-bulk shift, W_{Lb} and W_{Ls} are the Lorentzian widths of bulk and surface peaks, and I_s/I_b is the ratio of surface and bulk peak areas. All widths and shifts are given in meV.

$\langle N \rangle$	ΔE_{as}	ΔE_{sb}	W_{Lb}	W_{Ls}	I_s/I_b
100	-253	-189	98.5	1.5	1.46
250	-290	-186	104.1	0.1	0.90
600	-304	-185	96.7	11.5	0.80
900	-307	-187	102.3	16.0	0.71
1100	-310	-186	89.6	1.7	0.71

nonlinearly dependent on internuclear distance and coordination. As mentioned above, this causes a change in lifetime from about 85 fs for the Ne dimer to 3 fs for the central atom in Ne₁₃ [10]. As can be seen in Table I, we observe no clear changes in the Lorentzian width of the bulk peaks for the sizes we have investigated. This finding is expected, as according to the calculations from Cederbaum and co-workers the likelihood of ICD is strongly dependent on the internuclear distance [9,10]. When the first coordination shell has formed, the lifetime is not affected much by additional neighbors farther away, and hence bulk atoms can be expected to have an essentially constant lifetime width. The surface atoms have varying coordination numbers, less than 9, which makes the situation more difficult. According to Ref. [10], the estimated lifetime width changes from about 30 to about 90 meV for clusters with five and nine atoms, respectively. The geometries used in these calculations are not those expected for surface atoms in a larger cluster, but the predictions still show that variations in the lifetime width can be expected depending on which surface atom is ionized. The width that is measured in a photoelectron spectroscopy experiment is thus an average of different situations, and as surface coordination changes with size, a weak size dependence could be expected. In the spectra we have recorded, the Lorentzian width of the surface peak has some statistical scatter, but no trend concerning its size dependence can be observed (see Table I). We can definitely state that it is considerably smaller than for the bulk, and estimate the upper limit to about 20 meV. From these considerations we obtain a Ne 2s hole lifetime of 6 ± 1 fs for bulk atoms in clusters larger than a few hundred atoms, and on average longer than 30 fs for surface atoms. These lifetimes are larger than those predicted for Ne₁₃ in Ref. [10], but they are indeed of the same order of magnitude.

The calculation for Ne₁₃ assumed a face-centered-cubic geometry, and the distance between the center and the exterior atoms was assumed to be the same as in solid neon, $R = 3.13$ Å [10]. Recent calculations [23] suggest that Ne should form icosahedral clusters up to a size of several thousand atoms, but mass spectroscopy measurements [24] do not show any signs of the magic numbers expected for such a crystal structure. The unknown structure of small Ne clusters compounds the difficulties in estimating the lifetime of the inner-valence holes, but the assumptions of Ref. [10] will likely give a reasonable result.

In conclusion, we have found experimental support for the short lifetime due to the ICD effect of Ne 2s holes predicted by Cederbaum and co-workers for Ne clusters. We have also observed a difference in lifetime broadening between surface and bulk atoms, which also can be understood in the ICD picture. The interatomic character of ICD makes it more sensitive to the surrounding compared to the normal Auger decay, and the Ne 2s hole has a

considerably longer lifetime for surface atoms than bulk atoms due to the fact that they have fewer nearest neighbors than bulk atoms.

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Note added.—Jahnke *et al.* [25] have very recently made an unambiguous experimental observation of ICD in neon dimers, by detecting two Ne⁺ fragments in coincidence with the ICD electron.

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