Supporting information for:

One more attempt on ArXe

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Composition of core-shell clusters

Figure S1: Argon content of ideal icosaedric Xe-core, Ar-shell systems. The relative number of surface atoms decreases with increasing cluster size. The hatched area corresponds to the Ar content of the largest clusters produced in our experiments (label 'XL').

For icosaedric clusters, the number of atoms in every shell is given.[?] For a core-shell system in this ideal geometry, the relative content of both species can therefore readily be calculated. In Figure **??** we draw the Ar content of Xe-core, Ar-shell systems with one, two and three full Ar outer layers. A comparison of these graphs with Tables 1 and 3 of the main article shows that the largest clusters produced in our experiments ('XL'), for which a core-shell structure is probable, may have between 923 and 1415 atoms in total, corresponding to three and four Xe shells around a central Xe atom, followed by three Ar outer layers. The Xe content for these systems is 0.16 and 0.22, resp.

Electron-electron coincidence spectra

In this work, we use electron-electron coincidence spectroscopy to isolate electrons from autoionization decays of Ar $3s^{-1}$ vacancies from the remainder of the electron spectrum, mostly photoelectrons from outer valence levels and secondary electrons from intracluster inelastic collisions. By recording two electrons ejected in the same process, on an event-by-event basis, we are able to identify those secondary electrons which are ejected after Ar 3s photoionization. Here, we show a more detailed representation of the electron-electron coincidence data, from which figures in the main paper showing the ICD/ETMD spectra, and the pertaining Ar 3s photoelectron spectra, were derived.

A necessary condition for the ejection of two electrons by a single photon, irrespective of the mechanism by which this is accomplished, is a sufficient photon energy. In case of a sequential process, such as photoionization followed by ICD/ETMD, moreover the ionic state which is produced in the primary step must be located above the ionization threshold

for the doubly ionized systems. For Ar 3s autoionization, these conditions are discussed in detail in the main paper. For a general double ionization process, the required energy can be estimated as the sum of the single ionization energies of the final state holes (main paper, Table 3) plus the geometry-dependent Coulomb repulsion (main paper, Figure 1). Roughly, 27 eV are needed to produce an Ar $3p^{-1}$ Xe $5p_{3/2}^{-1}$ state, and about 2-4 eV less for $(\text{Xe } 5p^{-1})_2$ states. For photon energies exceeding this limit, the excess energy can be distributed to any, or both, of the released electrons. For photoionization followed by autoionization the energy imparted to the first electron is determined by the binding energy of the primary vacancy, however. This can be used to identify the pertaining second-step spectrum.

Figure **??**b shows a typical electron-electron coincidence spectrum recorded with a photon energy of 32 eV, a few eV above the inner valence ionization thresholds.

The Figure shows that a significant amount of slow electrons e_2 are recorded in coincidence with the primary 3s electrons (e_1), which have a kinetic energy of approx. 3.3 eV. Some background of electron pairs at other energies is also visible. It results from inelastic scattering of outer valence photoelectrons, and (in particular for the feature which has both electrons with kinetic energy less than 0.2 eV, upper left corner of Figure **??**b) due to inelastic scattering at parts of the analyzer.

More conventional, one-dimensional electron spectra pertaining to the photoelectrons and the ICD/ETMD electrons are obtained by summing up along one of the energy axis of the two-dimensional map, and are shown in (c) and (a). The peak in Figure **??**c at a binding energy of 28.7 eV pertains to the Ar 3s photoelectron line. No atomic counterpart of this line is visible in this Figure, as only the cluster photoelectrons lead to electron-electron coincidences. The trace shown in Figure **??**a is interpreted as the spectral shape of ICD/ETMD decays.

We have subtracted the background from random coincidences and coincidences due to electron scattering (electron impact ionization) from the signals shown in Figures **??**a,c. In order to do so, the regions between the two pairs of red horizontal bars in Figure **??**b were

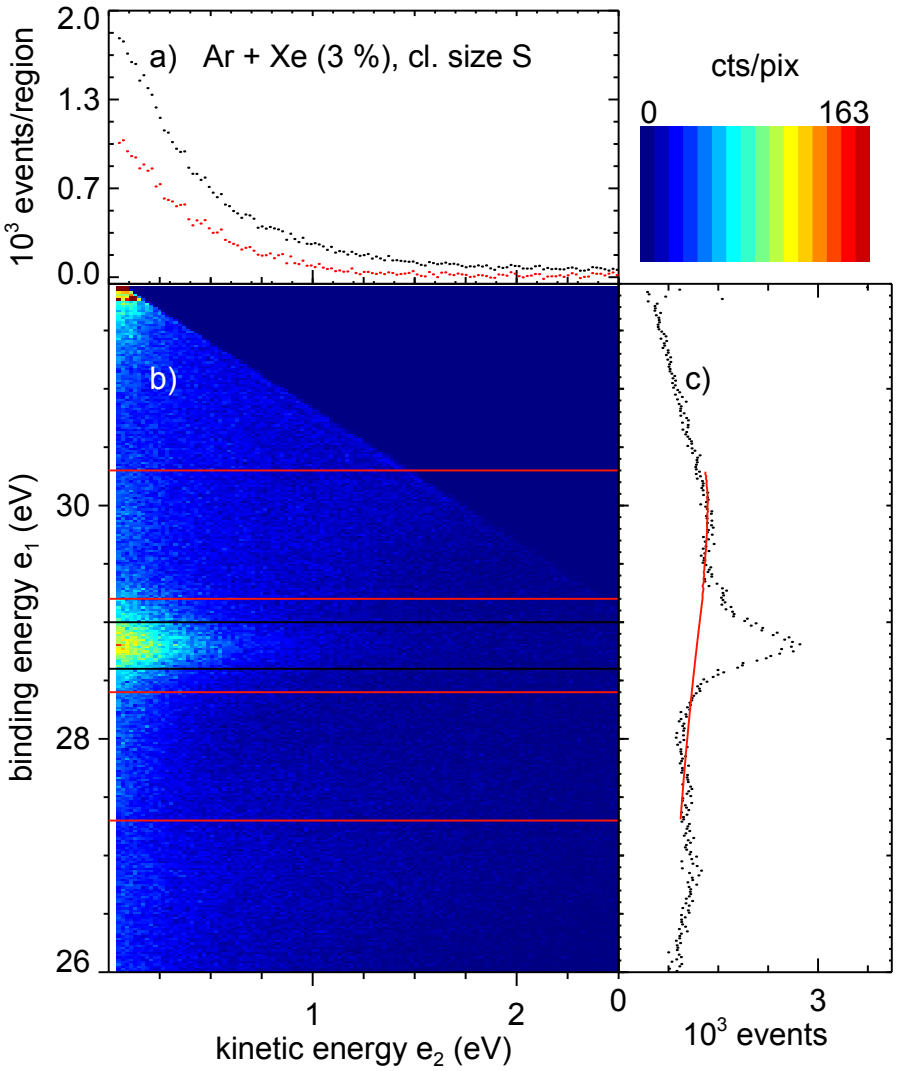

Figure S2: Photon excited electron-electron coincidence spectrum of mixed Ar-Xe clusters in the inner valence region. (b): Color-coded map of coincident electron pairs, with the electron of higher kinetic named e_1. The energy of e_1 is given as binding energy, using the photon energy of $h\nu = 32$ eV. (c): Energy spectrum of primary electrons e_1, irrespective of the energy of the secondary electron (summation of the coincidence map along horizontal lines). (a): Energy spectrum of all secondary (ICD or ETMD) electrons e_2 pertaining to the Ar 3s binding energy region marked by two black bars. See text for details. Intensity is expressed as coincident events/pixel of 20 meV^2 (b) or as coincident events per interval of 20 meV (a,c). In total, approx. 4×10^5 events are shown. The color scale of (b) is linear.

identified as background. The coincidence map was then subdivided into intervals of 0.5 eV width in the e_2 energy coordinate. For each interval, a second order polynomial was fitted to the background signal, and subsequently subtracted from the ICD/ETMD signal marked by the black bars. The summation of all background signals is shown as a wavy, solid red line in Figure **??**c, and the signal of secondary electrons, background subtracted, is shown as the lower trace of data points in Figure **??**a. Background subtracted ICD/ETMD signals are shown throughout the main paper.

These data were recorded under all expansion conditions listed in Table 1.

Similar figures were recorded for all combinations of expansion parameters listed in Table 1 of the main paper. A more detailed description of methods for analysing these data sets has been given.[?]

Experimental ICD/ETMD spectra

The background subtracted signal of secondary electrons e_2 being recorded in coincidence with a primary Ar 3s photoelectron e_1 is interpreted as the energy spectrum of ICD/ETMD of the cluster ensemble under study. Some representative examples for such spectra are shown in the main article. Here, we present a full account of these spectra. For better comparison, similar to the article they have been arranged into groups of spectra from either clusters of equal size, or of equal composition of the gas mixture (resulting in a similar ratio of condensed Ar to Xe, at least when averaged over the cluster ensemble). Thus, identical spectra appear more than once in the presentation.

As expected, the shape of the coincident e_2 spectra does not depend on the excitation energy (examples: Figure **??**).

As discussed in the main paper, the differences between clusters of different size (Figure **??**) are more substantial than those between clusters of different gas composition (Figure **??**).

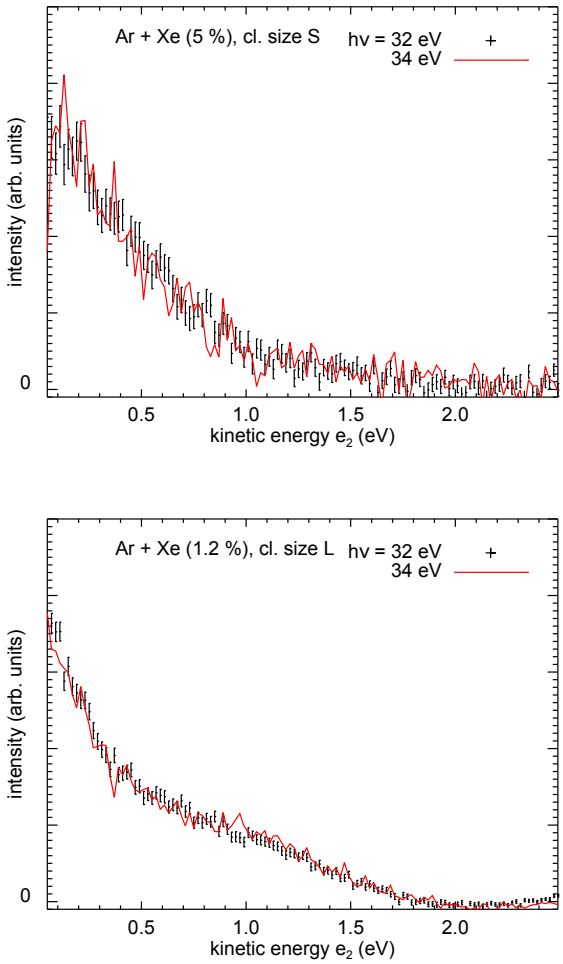

Figure S3: Energy spectrum of all coincident secondary (ICD or ETMD) electrons e_2 pertaining to primary electrons e_1 in the Ar 3s binding energy region. Spectra were recorded with photon energies of $h\nu = 32$ eV (symbols) and $h\nu = 34$ eV (trace). Spectra were normalized to equal area.

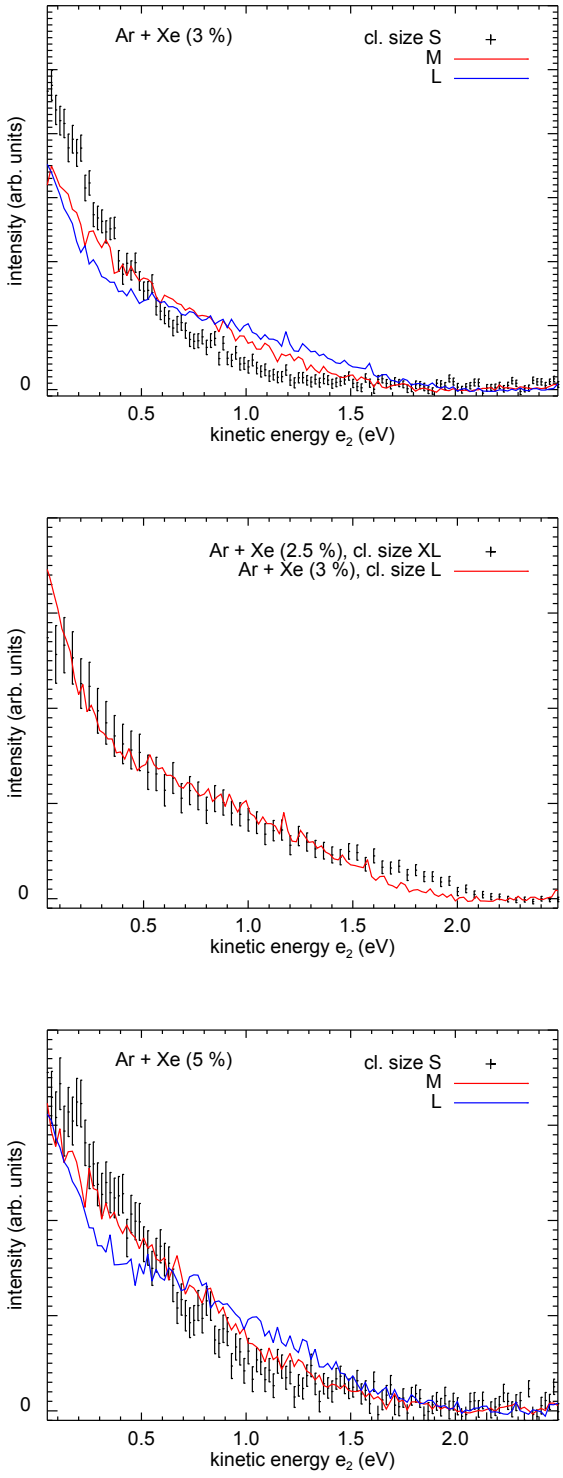

Figure S4: Energy spectrum of all coincident secondary (ICD or ETMD) electrons e_2 pertaining to primary electrons e_1 in the Ar 3s binding energy region. Comparison of the spectra from cluster ensembles of different mean size. Spectra were recorded at $h\nu = 32$ eV and were normalized to equal area.

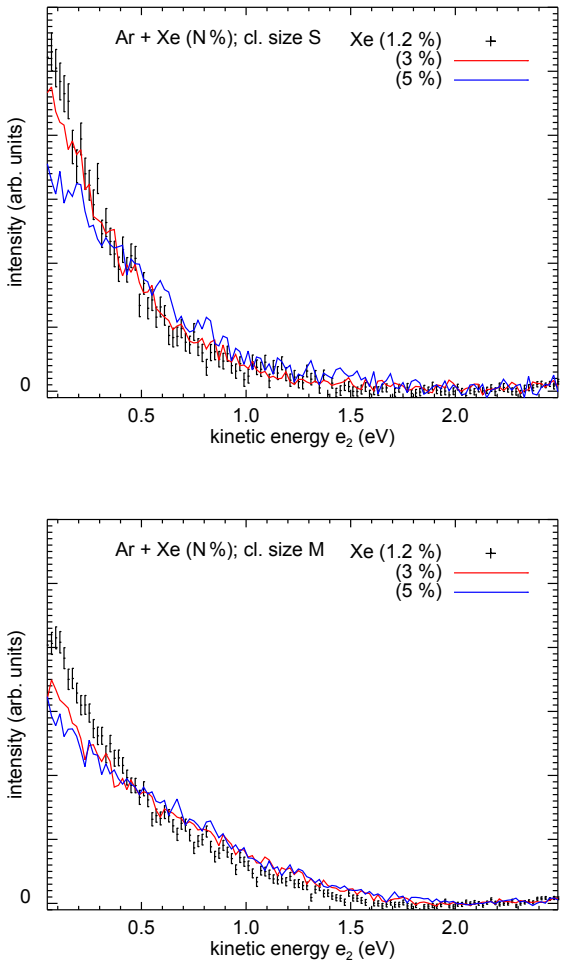

Figure S5: Comparison of the spectra from cluster ensembles of different gas composition, see Figure **??** for details.

Additional Theoretical ICD/ETMD3 Spectra

Clusters with $N = 38$ Atoms of Different Composition

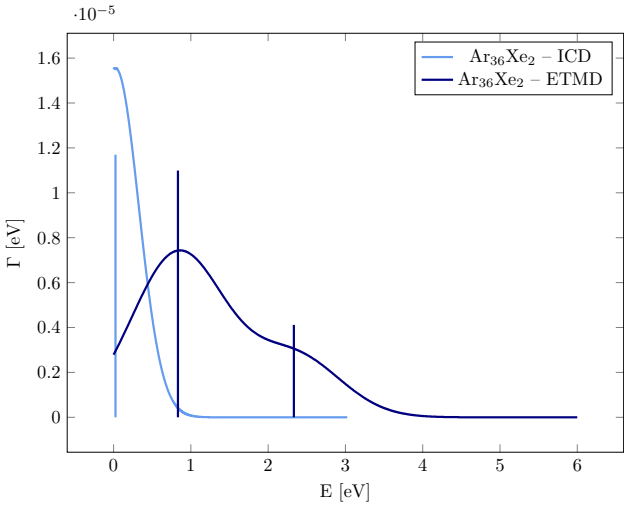

Figure S6

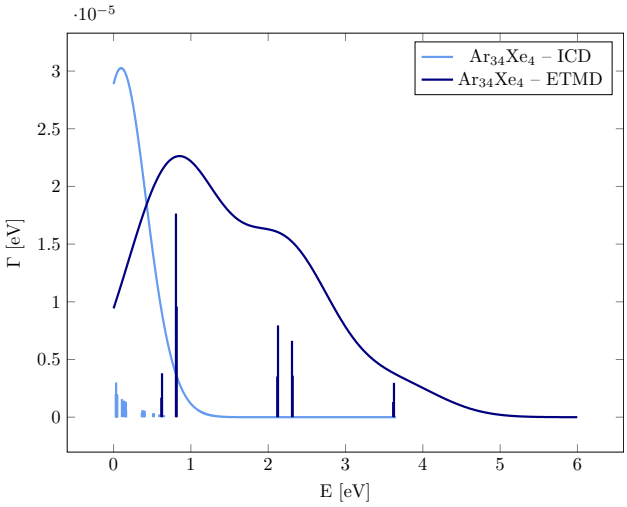

Figure S7

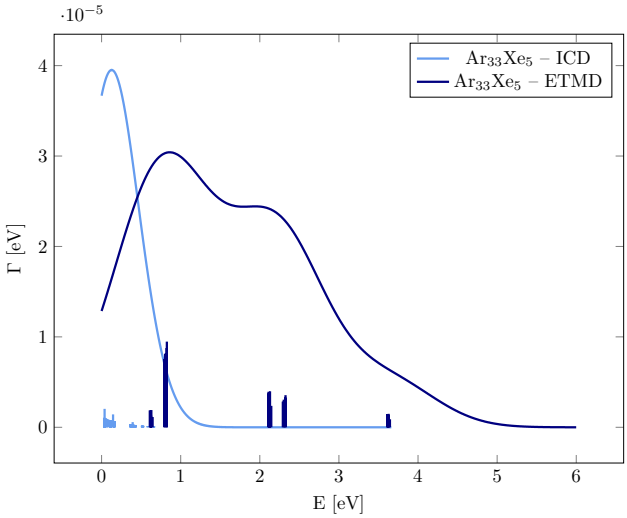

Figure S8

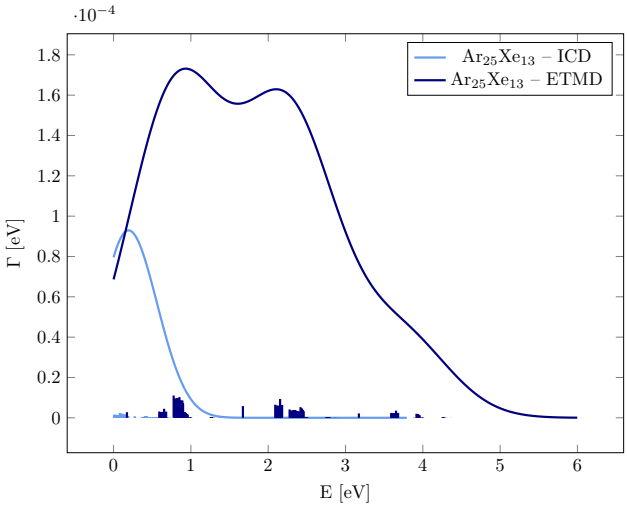

Figure S9

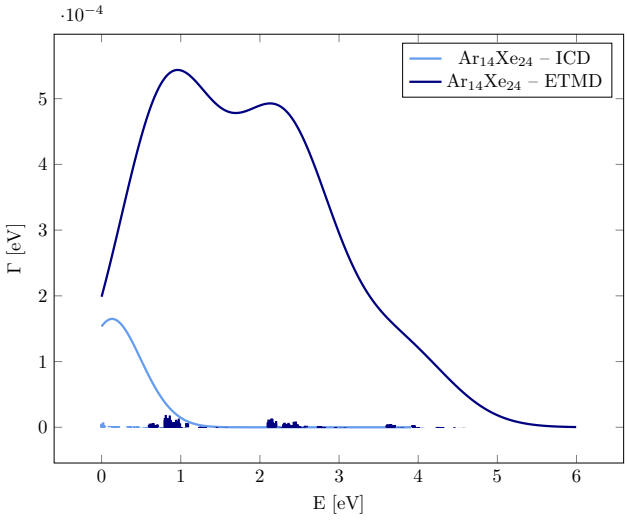

Figure S10

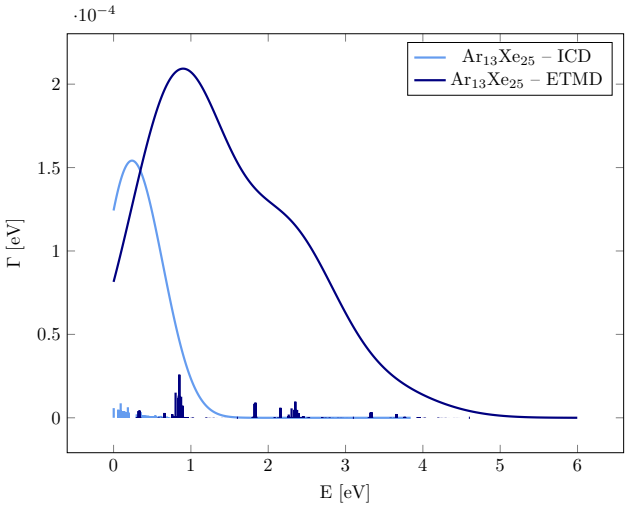

Figure S11

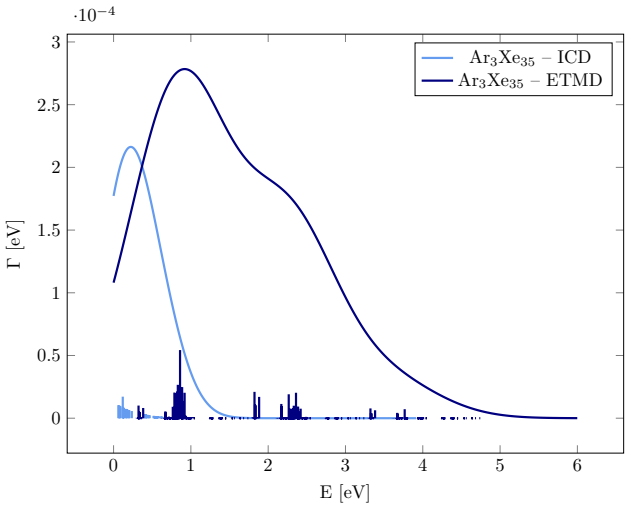
$\cdot 10^{-4}$
3
2.5
2
1.5
1
0.5
0
Γ [eV]
0
1
2
3
4
5
6
E [eV]
Ar_3Xe_{35} – ICD
Ar_3Xe_{35} – ETMD

Figure S12