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To the Editor

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Revision of Out Article jp-2016-06665e

Dear Editor,

Our paper has been reviewed by two of your Referees, who recommended it for the publication in the New Journal of Physics subject to minor amendments. We are thankful for the comments made by the Referees and respond to them below. Additionally, we took the opportunity to correct some typos or whatever.

Referee #1 raised the following points:

1. *In general, I find the manuscript clearly written but unnecessary long. Some details and discussions can be avoided without weakening the presentation. Here are some examples:*

   a) *ICD is explained twice in the introduction (top of page 3 and 3rd paragraph of page 3)*

   b) *the sentence: The notion of ICD requires that the electronic orbitals ... can be distinguished... make a distinction between ICD and Auger decay. does not bring important informations. Furthermore, using only a one-particle picture to define ICD may be misleading. For example, in molecular clusters ICD can be clearly identified after deep ionization (typically for binding energy above 20 eV) of one molecule. However, owing to the strong electronic correlation in this binding energy range the states cannot be described as ionization from a single orbital.*

c) *Page 9: the sentence "These atoms do not necessarily need to form bonds..." just rephrases what is already explained earlier in the manuscript on ICD.*

d) *Page 10: the definition of open and close channel is repeated. Explanations in page 9 and figure 1 are enough.*

e) *Page : the section "Cluster Structures" can be moved to Supporting information since only Table 2 is important to understand the results. Furthermore, it seems to me that the paragraph on previous study of the authors on large clusters does provide relevant informations on the reported results.*

f) *Page: the section Outer valence spectra is very detailed and the reader may lose the main point of this section which is, as far as I understood, to evaluate experimentally the percentage of Xe in the clusters. All extra details can be avoided. Just to help the readers, this section could be renamed to highlight the goal of the section like for example "Xe content".*

g) *Page: I think the section Inner valence spectra can be skipped without losing any relevant informations.*

2. *Page 8: the authors write that "the intensities of the peaks are proportional to the probability decay as well as the decay width". However, the probability and the width are simply related : Prob = Width*time/hbar.*
We included the relation between the decay probability and the decay width. However, the important information of this sentence is that the decay widths can be used to describe the intensities of the different peaks. Therefore, its proportionality is important. The sentence now reads:
The latter is proportional to the probability of the decay $P = \frac{\Gamma t}{\hbar}$ as well as the theoretically determinable decay width $\Gamma = \frac{\hbar}{\tau}$, which is inversely proportional to the lifetime τ of the decay process.

3. *Page 11: Eqs 6 and 7 the sums run over ALL pairs and ALL triples. In that case there should not be $N_{ICD,i}$ and $N_{ETMD,j}$ in the sums; otherwise those pairs and triples are counted several times.*
It now reads:
These are given by the sum over the decay widths of all geometrically different pairs i for the ICD and all geometrically different triples j for the ETMD(3), respectively, and over all channels β:

4. *Page 12: some symbols are not defined: Φ_{in}, χ_β, H_f for example. Since this part of theory has already been published, it can be shorten leaving just Eqs. 9 and 10.*
This part of the theory has indeed been published already. However, the general formula for the decay width of electronic decay processes serves as the best starting point for the explanation since it is known by a wider community. For the same reason, equation 11 should be shown, as it connects the earlier formulation and the new more abstract formulation in equation 10. We therefore rephrased the

paragraph to read:

$$\Gamma_\beta(E_{\rm res}) = 2\pi \left|\langle \Phi_{\rm in}|\hat{V}|\chi_\beta\rangle\right|^2, \tag{1}$$

where $|\Phi_{\rm in}\rangle$ and $|\chi_\beta\rangle$ are the initial and final state, respectively and $\hat{V}$ is the interaction operator between these two, can be approximated by its asymptotic behaviour. For the ICD the approximation reads:

$$\Gamma_{{\rm ICD},i,\beta} = (2J_{\rm in}+1)\,\frac{3c^4}{8\pi}\sum_{M'_{in}}\left|\begin{pmatrix} J'_A & 1 & J_A \\ -M'_A & M'_A - M_A & M_A \end{pmatrix}\right|^2 \frac{\sigma^{(X_E)}(\omega_{vp,\beta})}{R_i^6\,\omega_{vp,\beta}^4 \tau_{in,\beta}}, \tag{2}$$

where J_A, J'_A and M_A, M'_A denote the total angular momentum of the initially ionized atom (which is the same as the electron donor atom) in the initial and final state, respectively, which otherwise depends on intrinsic atomic properties which can be determined experimentally, like the ionization cross sections $\sigma^{(X_E)}(\omega_{vp,\beta})$, radiative lifetimes of the initially ionized state $\tau_{in,\beta}$ and the excess energy transferred to the emitting atom (the energy of the virtual photon) $\omega_{vp,\beta}$.

For the ETMD(3) the approximation reads

$$\Gamma_{{\rm ETMD},j,\beta} = \frac{c}{\pi}\sum_{m,M_{in,D'}} \frac{\Theta_{m,k}(\alpha_j)\sigma^{(X_E)}(\omega_{vp,\beta})\left|<\tilde{D}_{m,j,\beta}(M_{in,D'})>\right|^2}{R_j^6\omega_{vp,\beta}} \tag{3}$$

$$= \frac{c}{\pi R_j^6}\sum_{M_{in,D'}}\left(\left|<\tilde{D}_{x,j,\beta}(M_{in,D'})>\right|^2(2+\sin^2\alpha_j) + \left|<\tilde{D}_{z,j,\beta}(M_{in,D'})>\right|^2(1+\cos^2\alpha_j)\right) \times \frac{c\sigma^{(X_E)}(\omega_{vp,\beta})}{\omega_{vp,\beta}} \tag{4}$$

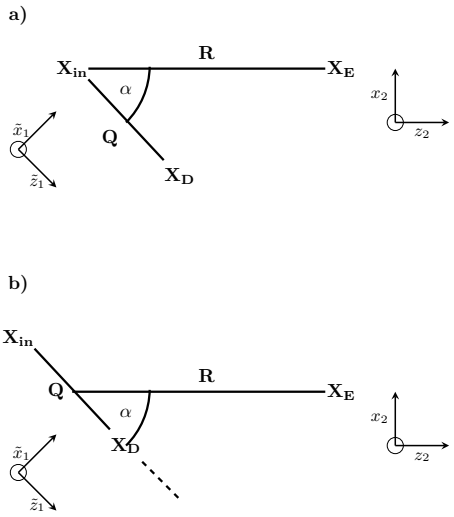
where $\tilde{D}_{m,j,\beta}$ are calculated transition dipole moments and $\Theta_m(\alpha_j)$ is a function depending on the angle α_j of the triple and the direction of the dipole transition moment m ...

5. *Page 12: ionization cross-sections, radiative lifetimes,... are not EXPERIMENTAL properties of atoms, they are intrinsic properties of atoms that can be experimentally measured.*
   Agreed. The sentence now reads:
   ... on intrinsic atomic properties which can be determined experimentally, like the ionization cross sections $\sigma^{(X_E)}(\omega_{vp,\beta})$, radiative lifetimes of the initially ionized state $\tau_{in,\beta}$ ...

6. *As far as I understand Figs 4-8 report Widths with respect to Electron energy and are thus not strictly speaking electron emission spectra. The authors should really compute the spectra. Furthermore, the lines which I guess are some convolution of the bars are not defined. And more importantly, how these "spectra" were normalized is not clear: in the cluster with 55 Ar atoms the central and inner layer of*

atoms can undergo ICD. A more intense band compared to 13 atoms is therefore expected. More explanations are needed.

7. *Page 18: it is stated that the decay width decreases like R-6 but in page 20 it decreases exponentially.*
   The reason is that it discusses different interatomic distances being the energy transfer distance R (R^{-6}) and the electron transfer distance Q (e^{-Q}) which can both be found in previous and coming papers about ETMD(3) (J. Chem. Phys. **138**, 014305 (2013). and Fasshauer *et al.* Mol. Phys. (2016), submitted.):



   Both on page 18 and 20, these distances are very clearly characterized in terms involved atom types or groups and which process is ongoing. To further clarify the matter, the sentences on page 18 now read:
   Two aspects have to be taken into account: an energy shift of the peaks due to different charge distances d in the final state (i.e. the interatomic Xe-Xe distance) and the decrease of the decay width with R^{-6}, R being the distance between the electron transfer unit and the xenon atom ionized in the final state. The larger the distance between the xenon atoms, the higher are the energies of the secondary electrons. For the case of xenon atoms on argon surfaces this at the same time means a larger distance between the Ar-Xe pair involved in the electron transfer and the electron emitting xenon atom. Hence, the decay widths are smaller. Therefore, a significant contribution from ETMD(3) compared to ICD is only seen if the two xenon atoms reside on two adjacent surfaces.

8. *Page 29: the efficiency of ICD is found below unity for clusters having few Xe atoms. I guess this is because in these clusters ICD and ETMD are closed for some Argon atoms which are anyway ionized. Maybe a statistical model may explain it. The theory could also help since it should be easy to determine the efficiency for all clusters considered in this study.*

Referee #2 raised the following points:

1. *ETMD(3) should be explained in the introduction by a sentence or two to aid the reader (at the moment, it is first explained in the theory section).*

2. *The authors mention that the 'nuclear dynamics may play an important role' but that they have been neglected in the calculations. While I understand that it is not feasible in such large systems the authors should at least briefly discuss the possible effect of nuclear dynamics e.g. peak shifts, broadening, ICD vs. ETMD, etc.*

3. *The spin-orbit splitting of the Ar $3p^{-1}$ state is briefly mentioned in Table 3 in the experimental section but it also stated that the a single value of the binding energy of Ar 3p equal to 15.3 eV is used for all of the simulations. The authors should explain the motivation for this choice in the theory section.*

4. *Page 13: The authors should justify the use of the 'unified force field' method for the calculation f the cluster structure (p13).* We added a sentence to justify our choice:
   After that, the cluster structures were optimized using the unified force field implemented in the Avogadro programme (version 1.1.0)[51,52] to give local minimum structures. The method was chosen due to its low computational cost, the possibility to find the next local minimum structure based on the chosen starting point and the necessary effort to produce reliable results with density functional theory (DFT) for v. d. Waals interactions since we in this work discuss structural trends and not absolute structures.

5. *Page 12: On page 12 last line there is to Tables II and III. I have not been able to locate these. The reference should be clarified.*
   The sentence has been changed to:
   In this work we evaluate the secondary energies and decay widths with the programme HARDRoC[20,49] using the experimental ionization energies of Table 3 and data from the literature given in Tables II and III of Ref. 34.
   The following sentence was removed.

6. *Page 20,21: it is not clear what structure of the larger clusters with 3871 atoms is used in the simulation. The authors mention icosahedral and cuboctahedral but no further details are given, e.g. Ar-Xe distance, Ar-Ar distance, etc.*
   The details were added to the Cluster Structures section. The last sentences now read:
   Furthermore, for comparison with the largest measured ArXe clusters, we constructed also larger core-shell structures (Table 2, #4 – 5). These were idealized icosahedral and cuboctahedral structures based on the v. d. Waals radii of argon and xenon r_{Ar} =1.88 Å[54] and r_{Xe} =2.16 Å[55].

7. *In fig. 9(a) it is specified in the text that Ar ¡N¿ =190 for the black trace but as far as I can tell no value is given for the other spectrum on the same graph.*

8. *It is not clear what the dotted lines in Figure 10 are?*

9. *The colour schemes of some of the figures lead to confusion when printed in grayscale. Some effort could be made to resolve this.*

I took the opportunity to shorten the title in order to not highlight only one out of several aspects. It now reads:
Non-nearest Neighbour ICD in Clusters

Sincerely yours,

Dr. Elke Faßhauer (corresponding author)