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## Core hole screening and decay rates of double core ionized first row hydrides

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# Core hole screening and decay rates of double core ionized first row hydrides

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Because of the high intensity, X-ray free electron lasers allow one to create and probe double core ionized states in molecules. The decay of these multiple core ionized states crucially determines the evolution of radiation damage in single molecule diffractive imaging experiments. Here we have studied the Auger decay in hydrides of first row elements after single and double core ionization by quantum mechanical *ab initio* calculations. In our approach the continuum wave function of the emitted Auger electron is expanded into spherical harmonics on a radial grid. The obtained decay rates of double K-shell vacancies were found to be systematically larger than those for the respective single K-shell vacancies, markedly exceeding the expected factor of two. This enhancement is attributed to the screening effects induced by the core hole. We propose a simple model, which is able to predict core hole decay rates in molecules with low  $Z$  elements based on the electron density in the vicinity of the core hole. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4801660>]

## I. INTRODUCTION

In ultra short X-ray pulse coherent diffractive imaging experiments with single macromolecules, Auger decay and ionization are the primary processes that lead to radiation damage and, ultimately to Coulomb explosion.<sup>1,2</sup> At the photon energies required for such experiments, photo ionization of core electrons is the dominant ionization process. For elements with a low atomic number  $Z$ , core ionization induces Auger decay, during which a valence electron refills the core, while a second valence electron is emitted. Thereby, the sample is charged up in sequences of photo ionization and Auger decay events, which eventually leads to a Coulomb explosion. To determine how this structure disintegration proceeds and whether it is possible to collect sufficient scattered photons of the unperturbed structure, knowledge of *molecular* Auger decay rates is essential.

At the high intensities required for single molecule diffractive imaging, the ionization rates become comparable to Auger decay rates and therefore electronic states with double vacancies in the K shell become relevant. Further, these states have a much smaller ionization cross section and thus can effectively suppress the formation of high charge states at short pulse durations — a phenomenon known as “frustrated absorption.”<sup>3,4</sup> For these reasons, the lifetimes of the intermediate single and double K-shell vacant states determine the competition of scattering and destruction of the sample.

The investigation of multiple core hole states has recently received attention also because multiple core hole spectroscopy opens up a way to sensitively probe electronic structure.<sup>5–8</sup> The Auger process in double core hole states in molecules of low  $Z$  elements, such as N, C, O has been

studied in a series of theoretical<sup>9–11</sup> and experimental<sup>10,12</sup> studies. However, to our knowledge only few attempts have been made to study the decay rate of doubly K-shell ionized states in molecules or atoms. Because in these states there are twice the number of decay channels available compared to the single core ionized case, one may be tempted to assume that the decay rate is simply twice the single core hole decay rate. Indeed, a recent calculation<sup>11</sup> of the double core hole decay (KK-KLL) of a series of small molecules seems to support such doubled rate, albeit this calculation may not have covered relevant relaxation effects sufficiently, and thus the authors estimated that the true value might be about 20% larger.<sup>11</sup> For atoms, Chen<sup>13</sup> calculated double K-hole vacancy Auger rates (KK-KLL) for atomic numbers  $Z = 10 \dots 36$  and found that for lower  $Z$  elements the Auger decay rate of double core shell vacancies was significantly larger than twice the Auger decay rate for the single core shell vacancy case. For the water molecule, we have recently calculated an even larger rate increase by a factor of three.<sup>14</sup>

A possible explanation for this pronounced rate increase over single core hole Auger decay are electronic relaxation effects. In particular, a single or double core hole in an atom or molecule induces relaxation of the surrounding electron density, such that the remaining electrons tend to screen the core hole. It can be anticipated that the valence electron density is deformed more dramatically in case of a double core vacancy, compared to that in the presence of a single core hole.

For atoms the additional contraction of electronic shells in a double core hole vacancy state results in an increased decay rate.<sup>13,15</sup> In molecules, additionally, the shift of valence electrons from neighboring atoms towards the core hole needs to be considered.<sup>16</sup> As we will show, this effect further increases the decay rates of double core ionized states.

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To systematically investigate such effects in small molecules, we have computed the Auger decay rates of a series of single and double core ionized molecules via *ab initio* quantum chemical methods and analyzed the respective electron density. We have chosen a sequence of iso-electronic molecules, namely, the neutral first-row hydrides methane CH<sub>4</sub>, ammonia NH<sub>3</sub>, water H<sub>2</sub>O, and hydrogen-fluoride HF, as well as their singly charged protonated states, CH<sub>3</sub><sup>+</sup>, OH<sup>-</sup>, H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, NH<sub>2</sub><sup>-</sup>, F<sup>-</sup>, and H<sub>2</sub>F<sup>+</sup>. All of these molecules have ten electrons, so that any variation of decay rates can be attributed solely to their different electronic structure.

## II. METHODS

### A. Theory

As described in detail before<sup>14</sup> Auger decay rates were calculated using a single center expansion of the electronic wave functions.<sup>17</sup> The bound part of the molecular states was calculated from Configuration Interaction (CI) calculations, while the continuum part was determined by solving the Schrödinger equation in the potential generated by the left-behind molecular cation. To this end, the molecular wave function was expanded into spherical harmonics on a radial grid. Accordingly, the molecular orbitals and single electron continuum wave function are given by

$$\phi_{i,\sigma}(\mathbf{r}) = \sum_{lm} \frac{P_{lm}^i(r)}{r} Y_{lm}(\theta, \phi), \quad (1)$$

where  $Y_{lm}(\theta, \phi)$  are spherical harmonics and  $P_{lm}^i(r)$  radial parts of the expansion. The exchange interaction of the bound electrons with the continuum electron was approximated here by the KSG<sup>18</sup> exchange interaction potential functional

$$V_{\text{XC}}[\rho(\mathbf{r})] = - \left( \frac{3}{\pi} \rho(\mathbf{r}) \right)^{\frac{1}{3}} \quad (2)$$

of the bound molecular electron density  $\rho(\mathbf{r})$ . From the determined continuum solutions, first order transition rates for Auger decay,

$$\Gamma_{\text{ini} \rightarrow \text{fin}}^{\text{Auger}} = 2\pi |\langle \psi_{\text{fin}} | H - E_{\text{ini}} | \psi_{\text{ini}} \rangle|^2, \quad (3)$$

were calculated for all relevant final states, including all available continuum channels. Under the assumption that the fluorescence decay channel can be neglected, these rates were finally summed up to obtain the total decay rate.

### B. Computational details

All molecular geometries used here were obtained by geometry optimization for the electronic ground state using GAUSSIAN 09<sup>19</sup> at the MP2/cc-pVTZ level of theory.<sup>20</sup> For both, initial and final electronic states, CI calculation were based on molecular orbitals (MOs), which were obtained from a restricted (open shell) Hartree-Fock calculation for the respective initial single or double core ionized electronic states using Dunning's cc-pVTZ basis set.<sup>21</sup> The

Hartree-Fock calculations and the transformation of two electron integrals were performed using a modified PSI3 quantum package.<sup>22</sup>

For the CI calculation we used a slightly different truncation scheme than that in Ref. 14. In particular we included all singly and doubly excited configurations from the respective reference(s). For the initial state, which is the singly or doubly core ionized state, we used a single reference, with a singly or doubly occupied core shell. For the final states of the Auger decay of a single core hole, we used multiple references with all possible combinations of rearranged two valence holes and refilled core shell. For the final states of the Auger decay of a double core hole, the same references were used but with a single occupied core shell. For all core vacant states, i.e., initial states and final states of the double core hole decay, single and double excited configurations were restricted by requiring the core orbital either singly or doubly occupied. This approach served to avoid any refilling of the core hole due to the pseudo continuum formed by the higher energetic valence orbitals.

We note that our rates for neon and water are slightly smaller (by  $\leq 10\%$ ) than those we have reported previously.<sup>14</sup> This difference is explained by the smaller CI space used in Ref. 14, in which double excitations were limited up to a certain Hartree-Fock orbital eigenvalue. The CI truncation scheme used in the present work allows a higher flexibility of the wave function and therefore improved the description of the final states based on MOs optimized for the initial core ionized state.

The computational parameters for the single center expansion were chosen as in Ref. 14. For the linear molecules HF, OH<sup>-</sup> and atoms Ne, F<sup>-</sup>, the number of  $m$  quantum numbers was reduced by exploiting molecular symmetries.

## III. RESULTS AND DISCUSSION

To validate our method, we first calculated molecular K-LL Auger decay rates for which calculated<sup>11,13,15,16</sup> or measured<sup>23-25</sup> values are available. As can be seen in Table I, the single core (K-LL) Auger decay rates we obtained agree with those obtained by Kolorenč and Averbukh<sup>11</sup> within 4%. For methane and water decay rates, which have been measured via the linewidth, also agree within 12% with our

TABLE I. Calculated K-LL Auger decay rates  $\Gamma_K$  in  $10^{-3}$  a.u.<sup>a</sup> compared with literature values.

|                  | Theory    |         |         | Experiment             |                        |
|------------------|-----------|---------|---------|------------------------|------------------------|
|                  | This work | Ref. 16 | Ref. 11 |                        |                        |
| CH <sub>4</sub>  | 3.2       | 3.5     | 3.1     | 3.4-3.5 <sup>b</sup>   | 3.1 ± 0.4 <sup>c</sup> |
| NH <sub>3</sub>  | 4.3       | 5.2     | 4.5     |                        |                        |
| H <sub>2</sub> O | 5.6       | 6.8     | 5.4     | 5.8 ± 0.2 <sup>d</sup> |                        |
| HF               | 7.3       | 8.3     |         |                        |                        |

<sup>a</sup>1 a.u. =  $4.13 \times 10^{16}$  1/s.

<sup>b</sup>From Ref. 23.

<sup>c</sup>From Ref. 24.

<sup>d</sup>From Ref. 25.

TABLE II. Calculated KK-KLL Auger decay rates  $\Gamma_{KK}$  in  $10^{-3}$  a.u. for neon compared with previous calculations.

|                           | This work | Ref. 15 | Ref. 13 |
|---------------------------|-----------|---------|---------|
| $\Gamma_K$                | 9.2       | 8.8     | 10.3    |
| $\Gamma_{KK}$             | 25.8      | 26.0    | 29.5    |
| $\Gamma_{KK}/(2\Gamma_K)$ | 1.4       | 1.5     | 1.4     |

results. Although the values calculated by Larkins<sup>16</sup> are systematically larger by about 15% than ours, the relative rate differences within the considered series of molecules also agree well with our results.

Table II compares the calculated single and double core hole Auger decay rates for neon with those calculated by Bhalla et al.<sup>15</sup> and Chen.<sup>13</sup> Again, the values we obtained agree within 13% to their calculations. Notably, for all double core hole decay calculations of neon, a marked enhancement  $\Gamma_{KK}/(2\Gamma_K)$  of about 1.4–1.5 is seen. From this comparisons we conclude that our approach yields sufficiently accurate results to quantitatively analyze the systematic trends discussed further below.

As the main result, we have calculated single (K-LL) and double (KK-KLL) core hole decay rates for the above iso-electronic series of molecules (Table III). As can be seen, with increasing atomic number  $Z$  of the central atom, the decay rate increases both for single and for double core ionized states. In contrast, the protonation state of the molecule seems to have only a minor effect on both single and double core hole decay rates. Overall, and in line with the results that have been obtained for atoms,<sup>13,15</sup> all molecular double core hole decays  $\Gamma_{KK}$  per core hole (i.e., divided by two) are markedly faster than that of the single core hole  $\Gamma_K$ .

Remarkably, for double core ionized states, the relative increase of the decay rate with  $Z$  appears to be slightly smaller. In fact, the ratio of double to single core hole decay rate per core hole,  $\Gamma_{KK}/(2\Gamma_K)$ , decreases monotonically with increasing  $Z$ , from about  $\Gamma_{KK}/(2\Gamma_K) = 1.8$  for methane to about  $\Gamma_{KK}/(2\Gamma_K) = 1.4$  for neon. Thus, not only the above systematic rate enhancement resembles the trend observed<sup>13</sup> for atoms with atomic number  $Z = 10 \dots 36$ , but also its systematic variation of the rate with  $Z$ .

We therefore asked whether and how this trend can be explained in terms of electronic structure changes due to the core hole, both as a function of  $Z$  as well as the number of hydrogen atoms. Specifically, we will analyze valence electron density shifts from the peripheral hydrogen atoms towards the central atom. To this aim, we will introduce a simplified model that relates the decay rates  $\Gamma_K$  and  $\Gamma_{KK}$  to the valence electron population on the central atom, applying a series of approximation steps.

Neglecting correlation effects, we first assume that the dominant contribution to an individual Auger transition rate results from a single pair of initial and final configuration state functions (CSF), both described by the same set of MOs. The amplitude for the Auger process from a CSF with single  $1s$  core hole to a final CSF with vacancies in the valence MOs  $v$  and  $v'$  with either singlet or triplet spin symmetry is

TABLE III. Auger decay rates in  $10^{-3}$  a.u. for single core ionized ( $\Gamma_K$ ) and double core ionized ( $\Gamma_{KK}$ ) molecules.

|                               | $Z$ | $\Gamma_K$ | $\frac{\Gamma_{KK}}{2}$ | $\frac{\Gamma_{KK}}{2\Gamma_K}$ |
|-------------------------------|-----|------------|-------------------------|---------------------------------|
| CH <sub>4</sub>               | 6   | 3.2        | 5.8                     | 1.8                             |
| CH <sub>3</sub> <sup>-</sup>  | 6   | 3.0        | 5.4                     | 1.8                             |
| NH <sub>4</sub> <sup>+</sup>  | 7   | 4.3        | 8.1                     | 1.9                             |
| NH <sub>3</sub>               | 7   | 4.3        | 7.2                     | 1.7                             |
| NH <sub>2</sub> <sup>-</sup>  | 7   | 4.1        | 6.9                     | 1.7                             |
| H <sub>3</sub> O <sup>+</sup> | 8   | 5.6        | 9.0                     | 1.6                             |
| H <sub>2</sub> O              | 8   | 5.6        | 8.8                     | 1.6                             |
| OH <sup>-</sup>               | 8   | 5.6        | 8.9                     | 1.6                             |
| H <sub>2</sub> F <sup>+</sup> | 9   | 7.2        | 10.8                    | 1.5                             |
| HF                            | 9   | 7.3        | 10.9                    | 1.5                             |
| F <sup>-</sup>                | 9   | 7.4        | 11.0                    | 1.5                             |
| Ne                            | 10  | 9.2        | 12.9                    | 1.4                             |

expressed by<sup>26</sup>

$$\frac{M_{vv'}}{\sqrt{2\pi}} = \begin{cases} \langle 1sk|1/r|vv' \rangle & \text{for } v = v', \text{ singlet} \\ \frac{1}{\sqrt{2}}(\langle 1sk|1/r|vv' \rangle + \langle 1sk|1/r|v'v \rangle) & \text{for } v \neq v', \text{ singlet} \\ \frac{1}{\sqrt{2}}(\langle 1sk|1/r|vv' \rangle - \langle 1sk|1/r|v'v \rangle) & \text{for } v \neq v', \text{ triplet.} \end{cases} \quad (4)$$

The above two-electron integrals are defined as

$$\langle 1sk|1/r|vv' \rangle := \int d^3r_1 \int d^3r_2 \phi_{1s}(\mathbf{r}_1)\phi_v(\mathbf{r}_1) \times \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_k(\mathbf{r}_2)\phi_{v'}(\mathbf{r}_2), \quad (5)$$

where  $\phi_{1s}(\mathbf{r})$  denotes the core orbital,  $\phi_k(\mathbf{r})$  the continuum wave function;  $\phi_v(\mathbf{r})$  and  $\phi_{v'}(\mathbf{r})$  are valence orbitals. The KK-KLL Auger decay rate of double K hole states is given by a similar expression, except that the final states have doublet spin symmetry, resulting in an additional factor of two for the rates.

Due to the strong localization of the hole  $\phi_{1s}$ , we further assume that the two-electron integrals in Eq. (4) are dominated by those parts of the valence electron wave functions  $\phi_v(\mathbf{r})$  and  $\phi_{v'}(\mathbf{r})$  which are close to the core hole  $\phi_{1s}$ ,<sup>27,28</sup> whereas the contribution of the remaining part of these orbitals to  $M_{vv'}$  is assumed to be small.

With the above assumptions, and following Refs. 29–32, we approximate each molecular Auger transition rate by

$$I_{vv'} = |M_{vv'}|^2 \simeq \sum_{aa'} C_{va}^2 C_{va'}^2 A_{aa'}. \quad (6)$$

Here,  $A_{aa'}$  is an atomic Auger rate for a final state with vacancies in the atomic orbitals  $a$  and  $a'$ , with populations  $C_{va}^2$  and  $C_{va'}^2$  in the molecular orbitals  $v$  and  $v'$ , respectively. Further, we assume that the atomic Auger rates  $A_{aa'}$  are independent of  $Z$ ; indeed, calculated Auger radial matrix elements<sup>33,34</sup> for atoms with  $6 \leq Z \leq 10$  vary by less than 6%. Also, the atomic Auger rates  $A_{aa'}$  for the different decay paths (i.e., two-hole combinations  $a, a'$ ) are replaced by an averaged rate

$\hat{A}$ , such that the variation of the molecular decay rate  $I_{v,v'}$  is determined solely by the changes of the populations  $C_{va}^2, C_{v'a'}^2$  of the atomic valence orbitals.<sup>28</sup>

If this scenario holds true, the total decay rate  $\Gamma$  of a core shell vacancy should be proportional to the number of possible combinations of creating two holes in the valence electrons that occupy the atomic orbitals of the central atom. To test this idea, we estimated the number of valence electrons  $n_{\text{val}}$  from the Mulliken population on that atom from the CI wave function for the single or double core ionized state, respectively. It follows that the rates should approximately obey

$$\Gamma = \begin{cases} \hat{A}^{(K)} \frac{1}{2} n_{\text{val}}^{(K)} (n_{\text{val}}^{(K)} - 1) & \text{for a single core hole,} \\ \hat{A}^{(KK)} n_{\text{val}}^{(KK)} (n_{\text{val}}^{(KK)} - 1) & \text{for a double core hole,} \end{cases} \quad (7)$$

i.e., the relationship between  $\Gamma_K$  and  $\Gamma_{KK}$  and the number of possible combinations of creating two holes,  $n_{\text{val}}(n_{\text{val}} - 1)/2$ , should be linear.

Overall, as can be seen from Fig. 1(a), both decay rates indeed follow this expected trend according to Eq. (7). To test whether the remaining deviations are mainly due to our particular — and somewhat arbitrary — choice of population analysis, Fig. 1(b) shows the same data, but with the number of valence electrons  $n_{\text{val}}$  derived from Löwdin populations<sup>35</sup> instead. Because only minor changes are seen, the deviations are likely to have a different origin.

To address this issue, we note that, whereas the effect of varying  $Z$  seems to be well described for neutral molecules by both approaches, the electron populations seem to be larger for the anions than expected from the respective decay rates, and smaller for the cations. In fact, inspection of the respec-

tive electron density distributions shows only little differences for varying protonation state in the vicinity of the central atom. Apparently, both population analyzes used above markedly exaggerate the changes of the electron density relevant for Auger decay caused by different protonation states.

We therefore asked if, instead, a simple estimate of  $n_{\text{val}}$  via the integrated *total* valence electron density within a sphere of a certain radius  $r$  around the central atom might better capture the total electron density relevant for the Auger two-electron integrals. We chose a value of  $r = 1.9a_0$ , a value close to the average bond length, for which the integrated electron density yields populations comparable with the Mulliken and Löwdin population. For this choice Eq. (7) predicts all decay rates much better [Figure 1(c)], except for neon. Qualitatively similar results are obtained for  $1.5a_0 < r < 2.5a_0$  (data not shown).

Overall, despite the relatively crude approximations used, Eq. (7) describes the Auger decay rates of the considered series of molecules with varying  $Z$  — both for the two wave function based and for the density based population estimates — remarkably well.

Notably, in Figs. 1(a)–1(c), the slope for  $\Gamma_{KK}/2$ , i.e., the averaged atomic decay rate  $\hat{A}^{(KK)}$ , is about 35% larger than that for  $\Gamma_K$ . This trend is quantified in Fig. 1(d), which displays the ratios  $\hat{A}^{(K)} = 2\Gamma_K/[n_{\text{val},K}(n_{\text{val},K} - 1)]$  and  $\hat{A}^{(KK)} = \Gamma_{KK}/[n_{\text{val},KK}(n_{\text{val},KK} - 1)]$  as a function of  $Z$ . Because a similar value of enhancement has been found for neon (40%), we attribute this 35% larger average atomic decay rate  $\hat{A}$  to an atomic effect.

Taken together, we have identified and quantified two effects which dominate the systematic differences and trends for single and double core hole Auger decay rates  $\Gamma_{KK}/2$  over  $\Gamma_K$  for the series of iso-electronic molecules studied here. The rate enhancement for the double core hole over single core hole is, first, due to an increased valence population in the vicinity of the core hole and, second, due to a systematic increase of the Auger decay rate per core hole and valence electron pair. The rate increase with atomic number  $Z$  can also be attributed to an increased valence electron population on the atom with the core hole. Generalizing these ideas, we propose that the presented approach is applicable to other molecules in which single and double core holes (single-sited) are located on elements with low atomic number  $Z$ .

We note that in this work effects of nuclear motion have been neglected. For the water molecule these effects have previously been found to affect the spectrum of the Auger electrons.<sup>14</sup> However, the *total* decay rate, which we address here, turned out to be nearly independent of the nuclear dynamics. We therefore assume that this is also the case for the molecules considered here.

## IV. SUMMARY AND CONCLUSION

In summary, we have calculated molecular Auger decay rates for single core hole (K-LL) and double core hole (KK-KLL) states for the iso-electronic series of first row hydrides with atomic numbers  $Z = 6 \dots 10$  and their singly charged protonated states. We demonstrated that decay of molecular double core hole states is 40% to 90% faster than twice the decay

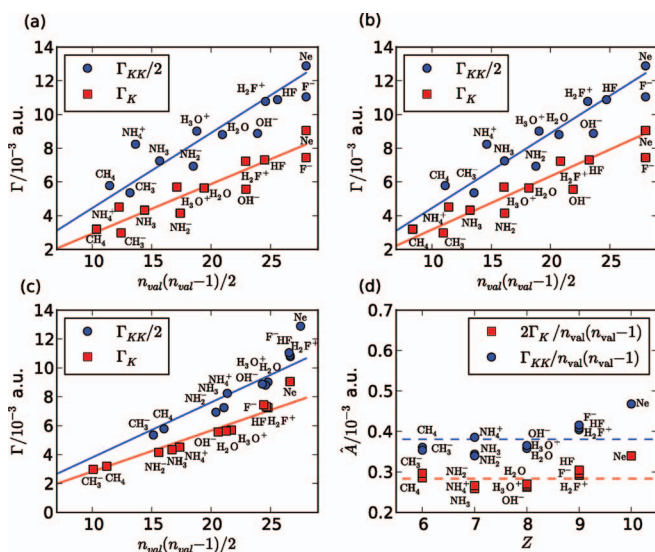


FIG. 1. (a)–(c) Decay rate per core hole as a function of the number of valence electron pairs  $n_{\text{val}}(n_{\text{val}} - 1)/2$  on the atom at which the core hole is located, estimated from the respective core ionized state wave function via (a) Mulliken and (b) Löwdin population analysis, as well as via (c) the integrated electron density within a sphere of radius  $r = 1.9a_0$  around the core hole. (d) Decay rate per core hole and per valence electron pair, where the number of valence electrons  $n_{\text{val}}$  was estimated as in Fig. 1(c). For all different methods for estimating  $n_{\text{val}}$  the decay rate  $\Gamma_K$  and  $\Gamma_{KK}$  is roughly proportional to  $n_{\text{val}}(n_{\text{val}} - 1)/2$ .

of the single core hole. This finding is partially explained by a valence electron shift towards the atom at which the core hole is localized. An unexpectedly simple model based on population analysis enables one to estimate Auger decay rates in molecules. As molecular Auger decay of multiple core holes is a crucial factor for the charging up of molecular samples in coherent diffractive imaging experiments with XFEL,<sup>1,2</sup> our approach should help to develop efficient descriptions and models of how radiation damage evolves after multiple core ionization also in larger molecules.

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