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K-shell Auger lifetime variation in doubly ionized Ne and first row hydrides

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We consider $1s$ Auger decay in doubly (core-core and core-valence) ionized Ne and in the isoelectronic first row element hydrides. We show theoretically that the presence of the spectator inner valence vacancy leads to Auger lifetime variation of up to about a factor of 2, relative to the Auger lifetimes in the singly ionized species. The origin of this effect is traced to spin selection rules. Implications on the modelling of the radiation damage in strong x-ray fields are discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3646204]

I. INTRODUCTION

Auger decay^{1,2} of core-ionized states is one of the basic manifestations of electron correlation in matter. On top of its fundamental significance for the understanding of electronic structure and dynamics, it has gained importance as a prominent analytical tool, e.g., in surface analysis.³ Auger decay can be triggered by photoionization of a core electron using x-ray radiation. Core ionization results in a formation of a highly excited cationic states that lie above the double ionization thresholds and, as a result, can decay by electron emission (Auger electrons). Recently, new-generation x-ray sources – X-ray free electron lasers (XFELs) – have become available at a number of facilities around the world.⁴ These sources are characterized by uncommonly high intensities (up to $\sim 10^{18}$ W/cm²) and, prospectively, also by very short pulse durations (down to ~ 1 fs).⁴ The unique characteristics of XFEL radiation led researchers to propose that it can be suitable for imaging of macromolecules in gas phase by single-molecule x-ray diffraction.⁵ Significant experimental progress with nanometer-resolution XFEL imaging has been achieved recently.⁶ Feasibility of extending this fascinating idea to atomic-resolution measurements depends on the extent of the radiation damage caused by the XFEL radiation. Thus, theoretical simulations of the radiation damage could be very helpful in choosing the optimal pulse characteristics for the envisaged atomic-resolution imaging.

State of the art molecular mechanics simulations of macromolecule-XFEL interaction⁵ rely on the classical description of atomic and electronic motion, in combination with quantum-mechanical rates for the electronic processes induced by the high-intensity x-rays. The latter include photoionization, predominantly of inner-shell electrons, and Auger processes following the creation of the corresponding inner-shell vacancies. In the high intensity regime necessary for obtaining the diffraction picture of a single molecule with atomic resolution, the target species become multiply ionized well within the XFEL pulse duration. It could be expected,

therefore, that many of the electronic processes leading to the radiation damage are modified by the presence of multiple positive charges. Concentrating specifically on the Auger decay, the core hole lifetimes could be affected by additional positive charges residing both on the atom bearing the core vacancy and on the neighboring atoms. In this work, we explore the effect of the double ionization of a single atom on the Auger lifetimes, leaving the effect of the neighboring positive charge to a separate publication.⁷ Since the Auger transitions of interest for the radiation damage in single-molecule x-ray diffraction are mainly induced by K -shell ionization of C, N, and O atoms, we specifically target doubly (KK - and KL -) ionized states of CH₄, NH₃, and H₂O as model systems, comparing them with the corresponding transition in the isoelectronic Ne atom. Using the Fano-ADC (algebraic diagrammatic construction) methods for the lifetimes of the singly and doubly ionized states,^{8,9} we predict that the lifetimes of the core-valence ionized states show an interesting behavior. In particular, lifetimes of the core-inner-valence ionized states change by up to about a factor of 2 depending on the spin multiplicity of the decaying state and can be different from the lifetimes of the singly core-ionized species by a similar factor. Section II briefly outlines the theoretical method we used in our calculations and gives a detailed account of the results.

II. AUGER DECAY WIDTHS OF SINGLY- AND DOUBLY-IONIZED STATES OF NEON ATOM AND METHANE, AMMONIA, AND WATER MOLECULES

A. Fano-ADC method for Auger decay rates

In all our Auger width calculations we are using Fano-ADC technique, first developed for the decay of singly ionized states⁸ and more recently generalized for the doubly ionized systems.⁹ The Fano-ADC approach for electronic decay widths is an \mathcal{L}^2 method that is based on the Fano expression¹⁰ for the decay width, Γ , through the matrix element of the full many-electron Hamiltonian (\hat{H}) between the boundlike (Φ) and the continuumlike ($\chi_{\alpha, \varepsilon_{\alpha}}$) components of

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the wave function at the energy of the resonance (E_r),

$$\Gamma = 2\pi \sum_{\alpha=1}^{N_c} |\langle \Phi | \hat{H} - E_r | \chi_{\alpha, \varepsilon_{\alpha}} \rangle|^2, \quad (1)$$

where the summation is over N_c decay channels and ε_{α} is the kinetic energy of the emitted electron for the α 's decay channel. The many-electron wave functions Φ and $\chi_{\alpha, \varepsilon_{\alpha}}$ are obtained using the *ab initio* method known as extended second-order algebraic diagrammatic construction [ADC(2)x]. In the case of the Auger decay of singly ionized states, ADC(2)x scheme for $(N - 1)$ electron systems is employed,¹¹ while the Auger decay widths of doubly ionized states are described by the ADC(2)x scheme for $(N - 2)$ electron systems,¹² N standing for the number of electrons in the closed shell ground state of neutral species. Finally, the interpolation and renormalization of the bound-continuum matrix elements obtained with \mathcal{L}^2 wave functions is achieved by Stieltjes imaging procedure¹³ that has been first applied to the problem of molecular Auger width in Ref. 14. In the center of the Fano-ADC computational procedure is the configuration selection scheme that sorts out the many-electron ADC basis states into those contributing to the expansion of the initial (boundlike) state and to the final (continuumlike) state. In all the calculations performed in this study, we employ the energy-based configuration selection scheme described in Ref. 8.

B. Auger decay in doubly ionized neon atom

The atoms of primary interest for the bio-molecular imaging applications are C, N, and O in their “natural” chemical state (i.e., as the one in proteins). The simplest chemical compounds modelling this chemical state are the corresponding hydrides, CH₄, NH₃, and H₂O which turn out to be isoelectronic to the Ne atom. Since Auger decay in Ne has been studied extensively in the past, first we would like to discuss Auger width variation in Ne²⁺ and to make connection to the previous work. Analogous Auger processes in the isoelectronic first row hydrides will be discussed in the next subsection.

Auger-active states of Ne²⁺ can be classified as stemming from $1s^{-2}$, $1s^{-1}2s^{-1}$, and $1s^{-1}2p^{-1}$ configurations. The first one of those, i.e., the “hollow atom,” has recently been observed in the XFEL studies.¹⁵ Looking at the spectator-core-

hole $KK-KLL$ Auger decay process in the hollow Ne, one immediately notices that it has twice the number of the decay pathways relative to the normal $K-LL$ Auger transition. In the simplest approximation, one would expect, thus, the $KK-KLL$ decay rate to be just twice the $K-LL$ one. Further, one notices that a couple of a bit more subtle effects can push the hollow Ne decay rate into opposite directions. First, double K -shell ionization leads to contraction of the valence orbitals in the initial state of the process, making the Auger matrix elements larger. Second, the kinetic energy of the $KK-KLL$ Auger electrons is a bit higher than that of the $K-LL$ (by about 70 eV (Ref. 16)) ones which could have just the opposite effect. Looking at the theoretical values for the $KK-KLL$ widths available in the literature, namely, 707 meV (Ref. 17), 804 meV (Ref. 18), and 623 meV (Ref. 19), one finds that all of them exceed the normal Auger width in Ne (240 meV (Ref. 20)) by more than twice, suggesting that the effect of the valence orbital contraction is the dominant one. The Voigt fit analysis of a 3 eV wide $KK-KLL$ feature in the experimental spectrum¹⁶ supports this conclusion.

In the present work, the Auger decay widths were calculated using the Fano-ADC method outlined above, starting from the restricted Hartree-Fock solution obtained using the MOLCAS 7.4 quantum chemistry package.²¹ In all our calculations on Ne atom, uncontracted cc-pCV6Z Gaussian basis²² augmented by $5s5p6d$ continuumlike diffuse Kaufmann-Baumeister-Jungen (KBJ) Gaussians²³ was utilized. Our Fano-ADC computation for the hollow Ne produces the decay width of 506 meV, which is lower than the available literature values and extremely close to twice the normal Auger width. In fact, we find that all the $KK-KLL$ decay channels attain about twice as larger partial widths than their $K-LL$ counterparts. Noteworthy, our Fano-ADC result for the normal Auger width (obtained in the same Gaussian basis), 251 meV, agrees rather well with the recommended literature value²⁰ and our partial width analysis for the $K-LL$ transition is in good correspondence with the available experimental and theoretical results²⁴ (see Table I). Nevertheless, the discrepancy between our result and the literature values (by themselves having a spread of more than 20%) could well result from the underestimation of the very strong relaxation effects in the hollow atom states by the second-order ADC scheme employed in our calculation. We believe that further work on the decay lifetimes of the hollow neon is needed.

TABLE I. Comparison of the branching ratios of the $KK-KLL$ and $K-LL$ Auger transitions in doubly and singly core-ionized Ne, respectively. Branching ratios are given in %, the total widths in meV. The experimental values for $KK-KLL$ transition are taken from Albiez *et al.*²⁹ (branching ratios) and from Avaldi *et al.*³⁰ (total width).

Ne ²⁺		Ne ⁺				exp.				
Transition	Present	Pelicon (Ref. 19)	Chen (Ref. 18)	Bhalla (Ref. 17)	Transition	Present	Kelly (Ref. 28)	Yarzhemsky (Ref. 24)	(Ref. 29 and 30)	
$KK-KL_{2,3}L_{2,3}$	² P	0.0	0.3	0.4	$K-L_{2,3}L_{2,3}$	³ P	0.0	0.0	–	
	² D	59.0	49.2	44.0		¹ D	50.5	61.2	58.2	60.9
$KK-KL_1L_{2,3}$	² S	8.1	9.2	12.6	$K-L_1L_{2,3}$	¹ S	9.5	9.6	10.2	9.5
	² P ⁽⁻⁾	6.9	1.1	0.7		³ P	10.6	6.1	9.3	6.3
$KK-KL_1L_1$	² P ⁽⁺⁾	22.6	33.0	31.6	25.0	¹ P	19.5	17.0	16.8	17.2
	² S	3.4	7.0	10.7	7.9	$K-L_1L_1$	¹ S	9.9	6.1	5.5
Total width (meV)	506	623	805	707		251	219	242	220 ± 30	

TABLE II. Fano-ADC total and partial Auger decay widths (in meV) for doubly ionized Ne atom. Electronic configurations and terms of the decaying states are specified in the first row. The literature values in parentheses are taken from Ref. 31.

Final state	$1s^{-1}2s^{-1}$	$1s^{-1}2s^{-1}$	$1s^{-1}2p^{-1}$	$1s^{-1}2p^{-1}$
	1S	3S	1P	3P
$2p^{-3}4S$...	0	...	0 (0)
$2p^{-3}2D$	0	0	78 (75)	77 (76)
$2p^{-3}2P$	1	0	31 (37)	33 (37)
$2s^{-1}2p^{-2}4P$...	0	...	12 (11)
$2s^{-1}2p^{-2}2D$	127	135	7 (0)	23 (28)
$2s^{-1}2p^{-2}2S$	16	15	4 (0)	6 (6)
$2s^{-1}2p^{-2}2P$	0	0	53 (52)	26 (23)
$2s^{-2}2p^{-1}2P$	123	16	24 (23)	25 (23)
Total width	267	166	197 (187)	202 (204)

Auger dynamics of a hollow Ne atom presents a particular interest because a three-electron $KK-LLL$ process can contribute to the decay of the core vacancies. Such a process, in which two valence electrons recombine into the core orbital to produce an extra-energetic free electron, has been first observed in doubly L -shell-ionized Ar atoms²⁵ and later in Kr and Xe.²⁶ The corresponding partial decay width in LL -ionized Ar was estimated to be in the range of 0.01–1 meV. To our knowledge, there are so far no theoretical or experimental data available for such a three-electron Auger transition in hollow Ne. Our Fano-ADC calculation for the Ne $KK-LLL$ process gives the partial decay width of about 0.05 meV, well within the range of the estimated $LL-MMM$ Ar values. Assuming that our calculation underestimates the valence orbital contraction effect, this figure presents a lower bound for the three-electron process width. While clearly negligible relative to the total hollow Ne decay width, the $KK-LLL$ process can well be observable, as in the case of heavier rare gas atoms, since it produces highly energetic electrons well outside the energy region of the two-electron transitions. Interestingly, a similar “collective” inter-atomic three-electron process can turn out to be the main decay channel in doubly inner-valence ionized clusters.²⁷

Going from hollow Ne to core-valence ionized Ne, we should consider two types of configurations, namely, $1s^{-1}2s^{-1}$ and $1s^{-1}2p^{-1}$ ones, which lead to both singlet and triplet states and turn out to have distinctly different patterns of lifetime variation with the spin multiplicity. The results of our Fano-ADC calculations of Auger widths for

core-valence ionized Ne are given in Table II. Looking at the results of these *ab initio* calculations, one readily notices that while spin multiplicity plays no role for the Auger widths of the $KL_{2,3}$ states, the widths of the KL_1 states depend crucially on whether the two holes form a singlet or a triplet. Indeed, the corresponding 1S state decays about 1.6 times faster than the triplet state. The origin of this trend becomes apparent if one looks at the partial widths of the KL_1 states (see Table II). In the decay of the singlet initial state, the recombination from $2s$ orbital to $1s$ one is operative and $2s^{-1}2p^{-2}$ and $2s^{-2}2p^{-1}$ electronic configurations of the Ne^{3+} final states are about evenly populated. In the case of the triplet decaying state, however, the single electron in the $2s$ orbital has the same spin as the one in the $1s$ orbital and, therefore, cannot fill the $1s$ vacancy. The $Ne^{3+}(2s^{-2}2p^{-1}2P)$ channel is still accessible but only via higher order processes comprising three-electron transitions. This leads to a radical drop in efficiency by nearly 90%. This effect fully explains the difference between the total Auger rates for the singlet 1S and triplet 3S initial states. Comparing this situation to the decay of the $KL_{2,3}$ states, one notices that the partial decay widths for all Ne^{3+} configurations remain more or less unchanged when going from singlet to triplet initial states, up to some redistribution of intensity between different terms of the $2s^{-1}2p^{-2}$ final configuration. In total, the decay widths of both singlet and triplet $1s^{-1}2p^{-1}$ states are about 80% of the Ne $K-LL$ Auger rate which is close to what is expected on the basis of the simple counting of the available Auger decay pathways.

C. Auger decay in doubly ionized methane, ammonia, and water molecules

Let us now consider the effect of a spectator vacancy on the Auger rate of the C, N, and O core hole in CH_4 , NH_3 , and H_2O molecules, respectively. These molecules are isoelectronic with Ne; however, the degeneracy of the outer valence orbitals is preserved only in the tetrahedral CH_4 . Our Fano-ADC calculations of the Auger widths in the first row hydrides were found to converge with respect to the single electron basis for the following Gaussian basis sets: CH_4 – uncontracted cc-pCV5Z basis set augmented by $4s4p4d$ KBJ Gaussians on C atom and uncontracted cc-pV5Z basis set on H (to within $\sim 5\%$); H_2O – uncontracted aug-cc-pCV5Z basis set further augmented by $4s4p4d$ KBJ Gaussians on O and uncontracted cc-pV5Z basis

TABLE III. Comparison of the Fano-ADC results with the available theoretical and experimental values for the $K-LL$ Auger decay widths in CH_4 , NH_3 , and H_2O molecules. The decay widths are in meV, citations are given in square brackets. Experimental value for ammonia is lacking because of the vibrational broadening in the Auger electron spectrum of ammonia (Ref. 41).

	Present	Theory				Experiment			
		(Ref. 32)	(Ref. 33)	(Ref. 34)	(Ref. 35)	(Ref. 36)	(Ref. 37)	(Ref. 38)	
CH_4	85	75	96	96	107 ± 10	120 ± 10	83 ± 10	94 ± 1	
		(Ref. 39)							
NH_3	123	106							
		(Ref. 14)			(Ref. 40)				
H_2O	148	150			160 ± 5				

TABLE IV. Fano-ADC total Auger decay widths (in meV) for different electronic states of doubly ionized CH₄, H₂O, and NH₃ molecules. The Fano-ADC Auger decay widths of the single core vacancies are given for each molecule in parentheses. To facilitate the comparison, the Fano-ADC results for Ne atom are also given.

Decaying state Γ (meV) Ne ($\Gamma_{1s^{-1}} = 251$ meV)		Decaying state Γ (meV) CH ₄ ($\Gamma_{1a_1^{-1}} = 85$ meV)	
$1s^{-1} 2p^{-1} 1P$	197	$1a_1^{-1} 1t_2^{-1} 1T_2$	68
$1s^{-1} 2p^{-1} 3P$	202	$1a_1^{-1} 1t_2^{-1} 3T_2$	69
$1s^{-1} 2s^{-1} 1S$	267	$1a_1^{-1} 2a_1^{-1} 1A_1$	90
$1s^{-1} 2s^{-1} 3S$	166	$1a_1^{-1} 2a_1^{-1} 3A_1$	49
$1s^{-2} 2S$	506	$1a_1^{-2} 1A_1$	167
NH ₃ ($\Gamma_{1a_1^{-1}} = 123$ meV)		H ₂ O ($\Gamma_{1a_1^{-1}} = 148$ meV)	
$1a_1^{-1} 3a_1^{-1} 1A_1$	92	$1a_1^{-1} 1b_1^{-1} 1B_1$	110
$1a_1^{-1} 3a_1^{-1} 3A_1$	94	$1a_1^{-1} 1b_1^{-1} 3B_1$	116
$1a_1^{-1} 1e^{-1} 1E$	100	$1a_1^{-1} 3a_1^{-1} 1A_1$	121
$1a_1^{-1} 1e^{-1} 3E$	105	$1a_1^{-1} 3a_1^{-1} 3A_1$	118
		$1a_1^{-1} 1b_2^{-1} 1B_2$	122
		$1a_1^{-1} 1b_2^{-1} 3B_2$	126
$1a_1^{-1} 2a_1^{-1} 1A_1$	126	$1a_1^{-1} 2a_1^{-1} 1A_1$	157
$1a_1^{-1} 2a_1^{-1} 3A_1$	81	$1a_1^{-1} 2a_1^{-1} 3A_1$	99
$1a_1^{-2} 1A_1$	230	$1a_1^{-2} 1A_1$	311

on H (to within $\sim 5\%$); NH₃ – uncontracted cc-pCV6Z basis set with $4s4p4d$ KBJ Gaussians on N and uncontracted cc-pV6Z basis set on H (to within $\sim 10\%$). The Fano-ADC Auger widths of the singly core-ionized molecules are presented in Table III alongside the available literature data. The calculated total Auger widths for the Auger-active main electronic states of the doubly ionized molecules are given in Table IV. Our results for the molecular Auger decay widths reveal the trends analogous to the one observed in Ne atom. In particular, we find that inner-valence spectator vacancies in methane, ammonia, and water play the same important role as it does in neon: the singlet to triplet ratio of the decay widths ranges from 1.6 (NH₃, H₂O) to 1.8 (CH₄). As in the case of Ne atom, this very pronounced difference is due to the fact that the transitions involving inner-valence-core recombination are, at least in the first order of perturbation theory, forbidden in the decay of the triplet states. In the case of outer-valence spectator hole, the effect of the spin multiplicity on the Auger rate is small, beyond the accuracy of our computational method. Furthermore, we find that the Fano-ADC decay widths of the hollow ($1s^{-2}$) molecules is approximately twice larger than the corresponding normal Auger widths, in accordance with the doubling of the available decay pathways. Assuming that our calculation for hollow molecules suffers from underestimation of the relaxation in the initial state in the same way as our results for hollow Ne, the true decay rates of the $KK-KLL$ widths of the first row hydrides could be about 20% higher than our theoretical predictions.

III. CONCLUSIONS

In conclusion, we have presented a detailed picture of Auger decay widths in doubly ionized Ne atom and the iso-electronic hydrides of C, N, and O. Our calculations are performed using the *ab initio* Fano-ADC method that, as we

show, produces reliable results for the normal ($K-LL$) Auger widths in these species. Nevertheless, we believe that in the specific case of the hollow ($1s^{-2}$) states, our method does not take into account fully the characteristically strong relaxation effect, which probably leads to underestimation of the hollow atom or molecule decay rates by about 20% (the spread of the literature values for this type of transition is of about the same magnitude).

Our most important finding has to do with the core-inner-valence doubly ionized states. We have shown that the effect of the spin state of the two holes has a major effect on the rate of the Auger decay. While singlet core-inner-valence ionized states decay about as fast as the singly core-ionized ones, their triplet counterparts decay by up to a factor of 1.8 slower. This trend is found to be completely general and is easily explained by spin selection rules. Interestingly, the singlet-triplet factor is largest for methane which leads us to believe that sp^3 hybridized carbon Auger decay, in general, can proceed significantly slower in the presence of an inner-valence hole. Depending on how probable the inner-valence ionization is for the given experimental conditions, this effect can have significant implications on the time scale of the Auger dynamics in multiply ionized bio-molecules. Having in mind the role of Auger transition in the formation of radiation damage in the XFEL diffraction experiments,^{5,6} inner-valence holes are not very likely to be produced by photoionization directly, but could well be produced by the electron impact mechanism – both with photo- and Auger electrons. This effect can be studied in detail by incorporating the decay widths given in the present work into the molecular dynamics simulations of the radiation damage.

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