Nonradiative Electronic Deexcitation Time Scales in Metal Clusters

M. E. Garcia*, Ll. Serra, F. Garcias,

Departament de Física, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain

and K. H. Bennemann

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

(February 1, 2022)

Abstract

The life-times due to Auger-electron emission for a hole on a deep electronic shell of neutral and charged sodium clusters are studied for different sizes. We consider spherical clusters and calculate the Auger-transition probabilities using the energy levels and wave functions calculated in the Local-Density-Approximation (LDA). We obtain that Auger emission processes are energetically not allowed for neutral and positively charged sodium clusters. In general, the Auger probabilities in small Na\(_N\) clusters are remarkably different from the atomic ones and exhibit a rich size dependence. The Auger decay times of most of the cluster sizes studied are orders of magnitude larger than in atoms and might be comparable with typical fragmentation times.

36.40.-c, 32.80.Hd

Typeset using REVTeX
I. INTRODUCTION

The decay of an electronically excited cluster may take place by emission of electrons, atoms or photons. It is generally accepted that the radiative cooling is the decay channel with the largest time scale [1]. Another deexcitation channel is the evaporation of atoms, which occurs within a characteristic time which ranges between pico- and milliseconds, depending on the bonding character of the clusters and the excitation energy. The fastest relaxation channel is the emission of photoelectrons. In addition, and like in atoms, secondary electrons can be emitted if the excitation energy is larger than the ionization potential of the cluster. These electrons result from intraband Auger processes, i.e., Auger decay of a valence hole and subsequent emission of a valence electron.

In excited light atoms, the nonradiative decay through emission of Auger electrons has a much larger probability than the radiative decay and dominates the relaxation process [2]. In clusters there are so far neither experimental nor theoretical studies of the intraband Auger probabilities. Recently, two important experimental studies on the deexcitation channels of small clusters after optical excitation have been performed, from which the contribution of Auger-processes can be inferred. Ganteför et al [3] analyzed the kinetic energy distribution of electrons emitted from optically excited clusters. They found that the photoelectron spectra show contributions from three different processes: direct emission, thermionic emission, and “inelastic scattered electrons”. The latter appear within a definite and narrow range of kinetic energies. One could in principle interpret the inelastic scattered electrons as coming from intraband Auger-processes. Reiners and Haberland [4] studied the competition between electron and atom emission after photoabsorption as a function of the photon energy. They observed that atom emission occurs within an energy range which is smaller than the cluster bandwidth. This means that excitations consisting of a hole in the bottom of the valence band (i.e., in the deepest electronic shells) do not lead to atom emission, despite that their energy is larger than the binding energy. The authors conjectured that this is due to intraband Auger-processes which lead to a very short life-time of such holes.
In this paper we present the first calculations of the intraband Auger time scales in metal clusters and show that Auger emission probabilities strongly depend on size and are, in general, orders of magnitude smaller than atomic Auger probabilities.

II. THEORY

We consider only closed-shell $Na_N$, $Na^+_N$, and $Na^-_N$ clusters and make use of their spherical symmetry. For the description of the electronic structure of the clusters we use the jellium model. Through the Auger process, a vacancy in a state $|n''\ell''\rangle$, with $\varepsilon_{n''\ell''} \leq \varepsilon_F$ ($\varepsilon_F$ being the Fermi level), is filled by an electron coming from a higher bound level $n\ell$. The energy released by this transition is transferred to a second electron, initially in a bound state $|n\ell\rangle$, which is ejected (i.e., excited into a continuum state $k$). Thus, the initial state consists of one hole in a bound state, and the final state consists of two holes in bound states and one electron in a continuum state. One can, however, consider the Auger process as a two hole $\rightarrow$ two hole transition, where the initial state is given by $|\Psi_i\rangle = c_{n''\ell''\sigma} c_k |\Psi_k\rangle$, with $|\Psi_k\rangle = c_k^+ |\Psi_0\rangle$ and $\varepsilon_k > 0$, and the final state by $|\Psi_f\rangle = c_{n\ell\sigma} c_{n'\ell'\sigma'} |\Psi_k\rangle$, with $\varepsilon_{n'\ell'}, \varepsilon_{n\ell} \leq \varepsilon_F$. $k$ denotes the continuum state of the Auger electron and $n''\ell'', n\ell$ stand for the states corresponding to the two final holes. $|\Psi_0\rangle$ refers to the electronic ground state of the cluster. The Auger transition probability can be calculated using Fermi’s golden rule, and is given by

$$w_{fi} = \frac{2\pi}{\hbar} \left| \langle \Psi_f \mid \hat{V} \mid \Psi_i \rangle \right|^2 \rho(E_f),$$

where $\rho(E_f)$ corresponds to the density of final states and $\hat{V}$ is the operator describing the Coulomb interactions, which is written as

$$\hat{V} = \frac{1}{2} \sum_{\sigma_1 \sigma_2} V_{1234} c_{1\sigma_1}^+ c_{2\sigma_2}^+ c_{3\sigma_3} c_{4\sigma_4},$$

where the sum is over the cluster energy levels. In Eq. (2) the quantities $V_{1234}$ are the Coulomb matrix elements.
\[ V_{1234} = \int \int \psi_1^\ast(\vec{r}) \psi_2^\ast(\vec{r}') \frac{e^2}{|\vec{r} - \vec{r}'|} \psi_3(\vec{r}'') \psi_4(\vec{r}) \; d\vec{r} \; d\vec{r}' , \] 

expressed in the basis of eigenfunctions corresponding to the bound and continuum levels of the cluster.

In order to calculate the Auger-emission probability of Eq. (1) we have first to determine the wave functions of the three bound states and that of the continuum state which is involved in. This can be done by performing an approximation which is widely used in atomic physics \[2\], and consists in taking the wave functions and energy levels of the original system, i.e., the cluster before the creation of the initial vacancy. Therefore we solve the Kohn-Sham equations for the spherical metal cluster, given by

\[ \left[ -\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{\ell(\ell + 1)}{2r^2} + V_{\text{eff}}(r) \right] R_{n\ell}(r) = \varepsilon_{n\ell} R_{n\ell}(r). \] 

Here, \( V_{\text{eff}}(\vec{r}) \) is the effective one-electron potential

\[ V_{\text{eff}}(\vec{r}) = v_j(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \; d\vec{r}' + \frac{\delta}{\delta n} E_{XC}[n(\vec{r})] , \]

where \( v_j(\vec{r}) \) is the electrostatic potential created by the jellium distribution of charge and \( E_{XC}[n(\vec{r})] \) the exchange and correlation term \[3\]. \( n(\vec{r}) \) is the electronic density. From Eqs. (4) one obtains the bound states of the cluster. The numerical algorithm to solve Eqs. (4) imposes the condition of regularity at the origin \( R_{n\ell} \propto r^\ell \) and fixes the number of nodes \( n \) of \( R_{n\ell} \). There is only one solution for a fixed \( n \) and \( \ell \) which vanishes exponentially at infinity and the algorithm iterates to find it, as well as its associated eigenvalue \( \varepsilon_{n\ell} \). The number of occupied shells determines the number of possible Auger processes for a given hole in the shell \( n'\ell' \). Since the total energy is conserved during the transition \( (E_i = E_f) \), the kinetic energy \( \varepsilon_{k\ell_k} \) of the emitted Auger electron is given by \( \varepsilon_{k\ell_k} = |\varepsilon_{n'\ell'}| - |\varepsilon_{n\ell}| - |\varepsilon_{n\ell} | \).

For a Auger emission to take place it must obviously hold that \( \varepsilon_{k\ell_k} > 0 \). Since also the total angular momentum is conserved, the two-hole final state must have the same angular momentum as the two hole initial state \( (L_i = L_f = L) \). This requires for the angular momentum \( \ell_k \) of the Auger electron the condition \( |L - \ell''| \leq \ell_k \leq L + \ell'' \), where \( L \) must
satisfy the inequality $|\ell - \ell'| \leq L \leq \ell + \ell'$. Similar constraints are fulfilled by the spin of the Auger electron. For the calculation of the Auger continuum wave function we also use Eqs. (3). However, in this case the number of nodes is unknown and the continuum energy $\varepsilon_{k \ell_k}$ and the multipolarity $\ell_k$ are fixed. The same regularity condition is used to start the integration outwards, from the origin up to a fixed large radius $R_0$. We normalize the outgoing Auger wave function $\sim \exp(ikr)/r$ within a sphere of radius $R_0$. Thus, the density of final states is given by $\rho(E_f) = R_0/(2\pi \bar{v})$, where $\bar{v}$ refers to the velocity of the Auger electron [2].

In order to determine the Auger probability we first separate the matrix elements (3) into radial and angular factors. This is achieved by performing the multipole expansion $1/r_{12} = \sum_{\mu \nu} r^\mu_1 / r^\nu_2 C^*_\mu(\theta_1, \phi_1) C^{(2)}_{\mu \nu}(\theta_2, \phi_2)$, with $C_{\mu \nu} = \sqrt{\frac{4\pi}{2\nu+1}} Y_{\mu \nu}(\theta, \phi)$, being $Y_{\mu \nu}(\theta, \phi)$ spherical harmonics. Evaluation of the angular factors depends on the choice of the angular-momentum coupling scheme. Since for the valence electrons of clusters the spin-orbit coupling is negligible, the initial and final two-hole states of the cluster can be expressed in the (LSJM) representation. The total transition probability into all possible states of $L$ and $S$ is then given by [2]

$$w(n\ell, n'\ell', n''\ell'') = \sum_{L,S} \frac{(2S+1)(2L+1)}{2(2\ell''+1)} \sum_{\ell_k} \frac{1}{2\hbar} \sum_{\nu} \left[ d_\nu D_\nu + (-1)^{L+S+\ell+\ell'} e_\nu J_\nu \right] \rho(E_f)$$

(6)

where the functions $D_\nu$ and $J_\nu$ are the direct and exchange radial matrix elements, and the angular factors $d_\nu$ and $e_\nu$ are given by

$$d_\nu = (-1)^{\ell+\ell'+L} \left( \ell'' || C^{(2)} || \ell \right) \left( \ell_k || C^{(2)} || \ell' \right) \left\{ \ell'' \ell_k L \atop \ell' \ell \nu \right\}$$

(7)

and

$$e_\nu = (-1)^{\ell_k+\ell'+L} \left( \ell'' || C^{(2)} || \ell' \right) \left( \ell_k || C^{(2)} || \ell \right) \left\{ \ell'' \ell_k L \atop \ell \ell' \nu \right\}.$$ 

(8)

Here, $\langle \ell || C^{(2)} || \ell' \rangle$ is the reduced matrix element of the spherical harmonic, multiplied by $[4\pi/(2\nu + 1)]^{1/2}$ [2].
III. RESULTS AND DISCUSSION

We have calculated the Auger transition probabilities for spherical (closed-shell) Na$_N$, Na$_N^+$ and Na$_N^-$ clusters with $19 \leq N \leq 253$. For each cluster we have determined first the effective potential $V_{\text{eff}}(\vec{r})$, the bound Kohn-Sham states ($\{\varepsilon_{n\ell} < 0\}$) and the corresponding radial eigenfunctions $\{R_{n\ell}(r)\}$. For a given vacancy $n''\ell''$ we calculated the number of possible final states $\{n\ell, n'\ell'\}$. For each of the final states we determined the energy $\varepsilon_k$ of the emitted electron and the different possible values of its angular momentum $\ell_k$. Then, for each $\ell_k$, we determined the corresponding outgoing radial wave function. This allowed us to calculate the Coulomb matrix elements and, using Eq. (6), the probability $w(n\ell, n'\ell', n''\ell'')$. Finally, we have calculated the total probability for an initial vacancy $n''\ell''$ as $W(n''\ell'') = \sum_{\ell\ell'} w(n\ell, n'\ell', n''\ell'')$. The total probabilities $W(n''\ell'')$ can, of course, also be expressed as an energy width $[\Sigma_A(n''\ell'') = \hbar/W(n''\ell'')]$ or as a lifetime $[\tau_A(n''\ell'') = W(n''\ell'')^{-1}]$.

The first interesting result of our study is that, within the approximation used in Eq. (5) for the exchange and correlation term (LDA), for neutral and positively charged spherical sodium clusters intraband Auger processes are energetically forbidden. There is no possible transition $n''\ell'', n\ell, n'\ell'$ yielding $\varepsilon_k > 0$. This means that, according to our LDA calculations, excited spherical Na$_N^+$ and Na$_N^-$ clusters can only decay via fragmentation (evaporation) or photon emission.

Our results for negatively charged sodium clusters indicate that, in contrast to what occurs for Na$_N^+$ and Na$_N^-$, nonradiative electronic decay is possible. Due to the presence of the extra electron and the consequent extra Coulomb repulsion, the binding energy of the electrons in negatively charged clusters is smaller than in neutral or positively charged ones. As a consequence the whole band of bound states is shifted upwards and makes possible Auger transitions with $\varepsilon_k > 0$. An example of such Auger transitions for negatively charged sodium clusters is illustrated schematically in Fig. 1. Note that the Kohn-Sham effective potential $V_{\text{eff}}(r)$ shows a barrier for negatively charged clusters. This might have consequences for the magnitude of the nonradiative emission probabilities. For instance, the
wave function of an emitted Auger-electron with positive energy but smaller than the energy barrier could have a large weight inside the cluster due to trapping effects and influence the transition matrix elements used to calculate \( W \). For holes in the first two shells of \( \text{Na}_N^- \) there are many possible transitions. For instance, there are 6 ways of filling a 1\( s \)-vacancy in \( \text{Na}_{39}^- \) by emitting an electron. For \( \text{Na}_{91}^- \) the number of such transitions is 11; for \( \text{Na}_{137}^- \), 14, and for \( \text{Na}_{253}^- \), 19.

Our calculated Auger widths of \( \text{Na}_N^- \) clusters are, for some cluster sizes, of the order of \( 10^{-1} \) eV, i.e., as large as for light atoms. In Fig. 2 the Auger life-time of a hole in the first (1\( s \)) and second (1\( p \)) shells of spherical \( \text{Na}_N^- \) clusters is shown as a function of the cluster size. The size dependence of \( \tau_A(1s) \) and \( \tau_A(1p) \) is very rich and shows no monotonical behavior. Furthermore, the life-times oscillate over many orders of magnitude. For instance, an initial 1\( s \)-hole in excited \( \text{Na}_{39}^- \) and \( \text{Na}_{67}^- \) lives only few femtoseconds, almost as short as a 1\( s \)-vacancy in light atoms with \( Z < 10 \) \[2\]. For these clusters the Auger emission is faster than any other deexcitation mechanism. This means that one can separate the time scales for the electronic and atomic relaxation. Thus, if one is interested in studying, for instance, the atomic motion after optical excitation of \( \text{Na}_{39}^- \) and \( \text{Na}_{67}^- \), one can assume that the Auger process occurs immediately after the excitation and has no further influence on the fragmentation (evaporation) behavior. On the other hand, \( \tau_A(1s) \) for \( \text{Na}_{57}^- \) and \( \tau_A(1p) \) for \( \text{Na}_{39}^- \) and \( \text{Na}_{57}^- \) are remarkable large, of the order of nanoseconds, i.e., larger than the life-times for any other deexcitation channel. For this other extreme case one can again separate the time scales and assume that the hole lives infinitely long (compared with the atomic relaxation).

However, it is not always possible to perform this separation of time scales. Fig. 2 also shows that for most cluster sizes \( \tau_A \) lies between pico- and nanoseconds. This magnitudes are comparable to the Auger life-times of positively charged ions approaching a metal surface at a distance of at least 2 Å \[7\]. This time scale is probably in the range in which excited clusters fragment \[8\]. Thus, results of Fig. 2 suggest that there might be competition between Auger-emission and fragmentation channels for a vacancy in a deep shell of a \( \text{Na}_N^- \) cluster.
In Fig. 3 the Auger life-time for initial vacancies in the different electronic shells of Na\textsuperscript{137} are shown. The solid line shows results obtained from the calculations as described before, whereas the dashed curve shows results obtained including relaxation effects in the final state (shake-off). The final state of the cluster corresponds actually to a system with \(N - 1\) electrons. This should have an influence on the Kohn-Sham levels, reflecting the fact that the many electron system relaxes due to the excess nuclear positive charge. For the cluster sizes considered, which have closed shells in the initial state, the final state with \(N - 1\) electrons is no longer a closed-shell system and cannot be calculated using the spherical jellium model \cite{1}. Thus, in order to take into account the relaxation effects we performed the following approach, commonly used in atomic physics \cite{2}. We considered for both the initial and the final state a cluster with \(N\) electrons, i.e., a closed-shell configuration. However, for the final state we solved the Kohn-Sham problem for a positive jellium background with charge \(Q = |e|(N + 1)\). In this way we simulated the excess charge. The relaxation effects calculated within this approach do not change the qualitative trend of the results, neither for the size dependence nor for the shell dependence (for fixed size) of the Auger life-times, as seen in Fig. 3. Regarding the shell-dependence of \(\tau_A\) for the different cluster sizes studied, there is no clear dependence on the level of the initial vacancy. \(\tau_A(1s)\) is in most cases the smallest life-time. For some clusters \(\tau_A(m)\) shows an alternation for increasing shell number \(m = 1, 2, ...,\) like for Na\textsuperscript{137}. For other cluster sizes there is a monotonic increase of \(\tau(m)\) with \(m\). In general one would expect a monotonic increase of the life-time, since the Coulomb matrix elements [Eq. (2)] should decrease with increasing kinetic energy of the Auger electron. However, due to the potential barrier shown in Fig. 1 and discussed below, for some values of \(\varepsilon_k\) (resonances) the corresponding wave function could have a particular large weight inside the cluster, giving rise to deviations from the monotonic dependence of \(\tau_A\) with energy. The potential barrier for Na\textsuperscript{137} is 0.7 eV high.

In Fig. 4 we show the distribution \(P(\varepsilon)\) of the emitted Auger-electrons as a function of their kinetic energies for Na\textsuperscript{137} and Na\textsuperscript{253}. \(P(\varepsilon)\) is calculated as
\[ P(\varepsilon) = \frac{A\gamma}{2\pi} \sum_{\ell,\ell',\ell''} \frac{w(n\ell, n'\ell', n''\ell'')}{(\varepsilon - \varepsilon_{klk})^2 + (\gamma/2)^2}, \]  

where \( \varepsilon_{klk}(n\ell, n'\ell', n''\ell'') \) is the energy of the electron emitted in the \((n\ell, n'\ell', n''\ell'')\)-Auger process, and the width \( \gamma \) is taking to be 0.05 eV. \( A \) is a normalization constant. In both cluster sizes \( P(\varepsilon) \) is dominated by electrons originated in few transitions with large probability. For Na\(_{137}\) the large peak at 1.23 eV corresponds to a \((1s, 3p, 3p)\)-transition, whereas the smaller peak at 0.66 eV results from a \((1d, 3p, 3p)\)-process. For Na\(_{253}\) the Auger spectrum is dominated by the \((1p, 2h, 2h)\)-process with a kinetic energy of 0.5 eV, while a smaller peak appears at 0.99 eV which corresponds to the \((1s, 4s, 2h)\)-transition. These two examples are consistent with the intuitive idea that the most probable Auger processes are those involving two electrons at the Fermi-level (3\(p\) for Na\(_{137}\), and 2\(h\) in the case of Na\(_{253}\)). Results of Fig. 4 remain unchanged if we take into account shake-off effects. Note that the kinetic energies of the emitted electrons are, for all clusters studied, not smaller than 0.4 eV and not larger than 1.5 eV, which is roughly the difference between the bandwidth and the ionization potential of the clusters. Thus, the kinetic energies of the Auger electrons concentrate in a narrow energy range. Comparison with the experimental results by Ganteför et al \[3\] leads us to argue that the photoelectron signal which cannot be explained as coming from direct photoemission or thermionic effects is due to intraband Auger processes. Regarding a comparison with experimental results by Reiners and Haberland \[4\], one can see in Fig. 2 that the Auger life-time of a vacancy in the 1\(s\)-shell, \( \tau_A(1s) \), of Na\(_{91}\) is approximately 100 ps, whereas \( \tau_A(1p) \sim 10 \) ps. Since the time scale for evaporation is probably larger than these values, our calculations suggest an explanation for the fact that light induced evaporation in Na\(_{91}\) takes place within a photon-energy range which is smaller than the bandwidth.

It is important to point out that our results are not sensitive to the particular form of the functional used for the exchange and correlation term. We have found neither qualitative nor appreciable quantitative differences by using the LDA functionals terms proposed by Wigner \[10\], Gunnarson-Lundqvist \[11\], and the parametrizations by Perdew-Zunger \[12\] and Vosko et al \[13\] to the Monte-Carlo calculations of Ceperley and Alder \[14\].
We have also performed a Hartree-Fock (HF) calculation of the energy levels [15]. In contrast to the results obtained using LDA, the HF-treatment of the exchange term yields that Auger-transitions for neutral and positively charged clusters are energetically allowed. However, the number of possible transitions in Na\textsubscript{N} is much smaller than in Na\textsubscript{N}\textsuperscript{−}, and for Na\textsubscript{N}\textsuperscript{+} there are just a few Auger-processes. Thus, the HF-calculation confirms the general trends obtained using LDA.

IV. SUMMARY AND OUTLOOK

We have calculated the intraband Auger-decay probabilities of spherical sodium clusters. Our results suggest that, for certain cluster sizes, there could be a competition between non-radiative electronic and atomic deexcitation channels. We found that the Auger-probabilities of small metal clusters are remarkably different from the atomic ones. In view of the results presented in this paper it remains an interesting problem to study intraband Auger-probabilities in nanostructures and films and to compare them with the case of small clusters. Also the study of spin-dependent Auger-processes in small magnetic clusters appears as a possible interesting extension of this work.

V. ACKNOWLEDGEMENTS

This work has been partially supported by the Spanish Government through the grant PB95-0492, and by the Deutsche Forschungsgemeinschaft through the Schwerpunkt “Femtosekundenspektroskopie”.
REFERENCES

* on leave of absence from Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

[1] U. Frenzel, U. Kalmbach, D. Kreisle and E. Recknagel, Surf. Rev. Lett. 3, 505 (1996).

[2] W. Bambynek, B. Crasemann, R. W. Fink, H.-U. Freund, H. Mark, C. D. Swift, R. E. Price and P. Venugopala Rao, Rev. Mod. Phys. 44, 716 (1972), and references therein.

[3] G. Ganteför, W. Eberhardt, H. Weidele, D. Kreisle and E. Recknagel, Phys. Rev. Lett. 77, 4524 (1996).

[4] Th. Reiners and H. Haberland, Phys. Rev. Lett. 77, 2440 (1996).

[5] W. Ekardt, Phys. Rev. Lett. 52, 1925 (1984).

[6] M. P. Iñiguez, C. Baladrón and J. A. Alonso, Surf. Sci. 127, 367 (1983).

[7] R. Monreal and N. Lorente, Phys. Rev. B 52, 4760 (1995).

[8] C. Bréchignac, Ph. Cahuzac, J. Leygnier and A. Sarfati, Phys. Rev. Lett. 70, 2036 (1993).

[9] W. Ekardt and Z. Penzar, Phys. Rev. B 38, 4273 (1988).

[10] E. P. Wigner, Phys. Rev. 46, 1002 (1934).

[11] O. Gunnarson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[12] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[13] S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. B 58, 1200 (1980).

[14] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).

[15] E. Lipparini, Ll. Serra and K. Takayanagi, Phys. Rev. B 49, 16733 (1994).
FIGURES

FIG. 1. Schematic illustration of the Auger emission in a Na$_X^-$ cluster with a vacancy in a deep electronic shell. Note that the Kohn-Sham effective potential $V_{\text{eff}}(r)$ shows a barrier, in contrast to the case of neutral or positively charged clusters. The Auger probability for this particular process is given by the exchange matrix element $\langle k, n''\ell'' | \hat{V} | n\ell, n'\ell' \rangle$ (see text). The direct Auger transition is obtained by exchanging the indices $n'\ell'$ and $n\ell$.

FIG. 2. Size dependence of the Auger life-time (in picoseconds) for a hole in the a) first shell (1s), b) second shell (1p) of spherical Na$_X^-$ clusters.

FIG. 3. Auger life-time for holes on different shells of Na$_{137}^-$. The dashed line refers to calculations taking into account relaxation effects for the final state.

FIG. 4. Auger electron distribution $P(\varepsilon)$ as a function of the electron kinetic energy for a) Na$_{137}^-$, and b) Na$_{253}^-$. 
Energy

$\varepsilon_F$

occupied states

$V_{\text{eff}}(r)$

cluster radius
\textbf{Na}_n^-

\textit{1\textsuperscript{st} shell}

\textbf{Na}_n^-

\textit{2\textsuperscript{nd} shell}

Cluster Size

Life-time (ps)

(a)

(b)
(a) $N=137$

(b) $N=253$