Radiative electron attachment in sodium clusters

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The electron attachment to bound unoccupied levels of spherical neutral Na_n clusters ($n=8$, 20, and 40) is analyzed using electron-cluster collisions. In the direct process here studied the captured electron loses its energy in a single step via the emission of a photon. The aim of the present paper is to estimate the strength of this inverse photoemission (IP) mechanism, and its contribution to the total inclusive inelastic cross section recently measured. We perform a quantum-theoretical calculation for incoming electrons in the range 0–2 eV. The magnitudes of the total IP cross sections are dominated by transitions to the less bound unoccupied levels while their patterns depend mainly on quasibound states in the incoming channel. It is found that in the range of incoming energies here analyzed the IP process has a negligible contribution to the inelastic inclusive experimental data. [S1050-2947(98)00110-3]

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I. INTRODUCTION

Collisions between electrons and atomic clusters provide a powerful tool to study several properties of the cluster. In the last few years many theoretical papers have investigated, from a quantum-mechanical point of view, some of these processes. The simplest analyzed collision was the elastic [1–3] in which the incident electrons do not transfer energy, mass, or charge. But as is well known, other complex processes can occur. Between them, recent papers [4,5] have studied a particular inelastic collision where energy is transferred to the target promoting a valence electron from a level under the Fermi surface to another level above it. Also the excitation of the collective plasmon states of the clusters has been analyzed in the framework of the electron scattering theory [6].

Electron-cluster collisions have also gained the attention of experimentalists who measured, using cluster beam depletion spectroscopy, absolute total (inclusive) inelastic electron-sodium cross sections, in the energy range 0.1 eV to $\simeq 6$ eV [7–10]. There exist different mechanisms which can remove a neutral Na cluster from the beam. For low electron energies (less than bound and ionization energies) the dominant process is probably the capture or attachment of the incident electron and the temporary formation of a Na_n^- system followed by some relaxation process. On the other hand, for impact energies above $\simeq 1$ eV, the incident electrons can produce primary cluster fragmentation.

In this paper we want to study a particular process related to the electron attachment in which the incident electron loses a discrete amount of energy from the continuum state by making a direct transition to a bound unoccupied level via the emission of a photon. This kind of attachment or more precisely, inverse photoemission (IP) process, provides information on the state into which the electron falls. We will here estimate the contribution of IP process to the inclusive inelastic electron scattering cross section reported in Ref. [7].

II. FORMALISM

In a proper theoretical description of the process the Hamiltonian describing the e^--photon interaction has the form (neglecting spin and treating up to first order)

$$H_{\rm int}=-\frac{e}{2m_e c}[\vec{p}\cdot\vec{A}+\vec{A}\cdot\vec{p}], \tag{1}$$

where $\vec{A}$ is the vector potential of electromagnetic radiation and $\vec{p}$ is the linear momentum vector of the incoming electron. In the case of inverse photoemission the initial state has no photon, so photons are created in the process. It becomes necessary to quantize the electromagnetic field. The classical vector potential $\vec{A}$ is replaced by the field operator $\vec{A}(\vec{x},t)$ defined by

$$\vec{A}(\vec{x},t)=\frac{1}{\sqrt{V}}c\sqrt{\frac{2\pi\hbar}{\omega}}\sum_{\vec{k}}\sum_{\alpha}\,[a_{\vec{k},\alpha}(t)\hat{\epsilon}^{(\alpha)}e^{i\vec{k}\cdot\vec{x}} + a^{\dagger}_{\vec{k},\alpha}(t)\hat{\epsilon}^{(\alpha)}e^{-i\vec{k}\cdot\vec{x}}], \tag{2}$$

where $\hat{\epsilon}^{(\alpha)}$ ($\alpha=1,2$), the linear polarization vectors, are real unit vectors whose directions form a right-handed set with the photon propagation direction of the vector $\vec{k}$. The two operators $a^{\dagger}_{\vec{k},\alpha}$, $a_{\vec{k},\alpha}$ either create or destroy a photon in the state $(\vec{k},\alpha)$, respectively, and V is the normalization volume for the photon.

For inverse photoemission the initial state $\chi_i(\vec{q},\vec{r})$ (with no photons) represents the incoming electron moving in the mean field created by the cluster. The final state consists of an electron in a bound state $\chi_f(\vec{r})$ above the Fermi level and an outgoing photon, emitted in any direction with wave vector $\vec{k}$ where $|\vec{k}|=w/c$:

$$\chi_i(\vec{q}_i,\vec{r})=\frac{4\pi}{q_i r}\sum_{\ell',m'} i^{\ell'} f_{\ell'}(q_i,r)Y^{*}_{\ell' m'}(\hat{q}_i)Y_{\ell' m'}(\hat{r}), \tag{3}$$

$$\chi_f(\vec{q}_f,\vec{r})=\frac{u_{n\ell}(q_f,r)}{r}Y_{\ell m}(\hat{r}), \tag{4}$$

with q_i (q_f) the wave vector of the incoming (attached) electron of energy E_i (E_f) related by $E_i - E_f = \hbar\omega$. The radial wave functions $f_{\ell'}(q_i,r)/q_i r$ and $u_{n\ell}(q_f,r)/r$ are obtained solving numerically the same one electron Schrödinger equation with the potential

$$V(r) = V_{\mathrm{LDA}} - \frac{\alpha_p e^2}{2(r^2+d^2)^2}. \tag{5}$$

In Eq. (5), V_{LDA} is the mean field potential resulting from the solution of the Kohn-Sham equations in the local density approximation in the context of the jellium model [11] which was extensively and successfully used in cluster theory and it is still being used in more refined collision calculations [12]. In the scope of the present approach the jellium model provides a rough estimation of the magnitude of the IP cross section. We know that for dynamical quantities based on off-diagonal matrix elements such as the dipole transition calculated in this paper, the agreement among results from different potentials is qualitative. Details (but not the order of magnitude) quantitatively depend on the dynamics, that is, on the wave functions which could show some differences in each potential. The second term of Eq. (5) accounts for the polarization induced in the cluster by the incoming electron. In the approximation here adopted [13], α_p is the static electric polarizability of the cluster and d is a cutoff parameter of the order of the cluster size. In the following we will use the experimental values of α_p of Ref. [14] (in the calculations we assume atomic units for which $\hbar = m_e = e = 1$, $c \simeq 137$, and a_0 is the Bohr radius).

Making use of the time-dependent perturbation theory up to first order in the interaction [15–17], the transition probability with emission of photons into a solid angle $d\Omega$ per unit time can be written as

$$W_{fi} = \frac{V\omega^2}{\hbar^2 4\pi^2 c^3} \times \left| -\frac{e}{m_e}\sqrt{\frac{2\pi\hbar}{\omega V}}\,\langle f|a^{\dagger}_{\vec{k},\alpha}(0)e^{-i\vec{k}\cdot\vec{x}}\vec{p}\cdot\hat{\epsilon}^{(\alpha)}|i\rangle\right|^2 d\Omega, \tag{6}$$

where the initial and final vector states are the direct product of the corresponding electron state and photon state $|n_{\vec{k},\alpha}\rangle$. Introducing Eqs. (3) and (4) and taking into account that there are photons only in the final state, the matrix element, in the dipolar approximation, i.e., assuming $e^{-i\vec{k}\cdot\vec{x}} \simeq 1$, results:

$$\begin{aligned}\langle f|a^{\dagger}_{\vec{k},\alpha}(0)e^{-i\vec{k}\cdot\vec{x}}\vec{p}\cdot\hat{\epsilon}^{(\alpha)}|i\rangle &\simeq \langle\chi_f|\vec{p}\cdot\hat{\epsilon}^{(\alpha)}|\chi_i\rangle \\ &= -\frac{i\omega m_e 16\pi^2}{3}\sum_{\ell' m' \nu}\frac{i^{\ell'}}{q_i} \\ &\quad\times Y^*_{1\nu}(\hat{\epsilon}^{(\alpha)})Y^*_{\ell' m'}(\hat{q}_i) \\ &\quad\times R_{n\ell\ell'}(q_i)I_{\nu\ell' m'},\end{aligned} \tag{7}$$

where $I_{\nu\ell' m'}$ and the radial integral $R_{n\ell\ell'}(q_i)$ are, respectively,

$$I_{\nu\ell' m'} = (-1)^{m+\nu}\sqrt{(2\ell+1)(2\ell'+1)} \times \sqrt{\frac{3}{4\pi}}\begin{pmatrix}\ell & 1 & \ell'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell & 1 & \ell'\\ -m & -\nu & m'\end{pmatrix}, \tag{8}$$

$$R_{n\ell\ell'}(q_i) = \int u^*_{n\ell}(r) f_{\ell'}(q_i,r) r\,dr. \tag{9}$$

The differential cross section is obtained from Eq. (6) dividing by the incident electronic flux $j = (\hbar q_i/m_e)(1/V_e)$, where V_e is the box volume of normalization of the continuum electron state:

$$\frac{d\sigma_{n\ell}}{d\Omega} = \frac{2(4\pi)^2 e^2\omega^3(2\ell+1)}{c^3\hbar j 3q_i^2}\sum_{\alpha,m',m}|Y_{1,m-m'}(\hat{\epsilon}^{(\alpha)}) \times\{Y^*_{\ell+1,m'}(\hat{q}_i)G^{+}_{\ell mm'} + Y^*_{\ell-1,m'}(\hat{q}_i)G^{-}_{\ell mm'}\}|^2, \tag{10}$$

with

$$G^{\pm}_{\ell mm'} = \sqrt{2(\ell\pm1)+1}\; i^{\ell\pm1}R_{n,\ell,\ell\pm1}\begin{pmatrix}\ell & 1 & \ell\pm1\\ 0 & 0 & 0\end{pmatrix} \times\begin{pmatrix}\ell & 1 & \ell\pm1\\ -m & m-m' & m'\end{pmatrix}. \tag{11}$$

Integrating over the angles $\hat{q}_i$, averaging over the photon polarization directions, and using normalized continuum and bound electron wave functions, the integrated cross section for the capture of an electron into a particular final bound state (n,ℓ) is given by

$$\sigma_{n\ell}(q_i) = \frac{16\pi m_e e^2\omega^3(2\ell+1)}{c^3\hbar^2 3q_i^3}\sum_{m',m}\{|G^{+}_{\ell mm'}|^2 + |G^{-}_{\ell mm'}|^2\}. \tag{12}$$

Thus the total IP cross section can be obtained computing the sum of the cross sections for the allowed (n,ℓ) final states at a given incident electron energy:

$$\sigma_{\mathrm{tot}}(q_i) = \sum_{(n,\ell)}\sigma_{n,\ell}(q_i). \tag{13}$$

III. RESULTS AND DISCUSSION

In the present paper we perform calculations for a particular capture process on Na_8, Na_{20}, and Na_{40} clusters. Figure 1 shows a schematic diagram of IP mechanism and displays also the single particle bound states obtained using the potential of Eq. (5) for the Na_8 which is shown in the inset of Fig. 1. For this cluster we have analyzed the features of the main components which give rise to the total IP cross section of Eq. (13). We first studied the radial form factors, i.e., the integrand of Eq. (9) for each possible final state. They contain useful information about the magnitude and spatial distribution of the capture process to a single (n,ℓ) bound state and they allowed us to conclude (a) for unoccupied states close to the Fermi level the capture process has a considerable probability to occur around the cluster surface, mean-

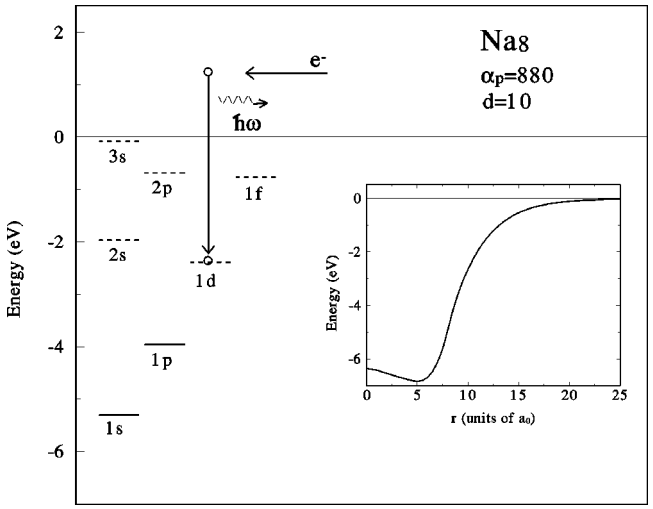

FIG. 1. Schematic diagram of the electron attachment process with emission of a photon. The bound levels correspond to the Na_8 target. The solid lines represent the occupied states and the dashed lines unoccupied states. The potential V_{LDA} plus the polarization term, for this system, is displayed in the inset.

while, for the less bound levels, the spatial distributions are spread out of the cluster. As an example we show in Fig. 2 the integrand at incoming energies 0.028 eV, 0.070 eV, 0.628 eV, and 1.50 eV for the $2s$ state (close to the Fermi surface) and for the $3s$ state which is near the continuum. (b) The form factors and, in consequence, their radial integrals increase considerably at some energies which are correlated

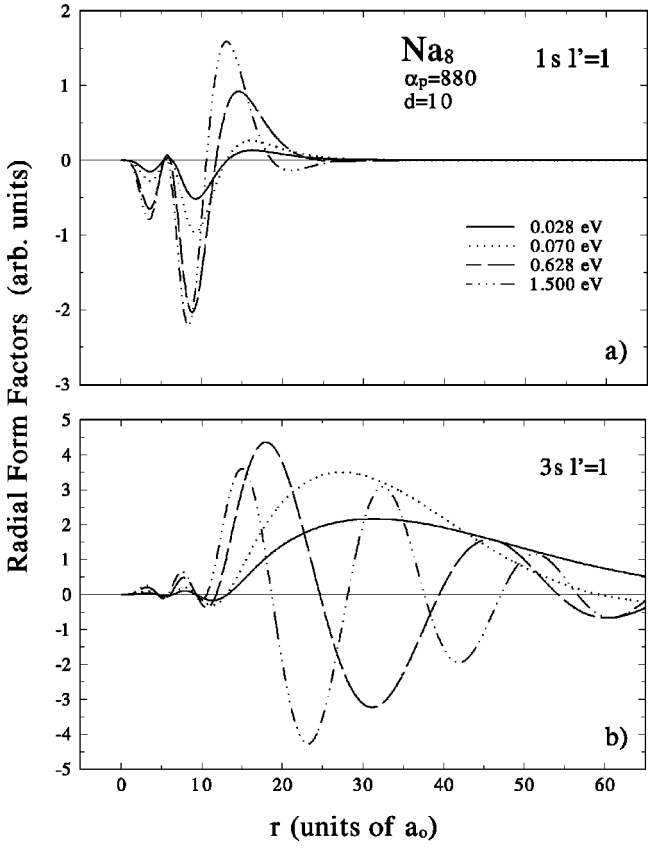

FIG. 2. Radial form factors for the system e^--Na_8 at different final states for some particular incident energies.

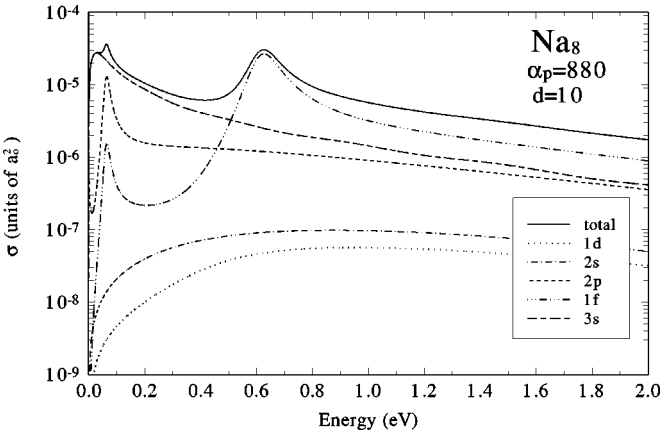

FIG. 3. Total and individual cross sections for the capture of an electron into final states n,ℓ in the Na_8 cluster.

with the energies and angular momentum of the elastic resonances discussed in Refs. [1, 4]. For the Na_8, from the analysis of these radial integrals $R_{n\ell\ell'}$ [Eq. (9)] it was found that when $\ell'=2$ is involved (according to selection rules this is the case for p or f bound levels) there is a strong maximum for incident energies around 0.07 eV where an elastic resonance occurs. Also the $\ell'=4$ is important around $E=0.628$ eV. These maxima are related with the maxima in the partial cross section for elastic electron scattering and are associated with the presence of quasibound states at those energies. If no resonance exists the radial integrals decrease for increasing incoming energies. Another general feature is that the most important contribution arises from the levels near the continuum. This effect can be observed in Fig. 3, which displays the full calculation for $\sigma_{n\ell}$ and σ_{tot} for energies ranging from 0.01 eV up to 2 eV. In this case, the main contributions to the total IP cross section arise from the $3s$ and $1f$ levels which are within the less bound states and the pattern depends on the presence of peaks in the partial contributions related with ℓ' resonances in the corresponding elastic process. The contributions to the capture to levels near to the Fermi surface are almost negligible. They are two or three orders of magnitude lower with respect to the capture in the states near the continuum.

We have made the same calculations and studies for Na_{20} and Na_{40} clusters as a function of the electron incoming energies. In the Na_{20} cluster the total IP cross section results from the sum of the transitions to the unoccupied levels considered, $1f$: -2.753 eV; $2p$: -2.115 eV; $1g$: -1.458 eV; $2d$: -0.946 eV; $3s$: -0.894 eV; $3p$: -0.182 eV; $1h$: -0.118 eV; $2f$: -0.044 eV; and in the Na_{40} cluster corresponds to the sum of the capture to the levels: $1g$: -3.023 eV; $2d$: -2.242 eV; $3s$: -2.011 eV; $2f$: -1.219 eV; $3p$: -1.039 eV; $1i$: -0.865 eV; $4s$: -0.313 eV; $3d$: -0.292 eV; $2g$: -0.291 eV. The overall magnitude and structure of the total cross sections obtained, as in the case of Na_8, were mainly determined by the strength and resonances which appear in the transitions to the less bound levels. Figure 4 displays a comparison of the total cross sections for the three considered systems. For the Na_8 the average value of the total cross section is around $10^{-5}a_0^2$. A similar strength was obtained in Ref. [16] for IP processes in adsorbed molecules. For the Na_{20} the average magnitude

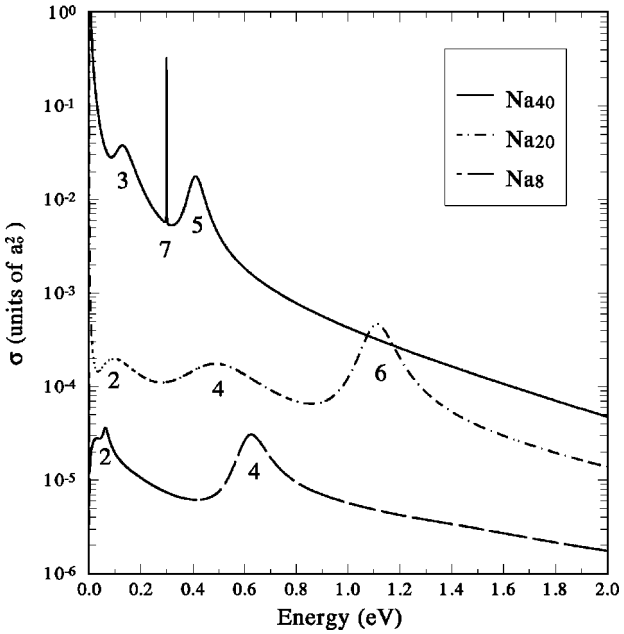

FIG. 4. Comparison of the total cross sections for the three clusters Na_n ($n=8$, 20, and 40). The numbers under the peaks correspond to the ℓ' values associated with the maxima and resonances of the elastic scattering.

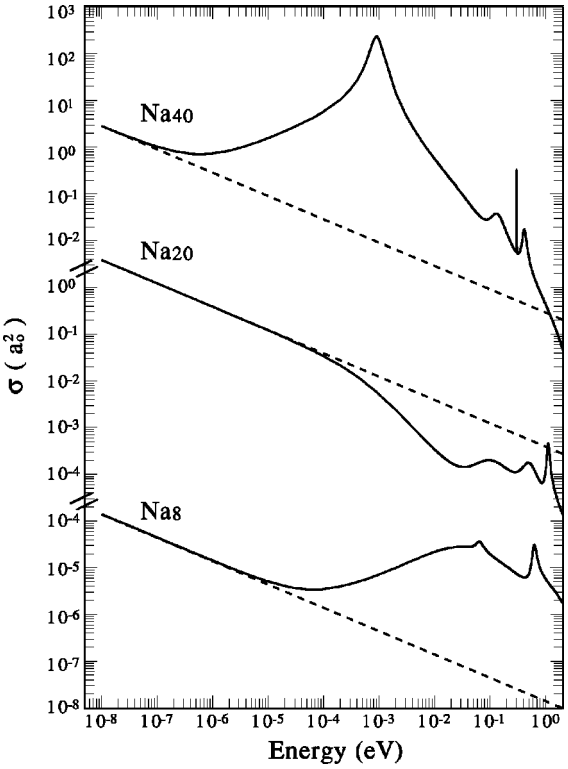

FIG. 5. Attachment cross sections for very low incoming electron energies for the three clusters here presented. Dashed lines represent the $1/q$ dependence predicted by the scattering theory at very low energies.

is $\sim 10^{-4} a_0^2$ and for Na_{40} it is approximately $10^{-3} a_0^2$ although it decreases two orders of magnitude at incident energies of 2 eV. This figure shows how the magnitude increases with the cluster size, in particular for energies lower than 0.6 eV where the IP process is relevant. This behavior can be understood in terms of the higher density of single particle states around zero (which have the most important contribution to the cross section) when the mass of the cluster increases. Thus it is expected that this trend persists for clusters with number of atoms greater than 40.

We have also investigated the theoretical behavior of the IP process at very low incoming energies as is shown in Fig. 5. At these energies only the scattering *s*-partial wave survives, populating the bound *p* levels and verifying the well known rule about the inverse variation with q of the low energy inelastic cross sections. This is obtained for Na_8, Na_{20}, and Na_{40} at energies less than 10^{-5} eV, 10^{-4} eV, and 10^{-7} eV, respectively, where the corresponding elastic dispersion is constant [see Figs. 5(a) and 8(a) of Ref. [1]].

We want to remark that the use of more reliable *ab initio* calculations to obtain the single particle energies and wave functions (which are very difficult to perform for the systems Na_{20} and Na_{40}) would not change the qualitative conclusions of the present paper with respect of the magnitude of the IP cross section. Such *ab initio* calculation or the use of other more refined potentials will have the effect of some shifting in the positions of the peaks in the IP cross sections.

In view of the large amount of experimental work on photoelectron spectroscopy of metal clusters (see Ref. [18]), it is interesting to compare the IP process with the one for the photoemission of the corresponding anion cluster Na_n^-. Assuming that the matrix elements of Eq. (6) are the same for both processes the rate between them can be written as $R=\omega^2/c^2 q_i^2$, which for the clusters here studied results approximately in the order of 10^{-6} at energies near resonances. The cross section for the photoemission would also be expected to present resonances now associated with quasibound states in the exit channel.

According to the results obtained it can be deduced that the one step inverse photoemission process has a negligible contribution in the experimental inclusive inelastic results of Ref. [7]. The electron capture referred to in [7] probably involves the creation of a resonant electron-cluster system followed by relaxation processes which differ from the emission of one photon here presented.

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