Photon Energy Dependent Valence Band Response of Metallic Nanoparticles

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We show that the valence band response to photon impact in metallic nanoparticles is highly energy dependent. This is seen as drastic variations of cross sections in valence photoionization of free and initially charge-neutral nanosized metal clusters. The effect is demonstrated in a combined experimental and theoretical study of Rb clusters. The experimental findings are interpreted theoretically using a jellium model and superatom description. The variations are attributed to the changing overlap with the photon energy between the wave functions of diffuse delocalized valence electrons and continuum electrons producing a series of minima in the cross section.

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Clusters constitute an intermediate phase between single atoms and solid state, and their properties evolve from atomic and molecular to bulklike as a function of size. In addition to exhibiting characteristics of these two extremes, clusters may have unique features not seen in other forms of matter. For unraveling these properties, research on clusters is an active area of science gaining endeavoring interest (see, e.g., [1–3]). For example, at certain conditions free clusters can be described as artificial atoms [4] or superatoms [5], where the wave functions of valence electrons are described utilizing tools known from atomic physics.

Photoelectron spectroscopy is a unique tool for mapping the electronic structure of nanoscale clusters. Most of the electronic structure studies on clusters have been carried out using conventional laser ionization [6], where the photon energy and its tunability are limited to the lower uv range. The energy limitations of lasers can be overcome using synchrotron radiation. The studies in the vuv to x-ray region so far have been performed mainly for rare-gas clusters and for the core levels (see, e.g., [7–10] and references therein).

A major part of the cluster studies concerns the evolution of properties as a function of cluster size. During recent years, an interest in the energy dependence of the photon-cluster interaction has emerged. Photon energy dependent studies using x-ray sources have been done for rare-gas clusters [11–14] and fullerenes [15–18]. Also, the energy dependence of photoelectron angular distribution of size-selected clusters close to the ionization threshold have been recently studied [3,19]. Interestingly, the valence-level cross sections have been observed to oscillate as a function of photon energy in C_{60} [15,16], C_{70} [17], and recently in some large molecules [20]. Similar oscillations have been also predicted to occur in free Na clusters [21–24], but hitherto have not been confirmed experimentally.

In the present Letter we report an experimental and theoretical study of the energy dependence of the valence band response to the photon impact in a resonance-free region far above the ionization threshold in nonsupported metallic nanoparticles. We show that the ionization cross sections of the valence levels oscillate drastically as a function of impact energy producing a series of minima. Rb has been chosen to display the effect due to its close-to ideal free-electron metallic character. The experimental observations are interpreted using jellium model calculations, which provide an understanding for the phenomenon. The experimental findings are interpreted as stemming from the oscillatory canceling of the r-weighted overlap between the bound electron jellium orbitals and continuum wave functions in the transition-matrix integral. The result highlights that the description of the valence structure of metallic clusters as an artificial atom provides good qualitative understanding for the observations.

The experimental work was carried out at the soft x-ray beam line I411 at MAX-laboratory, Lund, Sweden. The Rb clusters were produced using an exchange metal cluster source [25]. In the setup, a primary beam of rare-gas clusters is let through the atomic metal vapor that generates metal clusters in a pickup process. For further details of the setup, see Refs. [25,26]. In the present work Ar clusters were created by 2.0 bar Ar expansion through a liquid nitrogen cooled nozzle. The atomic Rb vapor was produced using a resistively heated oven at a temperature of 120 °C. The Rb vapor pressure inside the crucible was in the range 10^{-2}–10^{-3} mbar. The mean size of Rb clusters in the beam was estimated to be about $90(\pm 20)$ atoms. The size was obtained from the $4p$ core-level photoelectron spectrum of Rb clusters using a quantum-corrected conduction sphere approximation for clusters [27]. The stability of the clustering conditions was monitored by recording the $4p$ cluster spectrum between the valence-region scans. The photoelectrons were detected using a Scienta R4000 hemispherical electron energy analyzer. In order to obtain intensities proportional to the total photoionization cross sections, the electron spectra were measured at the so-called magic angle 54.7° with respect to the electric field vector of the linearly polarized synchrotron radiation. The photon energies used to carry out the experiment were 40.2, 48.6, and 58.6 eV. The experimental broadening including the analyzer contribution and photon energy bandwidth was about 150 meV.

In order to describe the energy dependence of the valence band response to photon impact, the calculation of the bound and continuum electron wave functions, as well as the photon-cluster interaction matrix elements even far above the ionization threshold are needed. This was highlighted in our recent paper [26] where the photoionization of K and Rb clusters was studied at a single photon energy. In the present work we have applied the jellium model approximation for clusters [26,28,29], and the so-called superatom description in the calculation of the wave functions.

In the present calculations, the radial parts of the valence jellium orbitals are calculated by replacing the Hartree-Fock mean field created by the nuclei and other electrons by a spherical well potential. The potential is parametrized by the cluster radius R_0 and the well depth V_0. Outside the well the potential is assumed to be a constant for the bound states and an r dependent Coulomb tail for continuum states. The potential in atomic units is given by

$$V(r) = \begin{cases} -V_0, & \text{if } r \leq R_0 \\ 0, & \text{if } r > R_0 \text{ (bound)} \\ -1/r, & \text{if } r > R_0 \text{ (continuum).} \end{cases} \tag{1}$$

The well radius is calculated using the relation $R_0 = r_s N^{1/3} + \delta_s$ and the depth using the expression $V_0 = \frac{1}{2}(\frac{9}{4}\pi N R_0^{-3})^{2/3} + W_N$ [29]. In these equations r_s is the Wigner-Seitz radius, δ_s is the spillout parameter, and N is the size of the cluster. W_N is the average ionization potential given by $W_{\text{wf}} + (\frac{1}{2} + c)R_0^{-1}$, where W_{wf} is the bulk work function and c is a quantum correction [27]. In the present case we have used values $r_s = 4.86a_0$, $\delta_s = 1.1a_0$, $W_{\text{wf}} = 2.16$ eV [26,30] and $c = -0.08$ [27]. Solutions of the Schrödinger equation with potential (1) for the bound states are spherical Bessel functions of the first kind in the inner region ($r < R_0$) and spherical Hankel functions in the outer region ($r > R_0$). The solutions for the continuum states are linear combinations of regular and irregular Coulomb functions [29].

The photoionization cross sections were calculated in the independent particle dipole-approximation. The cross section then takes the form [29]

$$\sigma_{nl\to\epsilon l'} = \frac{4}{3}\pi^2\alpha\omega(2l+1)\sum_{l'=l\pm 1}(2l'+1)\begin{pmatrix} l' & 1 & l \\ 0 & 0 & 0 \end{pmatrix}^2 \times \langle P_{\epsilon l'}(r)|r|P_{nl}(r)\rangle^2, \tag{2}$$

where $P_{nl}(r)$ and $P_{\epsilon l'}(r)$ are the bound and continuum electron radial wave functions, respectively. ϵ denotes the continuum electron kinetic energy, ω is the ionizing photon energy, and α is the fine-structure constant. The calculations were done far above the ionization threshold. Therefore the step function $\Theta_{\epsilon l'}$ and treatment of plasmon resonances introduced in [29] were neglected. Further complications such as thermal excitations and ellipsoidal deformations were also omitted.

Figure 1(a) shows experimental valence photoelectron spectrum of $\text{Rb}_{\langle 90\rangle}$ clusters measured at three different photon energies. The spectrum is composed of the peaks corresponding to the ionization of valence levels (i.e., jellium orbitals) at slightly different binding energies. The experimental spectra were normalized and energy calibrated using the 5s photoelectron line of atomic Rb at 4.18 eV binding energy [31]. Rb atoms are present in

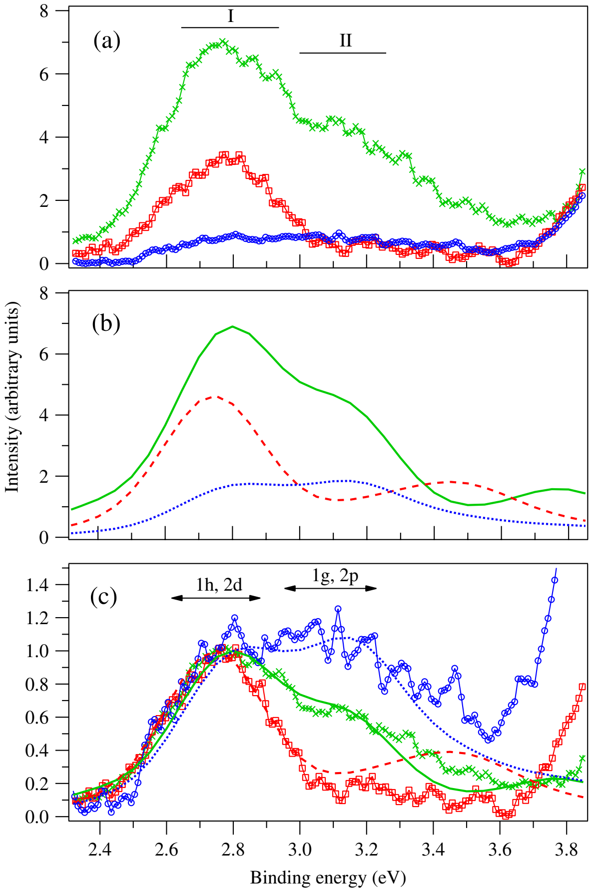

FIG. 1 (color online). Experimental (a) and simulated (b) valence photoelectron spectrum of neutral $\text{Rb}_{\langle 90\rangle}$ clusters at three different photon energies. In panel (a) (green) line with crosses show $\omega = 40.2$ eV, (red) line with squares 48.8 eV, and (blue) line with circles 58.6 eV. In panel (b) solid, dashed, and dotted lines show the same photon energies, respectively. Panel (c) shows the experimental and simulated spectra normalized in the binding energy region of 2.8 eV. Horizontal arrows in (c) mark the approximate positions of the four outermost jellium orbitals of the Rb_{90} cluster.

the interaction region due to the coexistence of metal-atom effusive beams in the interaction region. The rising edge of the atomic 5*s* line is shown in the region between 3.6–3.8 eV. The cluster/atom ratio in the interaction region was about 0.2, and it was monitored to be constant during the experiment. As expected, the total valence cross section decreases as the photon energy increases. More interestingly, the shape of the spectrum changes considerably with the photon energy. The relative intensities in the binding energy regions marked I and II, vary so that at 40.2 eV the I:II ratio is about 2:1, at 48.6 eV ~7:1 and at 58.6 eV ~1:1.

Figure 1(b) depicts simulated valence photoelectron spectra of $\mathrm{Rb}_{\langle 90\rangle}$ clusters at the same photon energies as the experiment in Fig. 1(a). In order to account for the mass distribution in the experiment, the spectra presented here were constructed by summing the spectra calculated for different sizes with weights obtained from a Gaussian distribution centered at the size $N = 90$ and half width of six atoms. In order to account for the experimental broadening, the calculated spectral lines were convoluted with a 150 meV Gaussian profile. The scale of the simulated spectra in Fig. 1(b) is chosen so that the highest point of the spectrum at 40.2 eV photon energy coincides with the experiment in Fig. 1(a). The simulated spectra were also shifted by +120 meV in binding energy. The small discrepancy in the energy position comes from the limitations of the potential (1). To ease the comparison, the experimental and simulated spectra are also shown in the same panel in Fig. 1(c), where the spectra are scaled to the same intensity at the binding energy of about 2.8 eV. The labels and the approximative binding energy positions of the most prominent jellium orbitals giving response in regions I and II are also indicated in Fig. 1(c).

The comparison of Figs. 1(a) and 1(b) shows that the well-potential jellium model used predicts the experimentally observed variations in the cluster valence band response to the photon impact surprisingly well. The decrease of the total cross section is accounted, and more importantly the changes in regions I and II are reproduced. The calculations deviate from the experiment at binding energies above 3.3 eV. For deeper levels the electron correlations are more significant, and the field felt by the electrons is not well enough approximated by a potential of the form (1). The agreement could be improved using, e.g., Woods-Saxon potential, but in this case one would not be able to get analytical solutions for the wave functions, while the main physics is already captured by the square-well potential.

The observed variations in the relative intensities illustrated in Fig. 1(a) can be explained by the oscillatory behavior of the photoionization cross sections of individual jellium orbitals as a function of photon energy. The existence of such oscillations in metallic clusters has been predicted for Na clusters of sizes 20, 34, and 40 [21–24]. Our independent calculations for slightly larger Rb clusters yield a similar result, and our experimental study confirms the prediction. Figure 2(a) shows the calculated valence total cross section, and Fig. 2(b) the individual-level cross sections for the four outermost orbitals of an Rb_{90} cluster as a function of photon energy. In Fig. 2(b) one can see that the photoionization cross sections of individual levels oscillate dramatically in the photon energy range under investigation. The cross section goes to nearly zero in the minima of each orbital. The largest oscillations are smeared out in the total valence cross section photon energy dependence shown in Fig. 2(a).

In the current calculations the oscillations of the cross sections stem from the following reasons. In metallic clusters the valence jellium orbitals are diffuse, extending to, for example, about 30 au in Rb_{90} clusters. If the photoelectron has high enough kinetic energy, the continuum wave function oscillates a few times in the region of the bound-state wave function. Therefore the *r*-weighted *r*-dependent overlap integrand in the radial matrix element (2) takes a wave-packet-like shape. At some kinetic energies, the negative and positive lobes of the integrand cancel each other when integrated over *r*. The oscillation frequency depends on the cluster size and steepness of the cluster potential, as discussed using the force gauge formalism in [21,22]. The described mechanism is similar to what is known to produce Cooper minima [32] in atomic photoionization. In the case of atoms the cancellations stem from a node in the bound-state wave function, whereas in clusters from the node(s) in the continuum wave function. A series of oscillations in the cross section has been also observed in solids [33], where the energy difference between two maxima was seen to be several tens of eVs. In solids the phenomenon is explained by translational symmetry of the solid material [33].

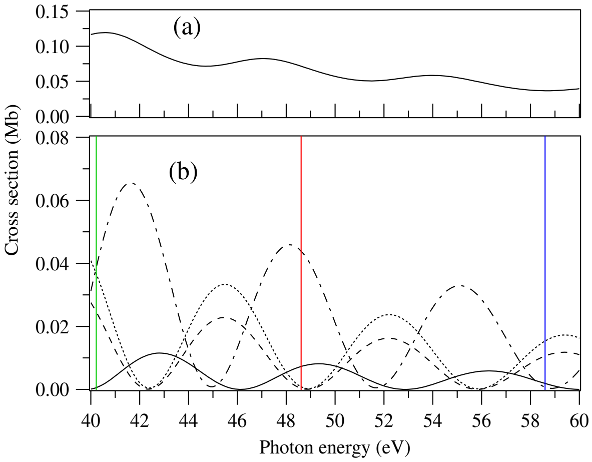

FIG. 2 (color online). Calculated total ionization cross section (a) and cross section of four outermost jellium levels (b) of Rb_{90} cluster as function of photon energy between 40 eV and 60 eV. In panel (b) a solid line depicts the cross section for $2p$, dotted line $1g$, dashed line $2d$ and dash-dotted line $1h$ orbital. Vertical lines mark the photon energies where the experiments were carried out.

The intensities in valence photoelectron spectra of fullerenes have been also shown to oscillate [15–17]. This behavior was explained by scattering of the photoelectron from the walls of the fullerene leading to standing waves inside the cavity [34]. Thus the reason for the changes in the shape of the spectrum in the case of metallic clusters is essentially different. In the case of molecular photoionization [20] the intensity variation in a spectrum has been explained by similar reasons as for fullerenes. At the same time, in the valence photoelectron spectra of rare-gas clusters no variations were seen [14]. The reason is that rare-gas clusters are bound by van der Waals forces, which keep the valence orbitals localized. The photons interact with single atoms in such a cluster, leading to atomiclike photoionization. On the other hand, in the case of core-shell ionization of rare-gas clusters the ratio between the bulk and surface components has been seen to evolve monotonically as a function of the photon energy [11,12]. This change was attributed to the electron scattering inside a cluster, which is an external process relative to photoionization. A similar photon energy dependence is expected for the core levels of metallic clusters also. Thus the intensity changes observed in the core ionization of clusters are due to the external to ionization process, whereas in the valence band response the reason is in an inherent quantum-mechanics property of the light-matter interaction.

A comparison of Fig. 2(b) to Fig. 1 shows that, for example, in the spectrum measured at 48.6 eV, the cross section of the jellium levels in region II ($1g$ and $2p$ orbitals) drops even slightly more than predicted by the calculation. In this case the ionization probability of $1h$ orbital has a maximum and of all other orbitals are close to minimum. At 58.6 eV, on the other hand, the ionization of $1g$ and $2d$ orbitals provides the highest intensities. The result highlights that the photon energy independent models of the valence band response based on approximations such as density of states (see, e.g., [2]), cannot be applied if the clusters are metallic and the valence levels are strongly delocalized.

We have shown experimentally that the valence band response of metallic clusters has a strong photon energy dependent nature even far above the threshold of photoionization, and that analytical jellium-model-based calculations provide a good description for the process. The current experiment and calculations verify the phenomenon predicted in [21,22]. The phenomenon in clusters is in a way similar to the Cooper minima known for the atomic ionization cross sections. Canceling out of the ionization-transition matrix elements has been demonstrated in an ‘‘infinite solid’’ [33]; there, however, the nature of the effect is in the periodicity of the crystalline structure, and thus is different from the case of clusters. Similar oscillations are expected to occur in most metallic clusters.

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