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Valence photoionization of free, neutral, and size varied alkali metal clusters

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Abstract. Valence photoelectron spectra of free, neutral, and size varied K and Rb alkali metal clusters are studied. The experimental spectra are simulated with jellium model based calculations with and without inclusion of dipole matrix elements and continuum wave functions. The simple jellium model used is found to provide good qualitative correspondence with the experimental results. It is shown that the dipole matrix elements provide a remarkable improvement to the standard density of states approach in understanding the photoelectron spectra of small to medium size metal clusters.

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1. Introduction

Clusters are particles that consist of finite number of atoms or molecules thus forming an intermediate phase of matter between individual atoms and solid state. Large clusters reflect properties of solid state metals whereas small clusters resemble the characteristic properties of molecules and atoms. Photoelectron spectroscopy is an established tool to investigate electronic structure of clusters and solids [1, 2]. Photoelectron spectra (PES) provide information about the structure and bonding mechanisms of clusters [3, 4]. Previously laser sources have been used for such experiments on free clusters, mostly on charged anionic or cationic species [5, 3]. The laser sources provide high radiation intensities, but are limited to energies well below 10 eV. Synchrotron radiation storage ring facilities offer tunable UV to Xray region photons which can be applied for valence and core level photoelectron spectroscopy measurements. The higher photon energy allows also valence studies which are free from, for example, complicated threshold effects and plasmon resonances [7, 8]. Binding energy values of inner level states can be used to carry out cluster size estimations using models describing ionization potentials of finite size metal droplets [9].

Metal cluster production methods have been developed during the past decades [5]. Recently described Exchange Metal Cluster Source (EXMEC) [10] has made it feasible to measure PES from free, neutral, and size varied metal clusters. The source

offers cluster size variation with a possibility to adjust the mean size distribution of produced neutral metal clusters.

Since the early days of cluster physics numerous theoretical papers have been published (see, e.g. [5, 6] and references therein). Most of the studies concerned the properties of ground states and simulation of the mass spectra [11, 12, 5, 13]. Recently, the emphasis has moved more into describing the dynamical processes (e.g. [14]). The most common way of interpreting photoelectron spectra of clusters is to use density of states (DOS) approach applying directly the quantum chemistry codes [15]. This, however, requires calculation of stable cluster structures which becomes increasingly demanding for larger clusters. In contrast to high level calculations one may use semiempirical methods. For example, jellium model has been recently used to predict the photoelectron angular distribution of size-selected anionic clusters [16, 17]. In those studies the model was used to describe the anisotropy of photoelectron emission of anionic clusters near to valence ionization energies.

Our goal in this study is to investigate how the simplest possible theoretical cluster model describes the valence photoelectron spectra of neutral small to medium size metal clusters recorded far above the ionization threshold. The emphasis is addressed to study on how the inclusion of the dipole matrix elements and simple continuum wave function changes the result in comparison to the standard DOS approach.

2. Experiment

Experiments were carried out at MAX-laboratory at the soft X-ray undulator beamline I411, in Lund, Sweden [18, 19]. A Scienta R4000 hemispherical electron kinetic energy analyzer was used for electron detection. Photoelectron spectra were recorded at 90° angle relative to the polarization direction of linearly polarized radiation. The photon energy of 40 eV was used in all experiments. Alkali metal clusters were produced using the EXMEC source. Detailed description of the setup is given in Ref. [10]. A resistively heated oven was used to evaporate solid samples. The vapor pressure inside the stainless steel crucible was estimated to be in the range of $10^{-2} - 10^{-3}$ mbar [20]. In the EXMEC method a distribution of clusters with different sizes is produced. Major part of the formed clusters are close to the mean cluster size $\langle N \rangle$ which can be used as an effective size of the clusters [21]. To obtain the most prominent effects, parameters of EXMEC set-up were varied in a way that the smallest and the largest possible clusters were produced. Cluster size variation was carried out by changing the temperature of the nozzle, pressure of inlet Ar gas, and temperature of the crucible. The inner valence K 3p and Rb 4p spectra recorded at the same time and settings [22] were used to carry out tentative size estimations of the produced clusters applying quantum corrected conduction sphere approximation [9].

3. Theory

The simulations were done utilizing simple model that accounts for the photoionization process in metal clusters. The model is described in detail in Ref. [23] (see also [17]) and only the main principles are reviewed here. The valence states are calculated using jellium model where the Hartree-Fock mean field created by the nuclei and electrons is replaced by a square well potential with radius R_0 and depth V_0 . For the bound states the potential outside the well is a constant, whereas for the continuum states the constant is replaced by r dependent Coulomb tail. This jellium potential in atomic units is given by

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

where $s = -1/R_0$ is the value of the Coulomb tail at $r = R_0$. The width and depth of the well are calculated from

$$R_0 = r_s N^{1/3} + \delta_s \tag{2}$$

$$V_0 = \frac{1}{2} \left(\frac{9\pi N}{4R_0^3} \right)^{2/3} + W_N + s, \tag{3}$$

where the Wigner-Seitz radius r_s and the spillout δ_s parametrize the size of the cluster, and N is the number of atoms in the cluster. The average ionization potential W_N is given by $W_N = W_{wf} + 3/(8R_0)$, where W_{wf} is the bulk work function. For K the size parameters are $r_s = 4.86 \ a_0$ and $\delta_s = 1.1 \ a_0$, and for Rb $r_s = 5.20 \ a_0$ and $\delta_s = 1.15 \ a_0$.

The most convenient form of the solution of the Schrödinger equation with potential (1) is obtained in the spherical coordinates. In the inner region $r < R_0$ the radial wave functions are spherical Bessel functions of the first kind. For the bound states the solutions in the outer region $r > R_0$ are spherical Hankel functions of the first kind, and for the continuum states the solutions are linear combination of regular and irregular Coulomb functions [23].

The photoionization cross sections were calculated in the dipole approximation. The angular parts of the photoionization matrix elements can be worked out analytically. Following Ref. [23] the cross section is then

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

where $P_{nl}(r)$ and $P_{\epsilon l'}(r)$ are bound and continuum single electron radial wave functions, respectively. The standard definition of the 3j symbol is used, ϵ denotes the (positive) energy of the continuum electron, ω is the frequency on the incoming photon 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 the plasmon resonances discussed in [23] were not needed. To maintain simplicity thermal excitations and ellipsoidal deformations were also neglected.

4. Discussion

Valence PES of K and Rb clusters for two different limit-sizes are presented in Figs. 1 and 2 together with the theoretical simulations. The PES include also atomic K 4s and Rb 5s photolines at 4.3 eV and at 4.2 eV which provide the binding energy calibration [25, 24]. The observed valence PES of alkali metal clusters are seen to locate above the solid work function of K at 2.30 eV and Rb at 2.16 eV [26]. The mean cluster size estimations obtained from conduction sphere approximation [9] using the binding energies of 3p and 4p orbitals of K and Rb, respectively, were 30 and 650 for K, and 50 and 200 for Rb. The cluster sizes in the jellium model calculations were chosen to correspond electronic magic numbers close the estimations obtained from

the conduction sphere approximation. The selected sizes were 34/40 and 676 for K, and 58 and 198 for Rb. The ionization potentials as well as the shape of the spectra display a clear cluster size dispersion especially in smaller clusters. Therefore in the case of smaller K clusters in Fig. 1(a) a reasonable agreement was obtained by using a sum of two cluster sizes 34 and 40 with equal weight distribution. Such a favoring of magic sizes in the size distribution may well be a property of the EXMEC method [10]. To account the several broadening factors in the experiment, such as experimental broadening, size distribution, thermal broadening, and nonspherical deformations, the calculated spectral lines were convolved with a 150 meV Gaussian function. The dotted lines depict the results obtained using the jellium model and the photoionization cross section (4) described above. To highlight the importance of including the continuum wave functions, dashed lines show the calculation without inclusion of the radial dipole matrix elements in Eq. (4). The approximation corresponds the DOS approach, where the intensities in photoelectron spectra are approximated using the number of electrons in each level.

Comparison of the experimental and calculated results in Figs. 1 and 2 shows that the jellium model applied gives surprisingly good agreement with the experiment. In the cases of smaller sizes of K and Rb clusters (upper panels) the peak profile is quite symmetric due to less dense array of occupied states. On the other hand, in the case of larger clusters (lower panels) the valence states approach rapidly the solid Fermi level shown as a vertical line. The increasing density of occupied high l orbitals closer to the Fermi level explains the sharp rise and slowly decreasing intensity profile. In the cases of larger clusters the binding energies are slightly underestimated. However, one may see that the peak profiles are well described.

Previous experiments have shown that the jellium model is applicable in the description of photoionization of anionic clusters [5, 16, 17]. This may be affected by the excess charge in the anionic cluster and the fact that the cluster is in a neutral state after the ionization. The case of initially neutral clusters is essentially different. The jellium-like potential is less evident and the continuum electron is moving in a positive charge of the ionic cluster. Our result is Figs. 1 and 2 show that the spherical well jellium model can indeed describe valence photoionization of initially neutral metallic clusters.

Comparison between the two calculations done with and without dipole matrix elements shows striking differences. Inclusion of the continuum waves and the radial dipole matrix elements improved the agreement remarkably in comparison to DOS approach in every case studied. The improvement is less evident in figures 1(a) and 2(b) which is due to slightly shifted binding energies in the calculations. The shift is caused by limitations of the potential. However, if the calculated spectra are shifted about +150 meV in binding energies, the agreement between the experiment and theory in for example 2(b) is remarkably good. It can be seen that the DOS spectrum tend to overestimate the relative intensities. This disagreement is systematically corrected by the radial matrix elements. As a specific example, in the case of smaller Rb clusters shown in Fig. 2(a), the ionization probability of an electron from the outermost 1g orbital around 2.6 eV is drastically overestimated by the DOS approach. Inclusion of the matrix elements modify the calculation in a way that the highest ionization probability is from the 1f orbital around 3.0 eV. Jellium orbitals 1q and 1f are nodeless and show very similar radial dependence, thus the result cannot be predicted without actual calculation of the radial matrix elements. Comparing the experiment and theory at higher binding energy region around 4 eV one can see that



Figure 1. Valence PES of size varied K clusters a) smaller and b) larger. Solid black lines present the experimental data. Dotted and dashed lines correspond the jellium model calculations. The intensities in dotted lines are calculated including the dipole matrix elements, whereas for dashed lies the intensity is obtained by the statistical weight of each jellium level. Position of the work function of solid K at 2.30 eV is shown as a vertical line. The smaller cluster PES in a) are simulated by sizes 34 (light gray line) and 40 (dark gray line). The larger cluster PES is in b) calculated using size 676.

the theory underestimates the intensities. This is due to lack of energy levels in the region. Most likely electron correlation plays a more significant role for the deeper levels and shift some levels into this region. Analysis of such effects is however left for the future.

It is a known fact that the theoretical description of ionization matrix elements and poly-centric continuum wave functions of many-atom systems is a very demanding



Figure 2. Valence PES of size varied Rb clusters a) smaller and b) larger. Solid black lines present the experimental data. Dotted and dashed lines correspond the jellium model calculations. The intensities in dotted lines are calculated including the dipole matrix elements, whereas for dashed lies the intensity is obtained by the statistical weight of each jellium level. Position of the work function of solid Rb at 2.16 eV is shown as a vertical line. The smaller cluster PES in a) is simulated using size 58 and the larger in b) using size 198.

task, which is the reason why DOS approach has been widely used in clusters. Our result has shown that the dipole matrix elements may change the result drastically. This indicates that much of the disagreement found in the DOS approach using high level Hartree-Fock or density functional theory calculations could be due to the omission of the dipole matrix elements and continuum wave functions. Therefore we may conclude that the way to improve high level calculations describing photoionization in clusters could be in including even a simple one-center continuum wave function and the dipole matrix elements instead of forcing the calculation for better bound state wave functions.

5. Conclusion

We have presented the valence photoelectron spectra of free, neutral, and size varied K and Rb clusters using synchrotron radiation. The model based on approximating the Hartree-Fock potential by a square well provides a good correspondence with the valence spectra far above the ionization threshold of neutral K and Rb clusters. It was shown that the inclusion of the radial matrix elements is important in obtaining reasonable agreement with the experiment. It demonstrates that the widely used DOS approach in more laborious theoretical frameworks could be significantly improved by including radial dipole matrix elements together with some approximate continuum wave function.

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