Core-Level Photoelectron Spectroscopy on Mass-Selected Metal Clusters using VUV-FEL Radiation

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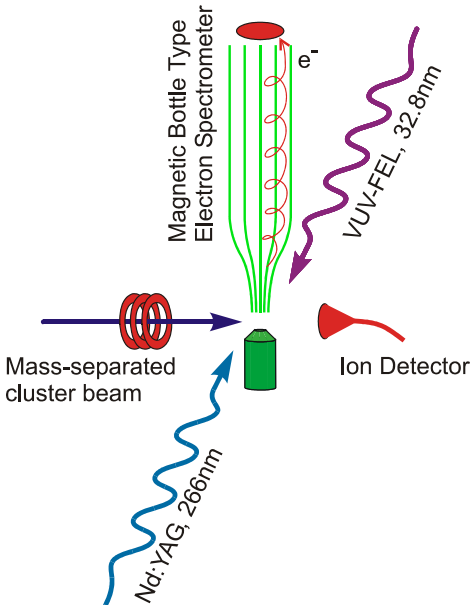
Electron confinement and size effects in metal clusters lead to novel optical, magnetic and chemical properties and therefore attract interest in fundamental as well as in applied sciences. Size-dependent catalytic activity, adjustable optical absorption or the generation of e.g., cluster-based soft magnetic materials are some of the prominent issues. Of particular importance is the correlation of the electronic with the geometrical structure. Despite the progress achieved so far, the evolution of the valence band towards the bulk is widely unknown and exhibits a fundamental scientific question which can now be addressed using the high photon energies and pulse intensities at FLASH.

Fig. 1: A metal cluster beam created in a laser vaporization cluster source and time-of-flight mass-separated in a Wiley-McLaren two-field arrangement is crossed by the light of the VUV free-electron-laser in the interaction region of a magnetic bottle photoelectron spectrometer. Detached electrons follow the magnetic field lines and are detected according to their arrival time on a channelplate detector. Alternatively, we use the third harmonics of a Nd:YAG laser (266 nm) in order to arrange, test and optimize the whole setup in advance or between the FEL shifts. Finally, a channeltron on the beam axis records the cluster ion mass spectrum in time. The interaction chamber is ultra-high-vacuum compatible and reaches a base pressure of about 10^{-10} mbar after baking. Furthermore, a liquid He cooling shroud serves to reduce further the local pressure at the interaction point.



As a first test case we concentrated on lead clusters with the 5d levels at binding energies of 18.1 eV ($5d_{5/2}$) and 20.7 eV ($5d_{3/2}$) below the Fermi level being accessible by the FEL. Lead shows one of the highest photoionization cross-sections of about 30 Mbarn at that energy. On the other hand, the experiment refers to former UV photoelectron measurements performed at BESSY on deposited lead clusters. There, a remarkable shift of the $5d_{5/2}$ level of about 300 meV between the atom and the bulk could be revealed [1].

During the last year several results were obtained by VUV photoelectron spectroscopy on mass-selected lead clusters anions. Due to the high brilliance of the FEL it became possible for the first time to record core level spectra from such highly diluted cluster targets. In particular an interesting cluster size-dependent core level shift is observed, showing a trend towards the corresponding bulk system.

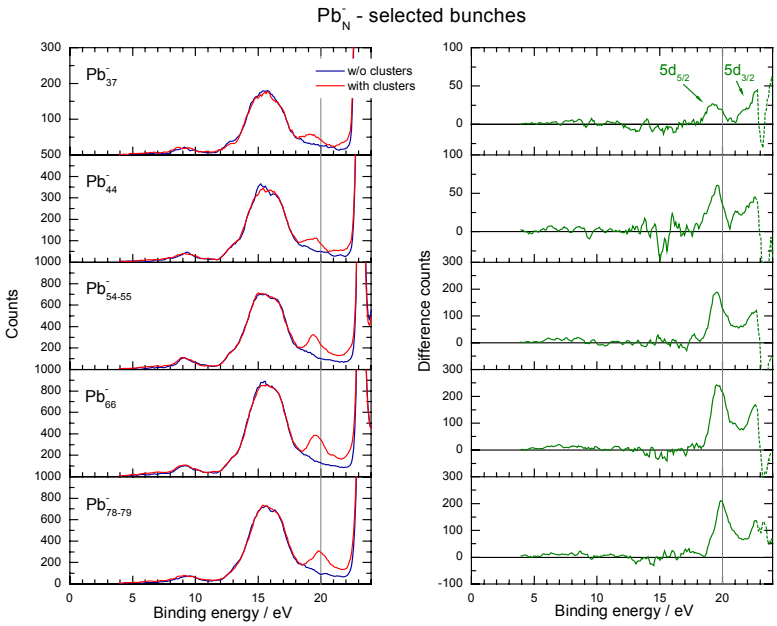


Fig. 2: Photoelectron spectra from lead clusters with atom numbers N from 37 to 78 (left: with and without cluster beam) and the corresponding difference spectra (right). The electron energy spectra shown here result from a conversion of time-of-flight measurements, the data are displayed with respect to E_{VAC}. The FEL was operated in the 20-bunch mode (each single bunch hitting another cluster size), with a pulse separation of 10 µs, at pulse energies in the range of 5-15 µJ at 32 nm wavelength.

Because the measurements are still in progress, most data are not yet evaluated. Nevertheless, Fig. 2 shows as example few shot-integrated spectra from clusters with atom numbers N ranging from 37 to 78. In spite of the vacuum close to 10^{-10} mbar and liquid He cooling around the interaction region, still some residual gas signal remains between 12 and 18 eV binding energy. Yet it has become possible to resolve with high statistics the $5d_{5/2}$ component of Pb at 20 eV. In the difference spectra on the right side of Fig. 2, the exact position of the 5/2 component appears very distinct, as well as the minimum between the spin-orbit split levels. The $5d_{3/2}$ component at 2.5 eV higher binding energy reaches into the strong Helium peak, originating from the cluster source processing gas.

When summarizing the $5d_{5/2}$ binding energies we observe a clear shift which depends on the exact number of atoms N in the cluster, see Fig. 3. Even with the more conservative estimate of the error bars it is obvious that the core level energies follow a clear trend towards the Pb bulk value, see the point in the upper left corner. Indeed, the linear fit through the data points including the bulk value corresponds to the 1/R dependence as expected for the ionization of negatively charged metal clusters within the liquid droplet model. Deviations from that trend could hint at, e.g., intrinsic core level shifts due to cluster size-dependent different ionization environments. In principle it should be possible to even discern different chemical influences. Besides such core level spectra, also in the valence band regime small but useful signals could be resolved. Moreover, a thorough evaluation of the single shot spectra will give information of the influence of e.g. the FEL pulse intensity on the photoelectron spectra in the near future.

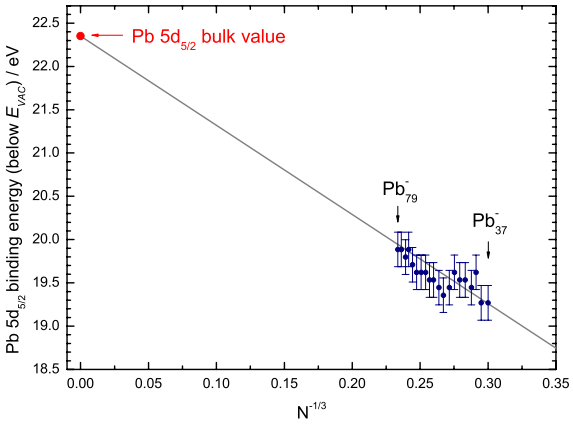


Fig. 3: Size dependence of the lead $5d_{5/2}$ binding energy. A clear trend to the corresponding bulk value can be observed in accordance with the classical charged sphere model.

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References

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