

Gold doped helium nanodroplets: from atomic spectroscopy to localized surface plasmon resonances in deposited nanoparticles

Florian Lackner^{*1}, Roman Messner^{*}, Alexander Schiffmann^{*}, Maximilian Lasserus^{*}, Martin Schnedlitz^{*}, Daniel Knez[†], Georg Haberfehlner^{†,‡}, Gerald Kothleitner^{†,‡}, Ferdinand Hofer^{†,‡} and Wolfgang E. Ernst^{2*}

^{*}Institute for Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

[†]Graz Centre for Electron Microscopy, Steyrergasse 17, 8010 Graz, Austria

[‡]Institute for Electron Microscopy and Nanoanalysis, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

We present the first electronic excitation spectrum of gold atoms inside helium nanodroplets as well as a new approach for the study of optical properties of deposited Au nanoparticles synthesized inside helium nanodroplets. The Au-He_N excitation spectrum exhibits characteristic blue shifted and broadened features caused by the interaction of the atom with the surrounding helium. For the study of deposited Au nanoparticles electron energy-loss spectroscopy is applied, enabling the investigation of localized surface plasmon resonances of selected, individual nanoparticles subsequently to their preparation in helium nanodroplets.

Gold nanoparticles are of great importance in a variety of fields such as catalysis, analytical chemistry, biology and even medicine because of their outstanding plasmonic properties combined with chemical inertness. Many of these applications are based on localized surface plasmon resonances.

We focus on the optical properties of Au atoms and nanoparticles and present the first investigation of the electronic excitation spectrum of single gold atoms isolated in helium nanodroplets as well as an investigation of the localized surface plasmon resonance in gold nanoparticles subsequently to their deposition on substrates.

In contrast to Au-He_N, the lowest excited states in Ag-He_N [1] and Cu-He_N [2] have already been explored. Using resonant two photon ionization spectroscopy, we recorded the lowest two electronic transitions in gold atoms inside helium nanodroplets. In addition to the characteristic broadening and blueshift, the bare Au mass channel exhibits a sharp line identified as a transition originating from the 5d⁹6s² ²D manifold, revealing that the helium environment opens up a relaxation channel which is forbidden in the free atom.

When deposited on suitable substrates, metal nanoparticles formed inside helium nanodroplets can be studied by means of transmission electron microscopy. Using electron energy-loss spectroscopy, localized surface plasmon resonances of individual nanoparticles can be characterized in a transmission electron microscope [3]. It is important to note that this method not only gives access to optically allowed dipole modes, but also to bulk and quadrupole modes. We will pre-

sent first results for gold nanoparticles with diameters less than 10 nm. Note that in contrast to the works by the Vilesov group on Ag particles in helium nanodroplets [4], our approach characterizes the nanoparticles after deposition. Furthermore, the flexibility of the helium droplet isolation approach allows the deposition of nanoparticles on other substrates such as fused silica in quantities that enable an investigation by means of UV/vis spectrophotometry. After finding suitable particle size regimes and deposition rates, this method may serve as complementary approach for the study of localized surface plasmon resonances in nanoparticles prepared by helium droplets.

Our work on Au nanoparticles points out an exciting new direction for the field of helium droplet assisted synthesis of nanoparticles. Considering that it has been shown that the method can be used to form core-shell nanoparticles [5,6], we think that it will become possible to produce and characterize novel, plasmonic core-shell nanoparticles which cannot be formed with conventional approaches.

References

- [1] Loginov *et al.* 2007, J. Phys. Chem. A, 111, 7504-7515
- [2] Lindebner *et al.* 2014, Int. J. Mass. Spec., 365, 255-259
- [3] Scholl *et al.* 2012, Nature, 483, 421-427
- [4] Loginov *et al.* 2012, Phys. Rev. Lett., 106, 233401
- [5] Haberfehlner *et al.* 2015, Nature Communications, 6, 8779
- [6] Thaler *et al.* 2014, Phys. Rev. B, 90, 155442

¹ E-mail: florian.p.lackner@gmail.com

² E-mail: wolfgang.ernst@tugraz.at