


Experiment title:

Systematic investigation of the charge transfer across the metal-ligand bond in monolayer protected gold nanoparticles and related magnetic phenomena

Experiment number:

HC-968

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Report:

This experiment was aimed at studying the charge transfer and magnetism induced by strongly interacting ligands on small gold nanoparticles. Such investigation was motivated by the current interest –and high degree of controversy– in understanding the origin of the unexpected strong magnetism observed in small gold nanoparticles. Small colloidal nanoparticles (Au_{small} , $d \sim 2$ nm) capped with carefully chosen organic molecules were prepared with the intention of correlating the electron-withdrawal and electron-donating features of the molecules to the density of charge carriers in the gold particles and ultimately to the induced magnetic moment. A second set of larger particles (Au_{large} , $d \sim 5$ nm) capped with a subset of the same molecule was also prepared as a control in which surface effects were expected to be much smaller. Each set of particles was prepared from a single synthesis in order to insure the maximum possible homogeneity in average size, size distribution and crystallinity of the different samples. The table below shows the combinations of gold particles and capping molecules that were prepared and characterised (TEM, XRD, SQUID) prior to the beamtime and measured during the experiment.

	Au_{small}	Au_{large}
Oleylamine	● (native)	
Hexadecylamine		● (native)
Dodecanthiol	●	●
Thioctic acid butyl ester	●	
Di-dodecyl sulphide	●	
Methyl-dodecyl sulphide	●	
Thiophenol	●	●
4-Nitrothiophenol	●	●
4-Methoxythiophenol	●	●
4-N,N'-Dimethylaminothiophenol	●	

All derivatives of Au_{small} were screened by measuring XAS spectra at the L_3 and L_2 edges of Au in the 11.75-12.17 keV and 13.61-14.03 keV energy ranges respectively, with particular attention to the transition at 11.94 keV, which yields information on the electron density in the $5d$ orbitals of the metal, thus is a direct probe of the possible charge transfer between capping molecules and gold. Due to the beam instability of the 16 bunch mode, a second set of measurements was carried out at the L_3 edge using a shorter integration time (1 s per point instead of 2 s), in order to keep acquisition of at least some subsets of samples

within the same refill time. The normalised spectra acquired in the second run are shown in Figure 1: as the zoom on the edge jump shows, no significant trend is observed at the 11.94 keV transition with respect to the electron withdrawing or donating properties of the capping molecules. Indeed, oleylamine -which is expected

to molecule interacting less strongly with the Au surface- shows the lowest intensity of the shoulder, indicating a higher electron density of the metal, and oleylamine is followed by 4-methoxythiophenol, whose methoxyl group is strongly electron donating. On the other hand, the differences are too small and sensitive to normalization to be significant, and all other capping molecules do not show differences. The same lack of a distinct trend was observed for the Au_{large} series (not shown), as expected due to the lower ratio between surface and volume Au atoms.

We measured XMCD at low temperature and high field (3 K, ± 17 T) on one sample: Au_{small}-Dodecanthiol; the choice of this sample was motivated by the relatively higher intensity of the transition 11.94 keV and the fact that it is the most robust system among the ones that have been prepared and the for which the highest density of sulphur atoms is expected, as a consequence of the small steric hindrance of the dodecanthiol molecule, which allows for a tighter packing of the particle surface. The acquisition protocol consisted in two series of 15 couples of spectra with alternating polarisation between LCP and RCP at positive applied field, followed by a second series at negative field; the energy range was 11.89-12.01 keV for the L₃ edge and 13.70-13.84 keV for the L₂ edge. Several scans had to be rejected due to beam instabilities causing significant shifts in energy, related to injection in the 16 bunch mode: in particular, a whole series of scans at the L₃ edge could not be used due to severe energy shifts between the positive and negative field series. The obtained XMCD spectra, shown in Figure 2, show no detectable signal down to the 10⁻⁴ range, indicating that a magnetic moment induced by ligands in these Au particles is either not present or very small.

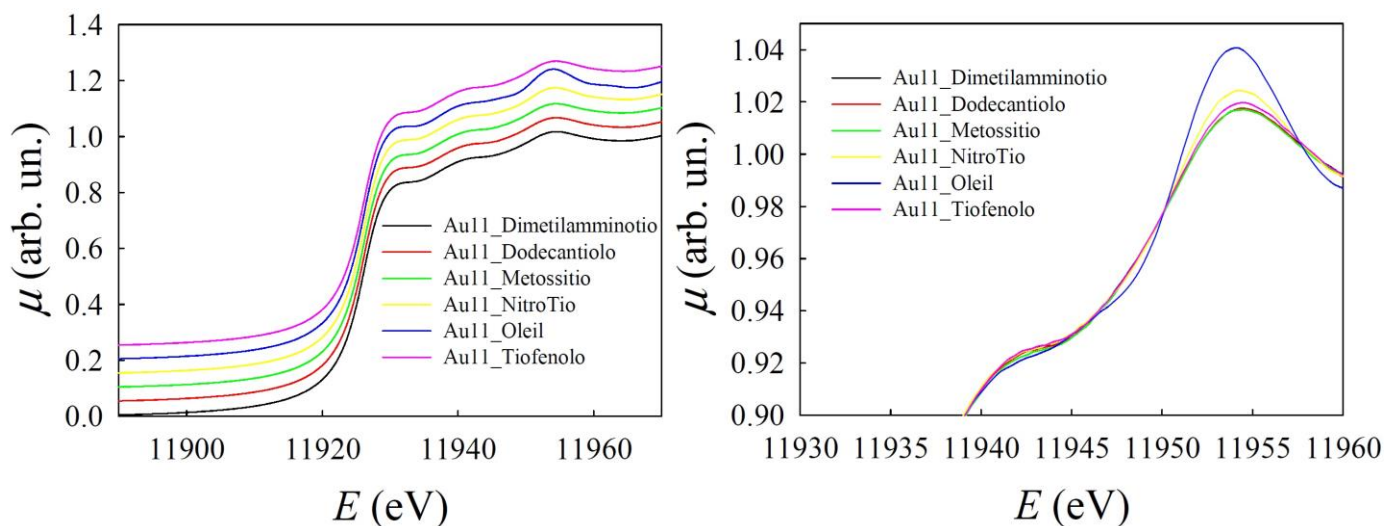


Figure 1. Selected normalised XAS spectra of the Au_{small} series and zoom on the edge jump area.

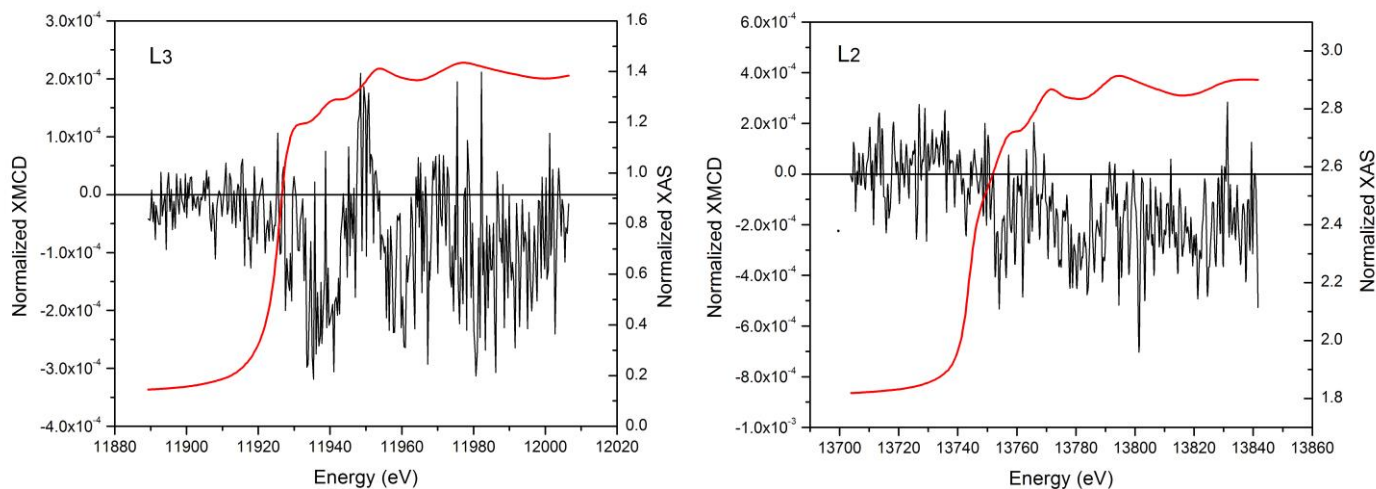


Figure 2. Normalized XMCD spectra of Au_{small}-Dodecanthiol at the L₃ and L₂ edges (3K, ± 17 T).

In conclusion, we prepared two sets of amine-capped Au nanoparticles and replaced the starting ligand with a series of electron-withdrawing and -donating thiols, obtained information on their influence on electron density on Au from XAS and found no significant trend. We measured XMCD on a selected sample and found no induced magnetism down to 10⁻⁴; beam instabilities prevented obtaining a more precise assessment of this quantity.