


**Experiment title:**

Orbital Moment in Pt nanoparticles  
supported in NaY zeolite

**Experiment  
number:**  
HE2381

**Beamline:**

ID08

**Date of experiment:**

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18

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We have recently reported on still smaller Pt clusters supported in NaY zeolites, containing 13 atoms [1]. These Pt particles are prepared in two chemical states: Pt<sub>13</sub> particles covered by H absorbed atoms (or deuterium) in one case, and Pt<sub>13</sub> particles in the bare neutral cluster case. Both show magnetic response in EPR and magnetization measurements, which varies as a function of the hydrogen absorption on the cluster surface [1]. From preliminary EXAFS experiments we have shown that the clusters have icosahedral structure comprising 13 atoms, therefore, all but one Pt atom are at the surface. Consequently, the surface effects attributable to the loss of local symmetry are maximized in this type of cluster, enabling us to ascribe the peculiar cluster physical properties to the surface atoms. In particular, the asymmetry of the surface d electrons bands is expected to produce an enhancement of the surface atomic orbital moment [2]. In the samples used, the NaY zeolite has been charged to a maximum of 6% Pt in weight, to ensure the isolation of the particles with respect to each other. The samples measured were three: Pt<sub>13</sub>D<sub>m</sub>, Pt<sub>13</sub>H<sub>m</sub>, and desorbed Pt<sub>13</sub>.

**Experiments.**

For the three samples the following experiments were performed: 1) XAS of the L<sub>2</sub> and L<sub>3</sub> edges of Pt, measured at T=7 K and H= 6 T; 2) XMCD of the L<sub>2</sub> and L<sub>3</sub> of Pt, measured at T=7 K and H= 6 T; 3) Field dependence of the XMCD of the L<sub>3</sub> edge of Pt, measured at T=7 K and field 6> $\mu_0$ H>6 T.

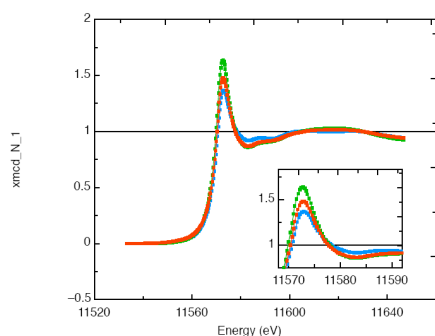


Fig. 1: L<sub>3</sub> edge XANES of the three Pt<sub>13</sub> samples

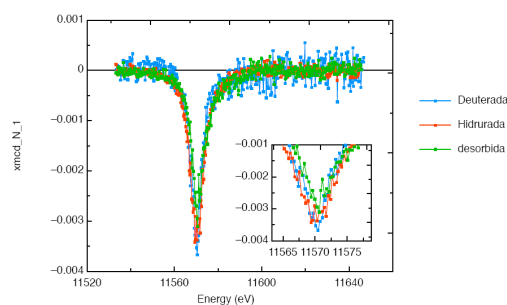


Fig. 2: L<sub>3</sub> edge XMCD of the three Pt<sub>13</sub> samples

**XAS**

The XAS L<sub>3</sub> edge of Pt data (Fig. 1) show a large white line which increases in the trend Pt<sub>13</sub>D<sub>m</sub><Pt<sub>13</sub>H<sub>m</sub><Pt<sub>13</sub> desorbed. It may indicate the partial oxidation of the samples Pt<sub>13</sub>H<sub>m</sub> and Pt<sub>13</sub> desorbed, or an increase in the number of holes in the Pt 5d band, or both. The EXAFS wiggles are almost identical for Pt<sub>13</sub>H<sub>m</sub> and desorbed samples, Fig. 1. Similar conclusions are obtained from the L<sub>2</sub> Pt edge XAS (not shown).

## XMCD

The  $L_3$  Pt edge spectra are very small (Fig. 1). There is an increasing trend as  $Pt_{13} \text{ desorbed} < Pt_{13}H_m < Pt_{13}D_m$ , namely peak intensity at the maximum  $= 3.0(2)$ ,  $3.3(2)$  and  $3.6(2) \times 10^{-3}$  for  $Pt_{13} \text{ desorbed}$ :  $Pt_{13}H_m$ :  $Pt_{13}D_m$ , respectively (The corresponding XAS spectra have been normalized to 1 at the center of the wiggles, and the scaling factor transported to the XMCD data. The  $L_2$  Pt edge peaks are nearly identical among them (not shown).

The signal of the  $L_{2,3}$  spectra obtained for Pt in a PtCo alloy [3], for which the total magnetic moment had been derived, allows to determine the scaling factor of XMCD intensity of the  $L_3$  Pt peak with the total moment. This factor is  $I_{\text{XMCD}}/m_T = 0.283$  where  $I_{\text{XMCD}}$  corresponds to the XMCD signal at the peak, when the  $L_3$  edge XAS high energy asymptote has been scaled to 1, and  $m_T$  is given in  $\mu_B/\text{Pt}$ . Using the scaling factor, we find that  $m_T = 1.1(1)$ ,  $1.1(1)$  and  $1.4(1) \times 10^{-2} \mu_B/\text{Pt}$  for  $Pt_{13} \text{ desorbed}$ ,  $Pt_{13}H_m$  and  $Pt_{13}D_m$ , respectively. The size of the  $L_2$  Pt edge XMCD spectra is so small that a proper use of the sum rules needs of further measurement time in order to determine the integrated XMCD with enough accuracy.

## XMCD hysteresis measurements

The measurements were performed between -6 and 6 T at constant energy; i.e. at the energy of the XMCD maximum, by changing the helicity of the incoming beam. They show that the  $L_3$  XMCD peak signal depends linearly with the field and do not show any curvature up to the highest field measured.

## Data analysis.

The XMCD experiment is element and shell selective, therefore we can be sure that we are only measuring the Pt contained in the sample, and the magnetic moment arising from the Pt 5d band. Other possible magnetic impurities different than Pt containing ones do not give a contribution, unlike in SQUID measurement, where all magnetogenic atoms may contribute. The smallness of the magnetization derived from the XMCD experiments and the linear field dependence induce us to think that the magnetic behaviour is rather Pauli Paramagnetic-like behaviour, although yielding to a larger value than in the bulk.

From the sharp peak of the  $L_3$  Pt edge XAS data the question whether there is an important contribution due to  $PtO_x$ . In reference [4] the XAS measurements performed on  $PtO_x$  layers are shown in Fig.3. In that paper it is shown that the  $PtO_{1.6}$  layer yields to a prominent white-line, that diminishes upon annealing till it has the shape of metallic Pt. At the same time the spectra are slightly shifted to lower energy. We have digitized their data and compared to our own XAS results. Very interestingly, the  $Pt_{13}D_m$  spectra peak coincides in height with the metallic Pt (Fig. 6 and 7), although the EXAFS wiggles are less pronounced in our sample. The  $Pt_{23}H_m$  coincides nearly exactly with the XAS curve of the so-called (annealed 555 K), and the desorbed is in between the annealed 545 and the 555 K spectra. From the fit of our  $Pt_{13}$  experimental  $L_3$  spectra to a linear combination of the Pt metal and  $PtO_{1.8}$  we can derive the percentual presence of one or the other component in the sample (Fig. 3). The percentages are 8, 23, 42 % for the  $Pt_{13} \text{ desorbed}$ ,  $Pt_{13}H_m$  and  $Pt_{13}D_m$ , respectively. The deuterated compound is the less oxidated, while the desorbed one is the most oxidated with up to 40%.

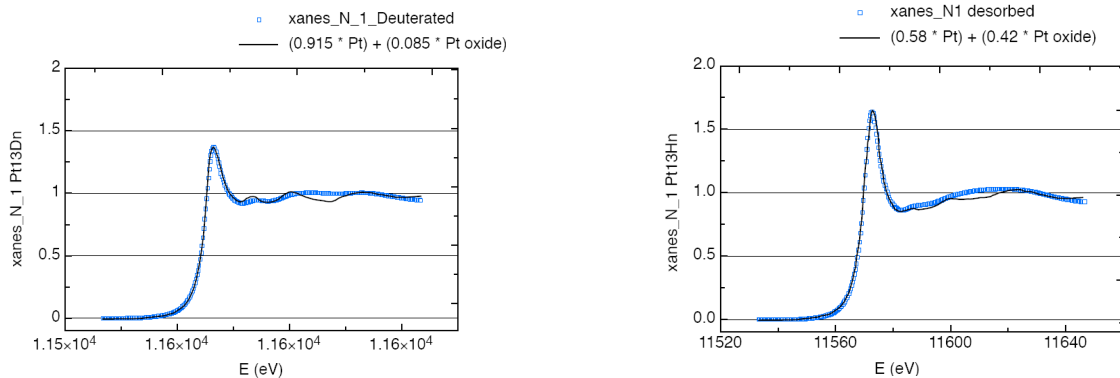


Fig. 3: Comparison between experimental  $L_3$  edge XANES of the two  $Pt_{13}$  systems and a linear combination of the available XANES spectra of pure and oxidized platinum, as explained in the text.

## References

- [1] X. Liu, H. Dilger, R.A. Eichel, J. Kunstmann and E. Roduner. J. Phys. Chem. B 110, 2013, (2006).
- [2] J. Stöhr, J. Magn. & Magn. Mat. 200, 470 (1999).
- [3] Grange et al. Phys. Rev. B 58, 6298 (1998).
- [4] Kolobov et al. Applied Phys. Letters 86, 121909 (2005).