ESRF	**Experiment title:** The structure of the $^3A_{2u}$ excited state of $Pt_2(P_2O_5H_2)_4{}^{4-}$ using microsecond resolved XAFS	**Experiment number**: CH760
Beamline: ID24	**Date of experiment**: from: 1-12-99 to: 12-12-99	**Date of report**: 18-02-99
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Report:

The experiment was aimed at performing a first attempt to observe the structure of a molecule in an excited electronic state using a dispersive XAS setup. We did not succeed but we think we have understood why, and have analysed a number of determinant factors. In this experiment report we summarize the main conclusions of this first attempt.

The experiment poses several difficulties due to the complex instrumentation setup. A laser is used to excite the system, which has to be kept at low temperature in a He cryostat. In fact, the excited-state lifetime of the complexes under investigation is of a few hundreds of microseconds at temperatures below 10K, and rapidly decreases to a few microseconds at T > 50K. Both the laser and the He cryostat were borrowed from other groups since ID24 did not dispose of its own equipment in Dec 99.

The choice of the samples was critical: we needed to find samples that were stable and available, that had a long-lived excited state and good quantum yields, that had edge energies that are compatible with the beam line, and that had large enough excited state distortions to be readily resolvable. The systems investigated during the allocated beam time for experiment CH760 were:

1 – UO_2Cl_4 at the U L_3 edge (17.166 KeV)

2 – $Pt_2(P_2O_5H_2)_4{}^{4-}$ at the Pt L_3 edge (11.564 KeV)

Both complexes are delicate, the first being weakly radioactive and the second very air-sensitive. The concentration of the solution had to be chosen large enough to obtain a

reasonable value of the Jump, but low enough to allow laser photons to penetrate as far as possible into the solution, as will be explained below. Last but not least, the solvents used for the solution had to be good "glass formers". This requirement limited the range of possible concentrations and made the sample preparation a non-trivial matter.

We started out with the U sample at T ~ 9 K. This sample was chosen because it has an exceptionally long excited state lifetime at this temperature, and also because the excited state distortion is expected to be very large. Fig.1 shows a simulation of the effect of the excitation on the EXAFS signal: the U-O distance is thought to expand of 0.1 Å yielding a large difference between the excited-state and groundstate signals. The static U L_3 edge spectrum had a Jump of ~ 0.2 in agreement with the calculated value for a concentration of ~ 25 mM.
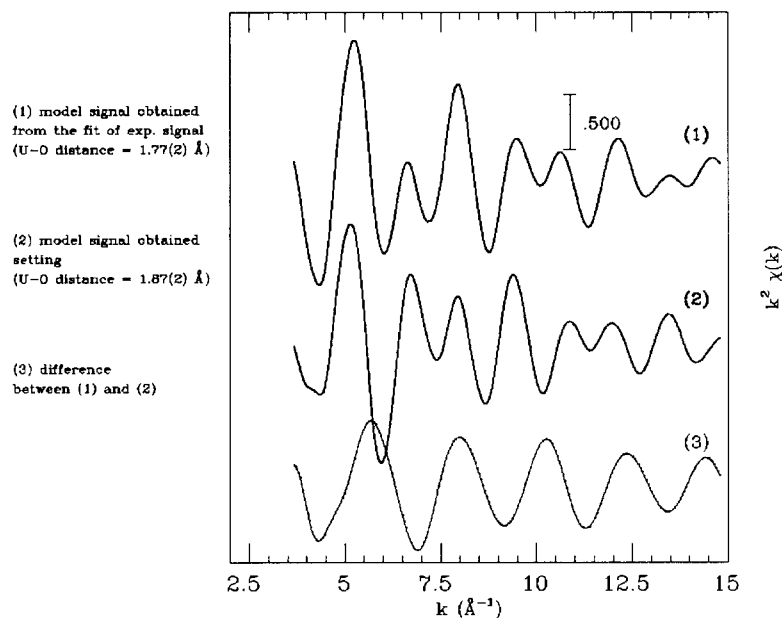

Fig.1: Top: model signal obtained from best fit of the static experimental spectrum (ground state). Middle: model signal obtained by increasing only the U-O distance of 0.1 Å, as expected for the excited state. Bottom: expected difference for an excited state population of 100%.

We acquired a series of 18 fast spectra (200 μs each) and fired the laser simultaneously to spectrum no. 6. We averaged over 50 repetitions. This cycle was then repeated without laser firing. We repeated the two cycles (with and without laser firing) 40 times, in order to improve the S/N ratio. We then subtracted the spectra "without laser firing" from those "with laser firing". Fig. 2 shows a series of "difference spectra" obtained by taking the difference between two successive spectra (i.e. spectrum no. 7 – spectrum no. 6). We do not observe any significant difference in the spectra following the laser excitation, even though the residual noise level is orders of magnitude smaller than the expected signal.

We believe that the failure to see an effect is related to the fact that we were not able to have a detectable excited-state population in the volume of the sample probed by

the X-ray beam. To do this we have to match the penetration depth d_{laser} of the laser photons (which we quantify as the distance from the laser window which yields, for the given sample concentration, an optical density (OD) of 1: $d_{laser} = d_{OD=1}$) to the depth of the sample probed by the X-ray beam d_{Xrays} (which is equal to the horizontal focal spot size, in the best of cases).
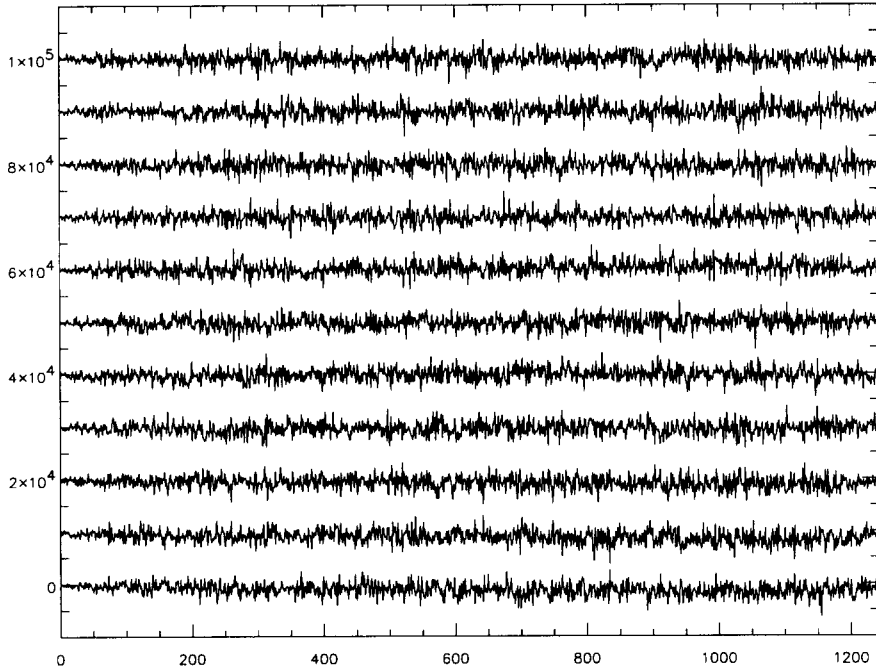

Fig. 2: From bottom to top: spectrum no. 4 – spectrum no.3 (first on the bottom), until spectrum no. 14 – spectrum no. 13 (last on top). The laser is fired simultaneously to spectrum no.6. No differences are detected following the excitation.

A sketch of the sample cell geometry is shown in Fig3. The direction of the X-ray beam is perpendicular to the paper.
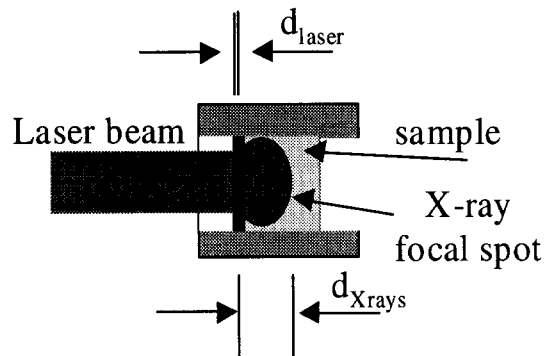

Fig.3: Sketch of the sample cell geometry: the X-ray beam direction is perpendicular to the paper.

For a given sample concentration, the penetration depth of the laser depends critically on the wavelength of the photons, through the optical absorbance (ε) of the

system. Unfortunately, it was not possible to tune the laser wavelength to the best value. In the future this problem will be overcome with the use of a dedicated laser with an Optical Parametric Oscillator.

For the U sample, the ratio d_{laser} / d_{Xrays} turned out to be far too small. For this reason, we decided to go back to the sample which had been initially foreseen in the proposal: $Pt_2(P_2O_5H_2)_4^{4-}$, which has a shorter excited-state lifetime at these temperatures, but for which it is possible to obtain a ratio d_{laser}/ d_{Xrays} much closer to 1.

The static Pt L_3 edge had a Jump of 0.2, compatible with the concentration of ~ 17 mM (Fig.4). This spectrum was recorded on ID24 and is representative of the data quality now possible on this beamline.
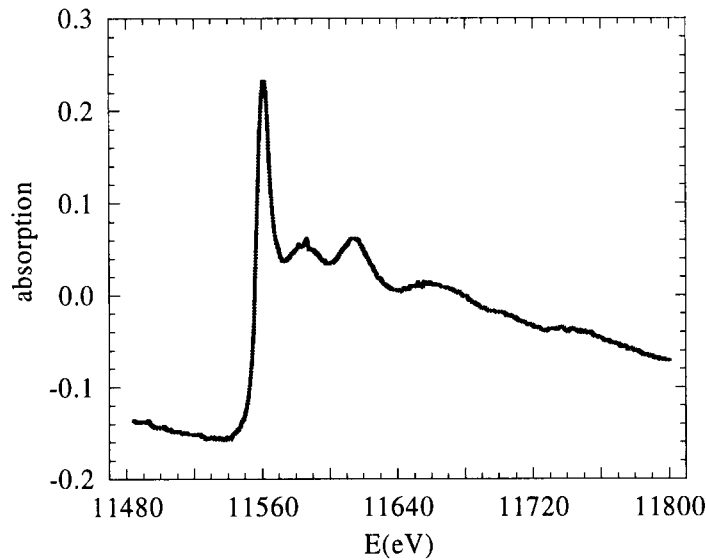

Fig.4: Static Pt L_3 edge spectrum of 17 mM $Pt_2(P_2O_5H_2)_4^{4-}$dissolved in a solvent composed of a ¾ mixture of H_2O and Ethil glycol.

Unfortunately, at this point we started having leakage problems with the teflon laser windows that we had mounted on the cryostat. This technical problem will be eliminated in the future with the use of a dedicated cryostat belonging to the beamline and optimized for this kind of experiments. Optical windows with good transmission properties in the wavelength range 0.2 – 1.0 μm are being purchased. They will be fixed to vacuum flanges on the cryostat using Ti joints which insure a strain-free mount throughout the whole temperature range. We plan to install an "in situ" monitoring of the excitation, by measuring the emission spectrum through a window opposite the laser entrance window.

We are also planning to perform off-line preliminary measurements of the optical spectra at low temperature in the ground states (and possibly also in the excited states) of the systems to be studied, as well as measurements of the lifetimes as a function of temperature. As a result of these measurements, we will be able to evaluate, prior to the experiment:

- the laser wavelength to be used for the best ratio d_{Xrays} / d_{laser}
- the most appropriate time resolution