



	<b>Experiment title:</b> X-ray absorption spectroscopy study of the electron transfer reaction $[\text{IrX}_6]^{2-} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	<b>Experiment number:</b> CH 1169
<b>Beamline:</b> ID 24	<b>Date of experiment:</b> from: 7 <sup>th</sup> Feb 2002 to: 14 <sup>th</sup> Feb 2002	<b>Date of report:</b> 18 <sup>th</sup> April 2002
<b>Shifts:</b> 21	<b>Local contact(s):</b> Sofia Diaz Moreno	<i>Received at ESRF:</i>
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## Report:

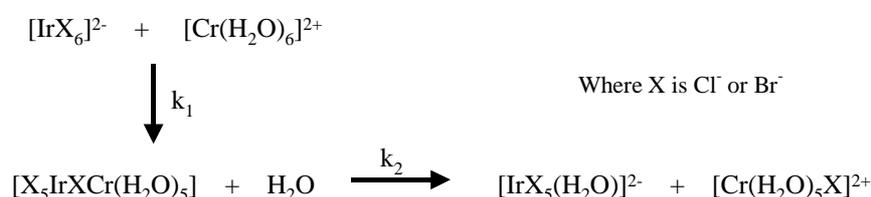
Electron-transfer reactions are a very important class of chemical reaction, that are known to proceed via two principal mechanisms [1]:

- (i) an outer-sphere mechanism, where the electron jumps through several layers of solvent and
- (ii) an inner-sphere reaction, where the transfer of the electron is made by a bridging group between the oxidant and the reductant.

Traditionally the characterisation of a reaction mechanism as inner-sphere requires the observation of a bridge ligand that is transferred from one metal centre to another [2]. However, ligand transfer is not an essential characteristic for all such reactions, and in those reactions where it does not take place, the detection of a bridged activated complex is considered sufficient evidence for assigning an inner-sphere mechanism to the reaction [3,4]. Though evidence for the existence of several of these latter reactive species has been obtained, no structural information has yet been obtained. It was the aim of this experiment to try and obtain via time resolved X-ray absorption spectroscopy the first data of this kind.

The system chosen for investigation was the redox reaction between  $[\text{IrX}_6]^{2-}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ , see Figure 1. This reaction is spectroscopically known [5] to proceed via the inner-sphere mechanism, though a fast outer sphere mechanism also occurs simultaneously that we anticipated would contribute a final state background to the data analysis.

Figure 1:



Time resolved experimental data were collected on the chloride ion balanced reaction at the Ir L<sub>III</sub> absorption edge using the Energy Dispersive X-ray Absorption Spectroscopy technique (EDXAS) and with the reaction initiated using the stopped flow cell methods developed at, and integrated into ID-24 [6].

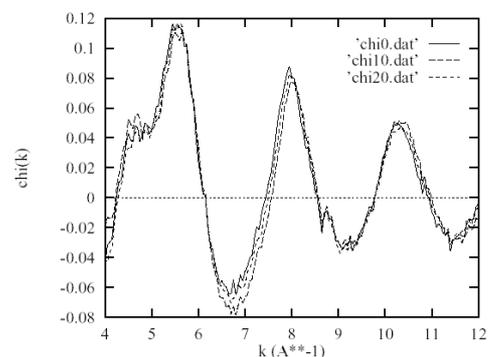
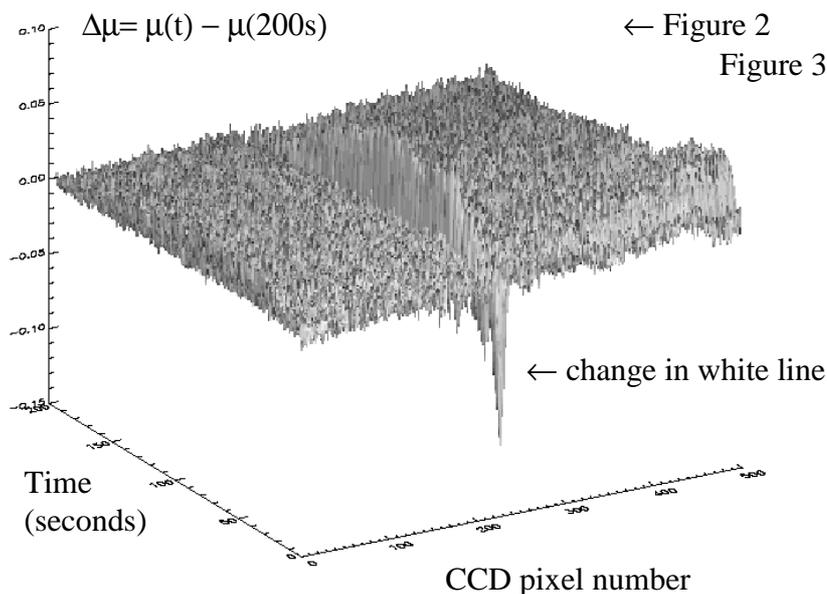


Figure 2 shows the difference spectrum calculated for the jump normalized experimental data collected in 1 second intervals over the first 200 seconds of the reaction. The varying feature corresponds to changes in the Ir L<sub>III</sub> white line obtained by

subtracting the 200 second (final state) spectrum from each of the spectra collected from the initiation of the reaction to 199 seconds later. The results show that there is a rapid transition that occurs in the first 20 seconds of the reaction followed by a region of stability from approximately 20 second to 160 seconds, before final relaxation to the state that occurs at 200 seconds. Figure 3 shows the small changes that occur in the EXAFS signal over the first 20 seconds of the reaction .

The slight variations in the EXAFS spectra appear to correspond to subtle structural changes in the local Ir environment over this time scale. Unfortunately the magnitude of the effect is too small to be able to reliably interpret structurally, though the reproducibility of the features between consecutive runs on different samples lends us a degree of confidence as to their existence. It was hoped that this difficulty could be overcome by collecting data on the bromine counter ion system where both Ir and Br edge data could be obtained. In principle this would have allowed us a complementary viewpoint, but unfortunately was prevented by the evolution of gas in that system. This gas producing side reaction was apparently unobserved in the earlier optical spectroscopy studies [5] due to the limitations of those techniques restricting them to the investigation of extremely dilute solutions only. Without the information from the counter-ion, the data analysis of the EXAFS was greatly hindered. This fact, in combination with the acknowledged dual character nature of the reaction system that results in a degradation of the ratio between spectral signal for the bridged activated complex versus the final state product, led to the inconclusive nature of the structural results. However, we believe the principle of the method has been demonstrated and more appropriate systems have now been identified.

- [1] Meyer, T.J. and Taube, H., "Comprehensive Coordination Chemistry", Vol. 1, pp. 331-84, Pergamon Press, Oxford, **1987**
- [2] Taube, H., Myers, H. and Rich, R.L., *J. Am. Chem. Soc.*, **1953**, 75, 4118.
- [3] Wilkins, R.G., "Kinetics and Mechanism of Reactions of Transition Metal Complexes", 2<sup>nd</sup> edc., VCH, Weinheim, **1991**, pp. 257-97.
- [4] Lippard, S.J., *Progress in Inorganic Chemistry*, **1983**, 30, 273.
- [5] (a) Sykes, A.G.; Thorneley, R.N.F., *J. Chem. Soc. (A)*, **1970**, 232. (b) Melvin, W.S.; Haim, A., *Inorg. Chem.*, **1977**, 16, 2016.
- [6] S. Diaz Moreno, in "From semiconductors to proteins: Beyond the Average Structure", edited by S.J.L. Billinge and M.F. Thorpe, 203-218, Kluwer/Plenum Academic Press, **2002**