

# Time-resolved pump-probe XAFS spectroscopy of copper based model complexes at beamline P11

B. Dicke<sup>1</sup>, M. Naumova<sup>2</sup>, B. Lebsanft<sup>1</sup>, A. Wetzel<sup>1</sup>, Alexander Hoffmann<sup>3</sup>, Johann Bielecki<sup>4</sup>, Jakob Andreasson<sup>4</sup>, Andriwo Rusydi<sup>5</sup>, Adam Neuba<sup>2</sup>, Gerald Henke<sup>2</sup>, Sonja Herres-Pawlis<sup>3</sup>, Michael A. Rübhausen<sup>1</sup>

<sup>1</sup>University of Hamburg and CFEL, Notkestraße 85, 22607 Hamburg, Germany

<sup>2</sup>University of Paderborn, Warburger Straße 100, 33098 Hamburg, Germany

<sup>3</sup>University of Munich (LMU), Butenandstraße 5-13, 81377 Munich, Germany

<sup>4</sup>University of Uppsala, Husarg. 3, 75124 Uppsala, Sweden

<sup>5</sup>National University of Singapore, 21 Lower Kent Ridge Road, 119077 Singapore, Singapore

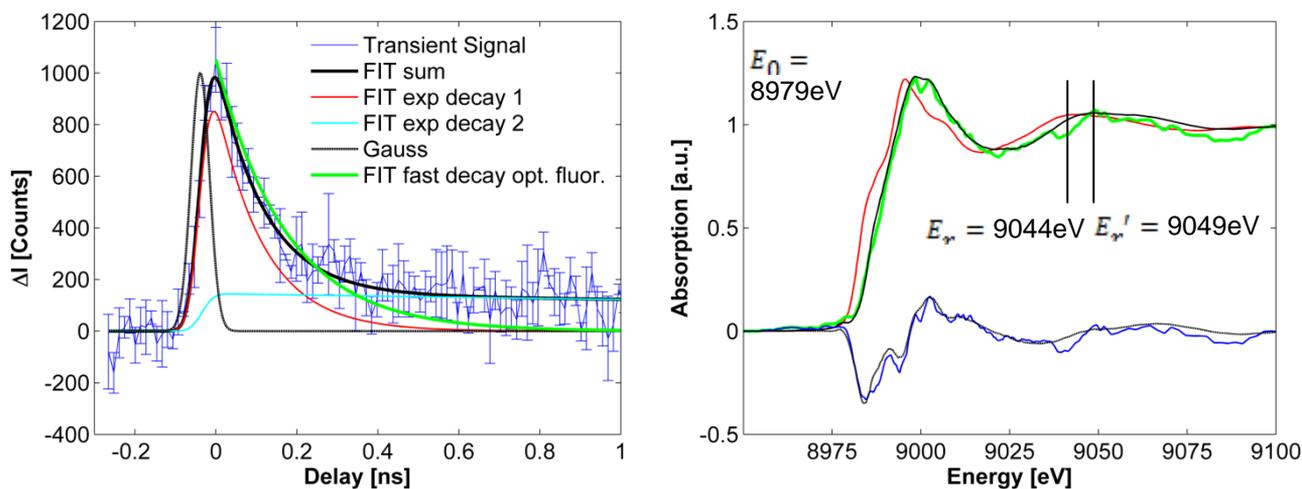
In Cu-Type-0 complexes it is possible to establish centers with a charge state of +I and +II which are coupled via metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT) processes, respectively. Typically this charge transfer is related to a transition from a tetrahedral to a square planar structure.

In a first beamtime in Oct. 2013 we studied two different complexes namely  $[\text{Cu(I)(TMGqu)}_2]^+$  and  $[\text{Cu(II)(TMGqu)}_2]^{2+}$  in which copper has an oxidation state of +I and +II respectively. A resonance raman study had shown that both, the MLCT as well as the LMCT transitions can be optically triggered [1]. We profited by this and studied the structural dynamics of the compounds with a time resolution of about  $\sim 70$  ps using time-resolved pump-probe XAFS [2].

In this technique the sample is pumped by a femtosecond laser pulse and then after a certain time delay probed by an X-ray pulse. In this way, two different types of measurements were performed: 1. Energy spectra: Scanning of the X-ray photon energy at a fixed time delay (see figure 1 right) and 2. Time-delay spectra: Scanning of the time delay between pump laser pulse and probe X-ray pulse at a fixed energy (see figure 1 left).

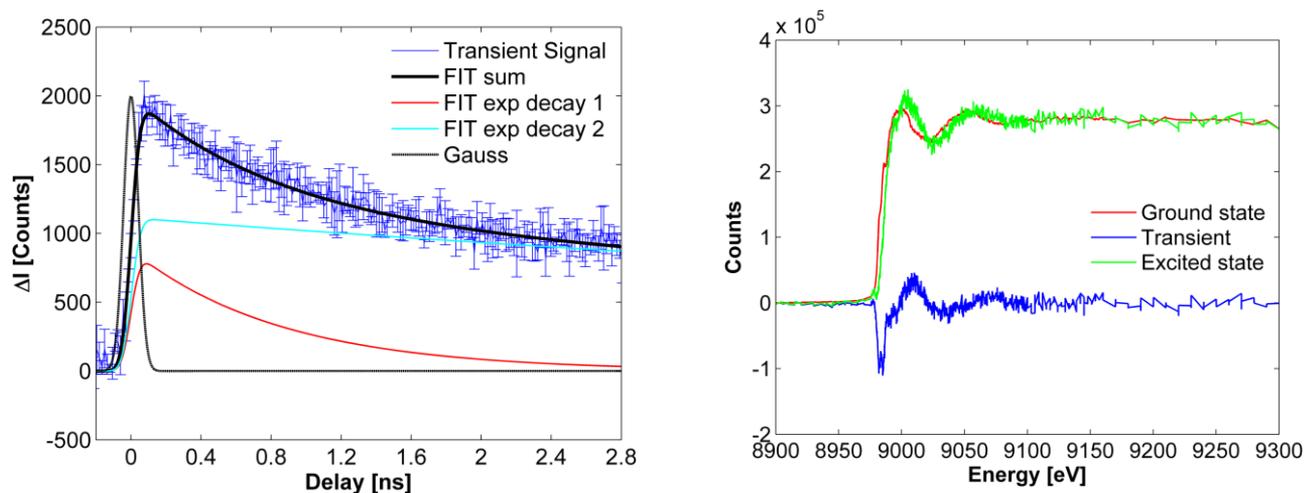
The decay of the time delay spectrum was dominated by a fast decay component with a time constant of  $\sim 130$  ps. However, we were unable to trigger the Cu(II) to Cu(I) transition, even though this transition is being accompanied by a visible fluorescence and being clearly identified by the resonance Raman study. We therefore confer that the dynamics of this state is beyond the time resolution of PETRA III. Furthermore, the XAS spectra of  $[\text{Cu(II)(TMGqu)}_2]^{2+}$  and of the photoexcited  $[\text{Cu(I)(TMGqu)}_2]^+$  ( $^*[\text{Cu(I)(TMGqu)}_2]^+$ ) show for higher energies up to 100 eV above the whitenline, a shift of the first resonance peak with respect to the one of  $[\text{Cu(I)(TMGqu)}_2]^+$  (see figure 1 right). This is related to the expected structural distortion between Cu(I) and Cu(II) complexes which involves a bond length contraction of the Cu-N<sub>gua</sub> bonds.

Furthermore, it is notable that both have the  $1s \rightarrow 4p$  transition blue-shifted by ca. 3.2 eV with respect to that one of the ground state of  $[\text{Cu(I)(TMGqu)}_2]^+$ . This can be associated with an oxidation state change of the Cu(I) species upon photoexcitation. In addition, a pre-edge is emerging upon the photoexcitation which can be clearly referred to a  $1s \rightarrow 3d$  transition and thus a  $3d^9$  configuration of Cu(II). Thus, these two observations together state the Cu(II) character of the MLCT state (compare also with Ref. [2]).



**Figure 1** (left) Transient difference spectrum between  $[\text{Cu(I)(TMGqu)}_2]^+$  and  $^*[\text{Cu(I)(TMGqu)}_2]^+$  as function of time delay at a fixed energy of 8985 eV with different fit components. For comparison a fast decay component observed in time-resolved fluorescence spectroscopy is shown. The decay component was determined to be  $\sim 130$  ps. (Right) K-edge energy spectra of  $[\text{Cu(I)(TMGqu)}_2]^+$  (red line),  $[\text{Cu(II)(TMGqu)}_2]^{2+}$  (solid black line) and  $^*[\text{Cu(I)(TMGqu)}_2]^+$  (green line). The latter two show the same features in the XANES region and also a blue shift of the first resonance peak after the whiteline with respect to that of  $[\text{Cu(I)(TMGqu)}_2]^+$ . The fraction of excited state molecules ( $\sim 6\%$ ) was determined by scaling the transient difference spectrum between  $[\text{Cu(I)(TMGqu)}_2]^+$  and  $^*[\text{Cu(I)(TMGqu)}_2]^+$  (blue line) to the difference spectrum between  $[\text{Cu(I)(TMGqu)}_2]^+$  and  $[\text{Cu(II)(TMGqu)}_2]^{2+}$  (dashed black line).

In a second beamtime in Jan. 2014 we studied the structural dynamics of a dinuclear copper(I) complex  $[\text{Cu}_2(\text{RSSR})_2](\text{OTf})_2$ . This complex showed a fast decay component with a time constant of  $\sim 1$  ns and a slow decay component with a time constant of  $\sim 11$  ns. The energy spectra show a shift of the first resonance peak for the excited state with respect to the ground state, a blue shift of the  $1s \rightarrow 4p$  transition and an emerging pre-peak upon photoexcitation, so that we can state that the spectral features are in full analogy to those of the TMGqu complex.



**Figure 2** (left) Transient difference spectrum between  $[\text{Cu(I)}_2(\text{RSSR})_2]^{2+}$  and  $^*[\text{Cu(I)}_2(\text{RSSR})_2]^{2+}$  as function of time delay at a fixed energy of 8985 eV with different fit components. (Right) K-edge energy spectra of  $[\text{Cu(I)}_2(\text{RSSR})_2]^{2+}$  (red line) and  $^*[\text{Cu(I)}_2(\text{RSSR})_2]^{2+}$  (green line). The blue line presents the transient difference spectrum, whereas an excited state fraction of 10 % was assumed.

## References

- [1] A. Hoffmann, S. Binder et al. *Angew. Chem. Int. Ed.* **53**, 299-304 (2014)
- [2] M. W. Mara, N. E. Jackson et al. *J. Phys. Chem. B*, **117**, 1921–1931 (2013)