

SLS Symposium on Electron Dynamics

Tuesday, September 7, 2010

10:00 to 12:15, WBGB/019

10:00 High repetition rate ultrafast time-resolved x-ray absorption spectroscopy
C.J. Milne, A. El Nahhasy, F. Lima, D. Amarasinghe, R.M. van der Veen, M. Reinhard, H. Rittmann-Frank, V.-T. Pham, C.N. Borca, D. Grolimund, R. Abela, Frank van Mourik and M. Chergui

10:30 Magnetic dynamics in the induced multiferroic CuO
S.L. Johnson, U. Staub, R. De Souza, E. Vorobeva, P. Beaud, A. Caviezel, G. Ingold, W.-S. Lee, Y.-D. Chuang, O. Krupin, L. Patthey, R. Moore, D. Lu, M. Yi, P. Kirchmann, W. Schlotter, J. Turner, M. Trigo, P. Denes, D. Doering, Z.X. Shen, Z. Hussain, A.T. Boothroyd

11:00 Coffee

11:15–11:45 Femtosecond laser-induced CDW melting in TiSe_2

E. Vorobeva, S.L. Johnson, P. Beaud, U. Staub, R. De Souza, Ch. Milne, J. Demsar, H. Schäfer, A. Titov and G. Ingold

11:45–12:15 Ultrafast dynamics in molecular complexes studied by time-resolved X-ray and optical spectroscopies

R.M. van der Veen, C.J. Milne, F.A. Lima, V.-T. Pham, A. El Nahhas, A. Cannizzo, D. Grolimund, C.N. Borca, S.L. Johnson, C. Bressler, R. Abela and M. Chergui

High repetition rate ultrafast time-resolved x-ray absorption spectroscopy

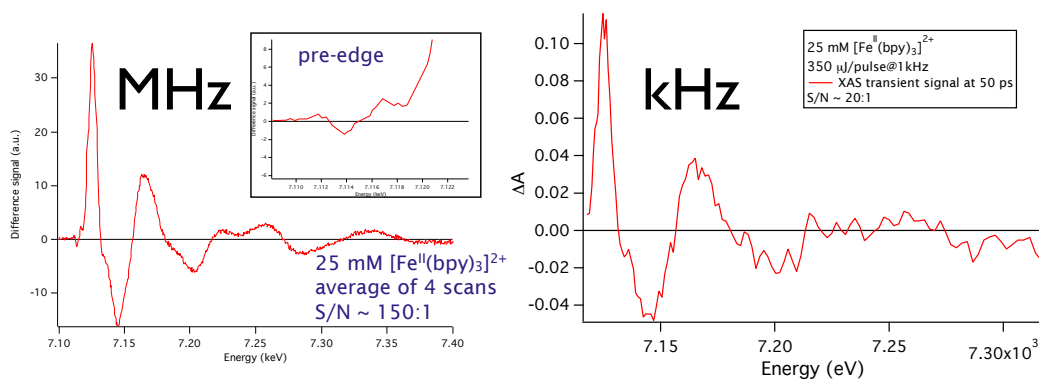
C.J. Milne^{*†}, A. El Nahhas[†], F. Lima^{*†}, D. Amarasinghe^{*†}, R.M. van der Veen^{*†}, M. Reinhard[†], H. Rittmann-Frank^{*†}, V.-T. Pham[†], C.N. Borca^{*}, D. Grolimund^{*}, R. Abela^{*}, Frank van Mourik[†], and M. Chergui[†]

[†]*Ecole Polytechnique Fédérale de Lausanne, Switzerland*

^{*}*Swiss Light Source, Paul Scherrer Institut, Switzerland*

chris.milne@psi.ch

Abstract: Using x-ray absorption spectroscopy (XAS) to probe laser-excited samples we can obtain excited-state structural and electronic dynamical information not available through other techniques.[1] One of the restrictions of most implementations of this technique is the 10^3 mismatch between x-ray and laser repetition rates. By using a laser capable generating significant pulse energies at MHz repetition rates we can eliminate this mismatch, thus greatly reducing measurement times and enhancing achievable signal-to-noise ratios. Two examples that demonstrate the strength of this technique will be presented. The first example is an investigation of a Re-based inorganic complex [ReBr(CO)₃bpy] in solution that DFT calculations indicate has a mixed metal-to-ligand charge transfer (MLCT) character in the ground-state with electron density being shared by the Re and halide moieties.[2] By monitoring the XAS signal at both the Re and Br absorption edges we can observe the charge density recovery dynamics after photoexcitation, confirming the MLCT-character of the ground-state. The second example that illustrates the significant gains to be had by increasing the data acquisition rate involves the photo-excitation of a dilute solution of the oxygen transport protein myoglobin (Mb). The Fe atom at the center of Mb can bind a small molecule such as O₂, CO, or NO, which is then released upon absorption of visible light. This allows us to investigate the ligand-recombination dynamics as well as the spin-state dynamics of the iron by measuring the time-dependent XAS signal at the Fe K-edge.



References

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2. A. El Nahhas, A. Cannizzo, F. van Mourik, A. M. Blanco-Rodriguez, S. Záliš, A. Vlček, and M. Chergui, "Ultrafast excited-state dynamics of [Re(L)(CO)₃(bpy)]ⁿ complexes: Involvement of the solvent," *J Phys Chem A* **114** (Jan, 2010) 6361–6369.

Magnetic dynamics in the induced multiferroic CuO

S. L. Johnson¹, U. Staub¹, R. De Souza¹, E. Vorobeva¹, P. Beaud¹, A. Caviezel¹, G. Ingold¹, W.-S. Lee², Y.-D. Chuang³, O. Krupin⁴, L. Patthey¹, R. Moore², D. Lu², M. Yi², P. Kirchmann², W. Schlotter⁵, J. Turner⁵, M. Trigo⁵, P. Denes³, D. Doering³, Z. X. Shen², Z. Hussain³, A. T. Boothroyd⁶

¹ Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

² Stanford University, Stanford, California 94305

³ Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

⁴ European XFEL, Albert-Einstein-Ring 19, 22761 Hamburg, Germany

⁵ SLAC National Accelerator Laboratory, Menlo Park, California 94025

⁶ Department of Physics, Oxford University, Oxford OX1 3PU, UK

steve.johnson@psi.ch

Induced multiferroics are materials that exhibit an unusual coupling of magnetism and ferroelectricity. CuO is a prominent example of such a material: whereas at low temperatures it displays antiferromagnetic order with an ordering wave-vector commensurate with the underlying lattice, at higher temperatures the magnetic order shifts to an incommensurate spiral and induces a small structural change that leads to ferroelectricity [1].

To investigate the interplay of magnetic, structural and electronic order in this system we have employed femtosecond time-resolved resonant diffraction at an x-ray free electron laser [2] to probe directly the dynamics of the magnetic order in response to a sudden electronic excitation from a 50 fs, 800 nm wavelength near-IR laser pulse. Although the data are still under analysis, preliminary results indicate that we are indeed able to resolve the time scale for growth of an electronically induced incommensurate, multiferroic phase.

[1] T. Kimura, Y. Dekio, H. Nakamura, T. Siegrist and P. Ramirez. *Nat. Mat.* **7**, 291-4 (2008).

[2] P. Emma et al. *Nat. Photon.* 2010 (doi:10.1038/nphoton.2010.176).

Femtosecond laser-induced CDW melting in TiSe_2

E. Vorobeva¹, S. L. Johnson¹, P. Beaud¹, U. Staub¹, R. De Souza¹, Ch. Milne^{1,2}, J. Demsar³, H. Schäfer³, A. Titov^{4,5} and G. Ingold¹

¹ Swiss Light Source, Paul Scherrer Institut, CH 5232 Villigen, Switzerland

² Laboratoire de Spectroscopie Ultrarapide, EPFL, 1015 Lausanne, Switzerland

³ Physics Department and Center of Applied Photonics, University of Konstanz, Germany

⁴ Institute of Metal Physics UrDRAS, Ekaterinburg, Russia

⁵ Institute of Metallurgy UrDRAS, Ekaterinburg, Russia

ekaterina.vorobeva@psi.ch

Charge density waves (CDW) are an example of a collective phenomenon in solids, which involves the development of a periodic modulation in the density of the electronic charges with a wave vector q that does not correspond to the reciprocal vector of the lattice. A common explanation for the CDW formation is Fermi surface nesting. It originates from the Peierls idea of electronic instabilities in purely 1D metals and is now often applied to charge ordering in real low-dimensional materials. This mechanism is, however, not unique. In 1T- TiSe_2 doubling of the lattice along the hexagonal crystal axes below 202K cannot be explained by existence of nesting vectors. Despite intense study over more than 30 years there is still no consensus on the mechanism driving this structural phase transition. With our work we contribute to this debate with the data obtained from time-resolved x-ray diffraction and optical reflectivity measurements. Our experimental x-ray data taken at FEMTO beamline at the SLS reveal an ultrafast laser-induced melting of a CDW state in TiSe_2 within the experimental time-resolution of 250 fs for laser fluences above $\sim 2 \text{ mJ/cm}^2$ at 140K (Fig. 1a). The optical reflectivity data show the presence of an A_{1g} amplitude mode of the CDW that softens as the temperature or laser fluence increase and finally disappears (Fig. 1b). By analyzing the x-ray data within the Landau model for second order phase transition we test one of the competing hypotheses that the doubling of the TiSe_2 lattice is driven by the electrons.

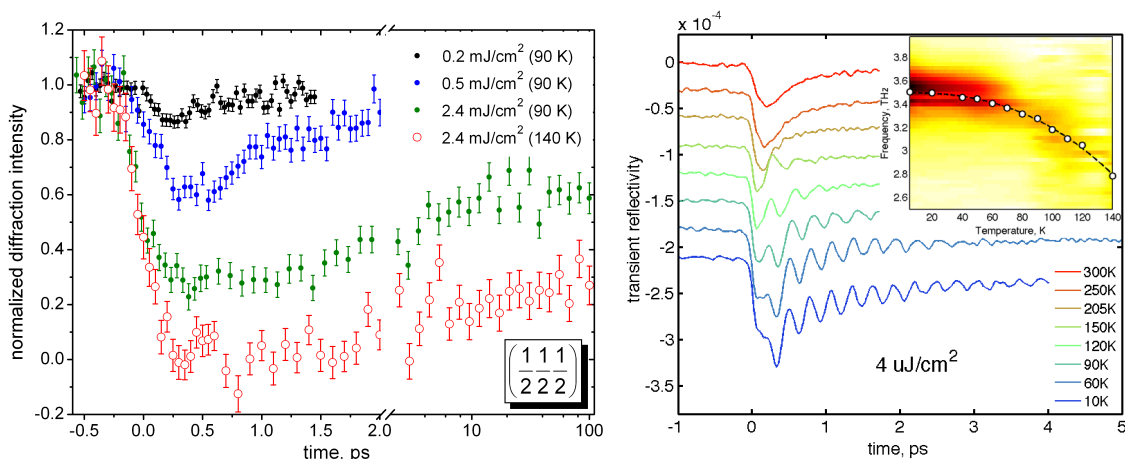


Figure 1. (a) Normalized intensity of the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ superlattice peak of TiSe_2 as a function of time at 90K and 140K; (b) Temperature dependence of the transient reflectivity signal of TiSe_2 measured at a laser fluence of 4 mJ/cm^2 . Inset shows the power spectrum of the oscillatory component of the data and the peak positions as extracted from a fit with a damped oscillator model.

Ultrafast dynamics in molecular complexes studied by time-resolved X-ray and optical spectroscopies

R.M. van der Veen^{1,2}, C.J. Milne^{1,2}, F.A. Lima^{1,2}, V.-T. Pham², A. El Nahhas², A. Cannizzo², D. Grolimund¹, C.N. Borca¹, S.L. Johnson¹, C. Bressler³, R. Abela¹ and M. Chergui²

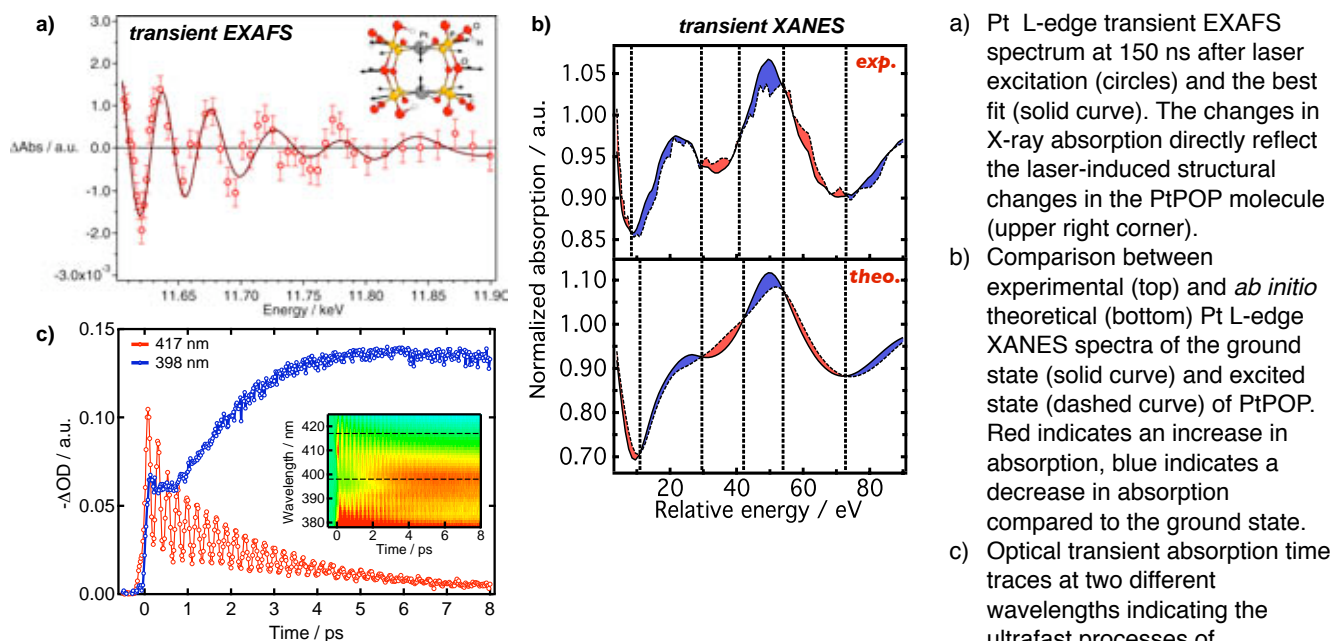
¹ Swiss Light Source, Paul Scherrer Institute, Switzerland

² Laboratoire de Spectroscopie Ultrarapide, Ecole Polytechnique Fédérale de Lausanne, Switzerland

³ European XFEL GmbH, Hamburg, Germany

Observation of the making and transforming of chemical bonds in the course of a chemical reaction is the dream of every chemist. The recent implementation of X-ray absorption spectroscopy in the ultrafast time domain allows studying the electronic and structural dynamics of photoexcited molecules in solutions. In this study we present the ultrafast dynamics of a photochemically active molecular complex ($[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$, PtPOP). X-ray pulses of 70 ps width from the FEMTO beam line at the Swiss Light Source are used to probe the transient structure after excitation with a femtosecond laser pulse tuned to the excited state absorption at 380 nm. A rigorous model-based statistical analysis of the difference (excited minus unexcited) X-ray absorption fine structure (EXAFS) spectrum shows a contraction of 0.31(5) Å of the Pt atoms and a ligand expansion of 0.010(6) Å in the triplet excited state. *Ab initio* calculations of the X-ray absorption near-edge structure (XANES) spectrum for both the ground and excited states are in good agreement with the time-resolved EXAFS results. However, further improvements in the theoretical treatment of XANES are necessary to make it a more quantitative tool in structural dynamics. Complementary to the time-resolved X-ray measurements, optical femtosecond transient absorption measurements have shown wavepacket dynamics and vibrational cooling in the impulsively excited singlet state. These results indicate that the solvent plays an important role in funneling the excited state excess energy.

The combination of ultrafast optical and X-ray techniques is a promising approach to obtain new insights in structural and electron dynamics of chemical and biological systems. The advent of intense sources of femtosecond X-rays (e.g. XFELs) make it possible to apply this method to more complex systems.



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