Time-Dependent X-ray spectroscopy as a Probe of Ultrafast Dynamics in Transition-Metal Photo-excited Complexes

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Photon-induced nonequilibrium electron dynamics in transition-metal complexes have drawn intense interest for numerous applications in diverse research fields such as solar energy conversion, photosynthesis, photodissociation, and photocatalysis [1]. The study of the time evolution of the light-driven state is crucial in creating a deeper understanding of these technologically-important phenomena. Often, the photo-induced state undergoes an ultrafast decay into a metastable state from which it relaxes more slowly back into the ground state. The use of ultrafast pump-probe x-ray spectroscopy would provide structural, electronic, and magnetic information on the nonequilibrium properties of an excited system.

After the absorption of a photon, the system is in a highly excited state from which it can relax back to the ground state or to a metastable state often cascading through several intermediate states. Understanding of this relaxation is of importance for photoinduced effects, such as photoinduced demagnetization or spin transitions, energy conversion processes including solar cell applications and photosynthesis, etc. Understanding pump-probe spectroscopy on these system requires the inclusion of dissipative effects that allow relaxation of the highly-excited state. A prototypical example is photoinduced spin crossover effects that occur, for example, in low-spin iron and ruthenium complexes [2]. After photoexcitation, the material relaxes into a metastable state with different spin and metal-ligand distances. In addition, the excited electron can in certain situations decouple from the system which is of importance for solar cell applications. An understanding of the ultrafast dynamics is therefore crucial. Time-dependent x-ray spectroscopy can give insight into the detailed nature of the intermediate states in the cascading process by providing time-dependent information on magnetic moments, the electronic configuration, and bond lengths. Other systems that have been studied with optical pump/x-ray probe involve fast demagnetization (100-300 fs) in thin metal layers such as nickel [3, 4]. These systems have been described using macroscopic models of the magnetization. However, such approaches do not allow a detailed interpretation of the spectral line shape. In order to understand these experiments, methodologies to understand pump/probe x-ray spectroscopy on materials away from nonequilibrium need to be developed. This requires the coupling of the local electronic system, where the x-ray process occurs, to a bath of states to absorb the excess energy from the pump mechanism.

In order to take full advantage of the x-ray based pump-probe capabilities currently developed at the Department of Energy's user facilities, new theoretical methodologies to describe these experiments need to be developed in addition to the experimental tools. Below are the key developments necessary to interpret these techniques.

First, methods need to be developed to allow the large-scale calculation of nonequilibrium processes, i.e, processes including dissipation . Often, nonequilibrium processes are described by studying the time dependent population of particular states. However, this is not sufficient for the understanding of x-ray absorption spectral lineshapes which are usually very sensitive to the detailed nature of ground-state properties, such as symmetries, ground-state expectation values of spin-orbit coupling, orbital and spin moments, etc. This generally requires the calculations of larger-scale systems. Generally, nonequilibrium processes are calculated using density-matrix methods that limit the size of the system that can be studied. Calculational techniques that allow for the calculation of large systems in the presence of dissipation, essential for describing x-ray spectroscopy, need to be developed.

Secondly, the interpretation of the time-dependent spectral lineshapes requires extension of existing codes to calculate x-ray spectroscopy into the time-domain. Currently, the number of calculations of x-ray pump-probe experiments is extremely limited. The lack of code development for spectral lineshape interpretation concurrent with the progress of experimental techniques would allow the experimentalist to make better use of the

Thirdly, a better understanding of x-ray pump-probe techniques needs to be developed. Although, intuitive ideas exist regarding the interpretation of, for example, an optical-pump/x-ray-probe experiment exist, no systematic understanding has been developed. More understanding needs to be developed of the effects of the time-dependence of both pump and probes on the interpretation of spectroscopy. A complicating factor is the higher-order nature of the process. Even in the absence of dissipative effects, higher-order spectroscopies, such as resonant inelastic x-ray scattering, are less straightforward to interpret. New concepts for interpreting x-ray pump-probe spectroscopies are essential for a broader ac-

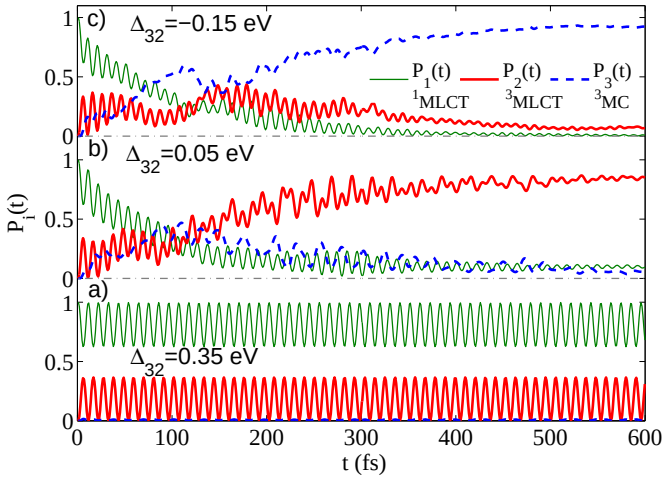

FIG. 1: The probability of the ^{1}MLCT ($P_1(t)$, green thin solid), the ^{3}MLCT ($P_2(t)$, red solid), and the ^{3}MC ($P_3(t)$, blue dashed) as a function of time for different values of the energy difference Δ_{32} between the ^{3}MC and ^{3}MLCT states. (a) $\Delta_{32} = 0.35$ eV; (b) $\Delta_{32} = 0.05$ eV; (c) $\Delta_{32} = -0.15$ eV.

ceptance of these techniques.

A typical example of the effects that can be studied are spin-crossover phenomena in transition-metal complexes. Crucial in the understanding of this process [5] is the change of the metal-ligand distance resulting from the transfer of electrons from the t_{2g} to the e_g orbitals that repel the ligands more strongly [6]. This mechanism underlies the spin crossover in Fe complexes [7]. However, a significant bond elongation is not present in all spin-crossover systems. In ruthenium complexes, such as $[\mathrm{Ru^{II}(byp)^3}]^{2+}$, spin flips occur within the t_{2g} orbitals and only a minimal change in metal-ligand bond length is observed [8]. Due to their wide frequency response, ruthenium compounds have been extensively studied. The ground state is a singlet with six electrons in the t_{2g} orbitals. Since Ru $4d^6$ multiplet excitations are dipole forbidden, the optical excitations are dominated by metal-to-ligand charge-transfer (MLCT) into the π^* orbitals of the organic ligands, creating a singlet $t_{2g}^5 L$ configuration, where L indicates an electron in the π^* ligands. The strong $4d$ spin-orbit coupling then causes spin flips in the t_{2g}^5 states leading to triplet MLCT states. The resulting triplet state is long-lived with a lifetime on the order of hundreds of ns [9–11].

Despite decades of research, the mechanism for the ultrafast decay from the singlet to the triplet MLCT states is still not understood. The radiationless ultrafast decay is generally accompanied by a pronounced change of the metal-ligand bond lengths [5]. However, one does not expect a significant change in the Ru-ligand distance for different t_{2g}^n configurations. This has been confirmed experimentally where for the ^{3}MLCT a bond contraction of only ∼0.03 Å [8] with respect to the ground state is observed. As a result, the Huang-Rhys factor, and hence the decay, between MLCT singlet and triplet is expected to be negligibly small. Therefore, the system should oscillate between the singlet and triplet states via the spin-orbit interaction. A possible explanation for the irreversible decay between the singlet and triplet MLCT is that a ^{3}MC ($t_{2g}^5 e_g$) state acts as an intermediary. Small hopping matrix elements due to deviations from pure octahedral symmetry allow a coupling between the ^{3}MC and ^{3}MLCT states. Depending on the relative position of the MC state with respect to the MLCT different decays can be observed ranging from an oscillation between the singlet and triplet MLCT states, a decay to the ^{3}MC state and a decay into the ^{3}MLCT. Optical-pump/X-ray-probe can provide valuable insights into the various mechanisms and the involvement of the ^{3}MC due to its sensitivity to the electronic and structural properties of the Ruthenium complex. The chemical selectivity of X-ray absorption also makes the interpretation less ambigous than techniques that work with visible light.

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[1] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. **84**, 85 (1988).
[2] P. Gütlich and H. A. Goodwin, Spin Crossover in Transition Metal Compounds (Berlin, Springer-Verlag, 2004).
[3] C. Stamm, T. Kachel, N. Pontius, R. Mitzner, T. Quast, K. Holldack, S. Khan C. Lupulescu, E. F. Aziz, M. Wietstruk, H. A. Dürr, and W. Eberhardt, *740 Femtosecond modification of electron localization and transfer of angular momentum in nickel*, Nature Materials **6**, 740 (2007).
[4] H.-S. Rhie, H. A. Dürr, and W. Eberhardt, *6 eV PES Femtosecond electron and spin dynamics in Ni/W(110) films*, Phys. Rev. Lett. **90**, 247201 (2003).
[5] M. van Veenendaal, J. Chang, and A. J. Fedro, Phys. Rev. Lett. **104**, 067401 (2010).
[6] Ch. Bressler *et al.*, Science **323**, 489 (2009).
[7] J. Chang, A. J. Fedro, and M. van Veenendaal, Phys. Rev B **82**, 075124 (2010).
[8] W. Gawelda, M. Johnson, F. M. F. de Groot, R. Abela, C. Bressler, M. Chergui, J. Am. Chem. Soc. **128**, 5001 (2006).
[9] N. H. Damrauer *et al.*, Science **275**, 54 (1997).
[10] A. T. Yeh, C. V. Shank, and J. K. McCusker, Science **289**, 935 (2000).
[11] C. Creutz, M. Chou, T. L. Netzel, M. Okumura, N. Sutin, J. Am. Chem. Soc. **102**, 1309 (1980).
[12] J. Chang, A. J. Fedro, and M. van Veenendaal, to be published.