Attosecond Stimulated X-ray Raman Probes of Energy and Electron Transfer in Porphyrin Dimers and Proteins

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Abstract: Energy and electron transfer processes in molecular complexes can be measured at unprecedented spatial and temporal resolution by novel X-ray spectroscopy techniques. Multidimensional broadband X-ray signals are simulated for a metalloporphyrin dimer and a Re-modified azurin model system of long-range biological electron transfer.

1. Introduction

Excitation energy transfer (EET) and electron transfer (ET) in biological systems are essential for living species, e.g. they play important roles in photosynthesis and cell respiration. Conventionally EET and ET are observed by time-resolved fluorescence spectroscopy or time-resolved infrared techniques. Ultrafast X-ray spectroscopy is a powerful tool to follow electronic dynamics, and novel intense X-ray technology will make even the single molecule measurement possible.[1] Here we propose using ultrafast X-ray pulses to take snapshots of these processes. Stimulated X-ray Raman spectroscopy(SXRS) and transient X-ray absorption signals connect directly to the change of electron densities around the specific atoms excited by the X-ray pulses. Comparing to optical or infrared pulses, the much shorter X-ray pulses can create excited state superpositions localized to the target atoms, resulting in much higher temporal and spatial resolutions. In this study we apply this technique to porphyrin dimers and the Re-modified azurin and demonstrate the power of ultrafast X-ray spectroscopy in probing EET and ET dynamics. The SXRS technique is illustrated in Fig. (a).

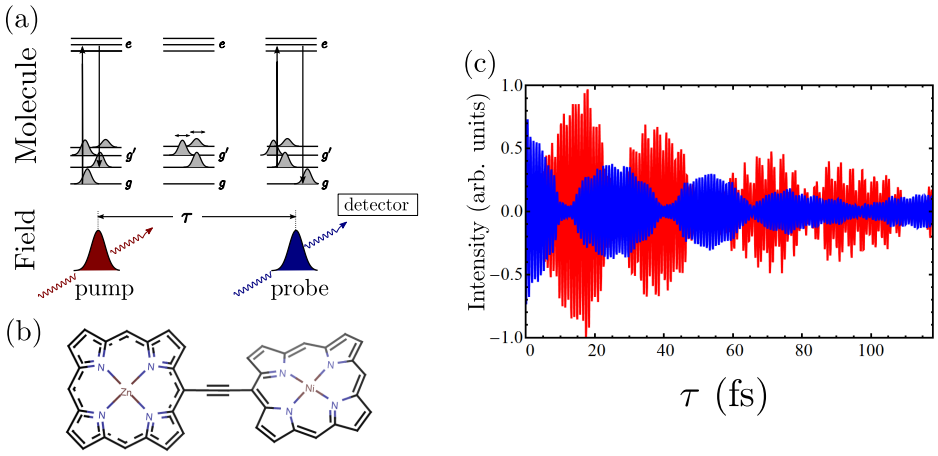

Figure 1: (a) The mechanism of SXRS technique. The system is initially in the ground state g. The pump pulse creates a valence excitation g' through a Raman process with the transient occupation of a core-excited state e. After a time delay τ, the probe pulse returns the system to the ground state via another Raman process. The signal is given by the difference in the transmitted intensity of the probe with and without the pump. (b) The zinc-nickel porphyrin dimer studied. (c) The time-resolved SXRS signals for the porphyrin dimer. Shown are single-color Zn2p/Zn2p signal (in blue) and two-color Zn2p/Ni2p signal, with a zinc pump and nickel probe (in red).

2. Energy Transfer in Metalloporphyrin Dimers Detected by Stimulated X-ray Raman Spectroscopy

Porphyrin rings are the nature's choice for converting sunlight energy into chemical bonding energy. With different metal centers, porphyrins form the basic structure of many bio-molecules. In the light-harvesting antenna complex, porphyrins absorb the sunlight photons and get excited, then the excitation energy is transferred to the reaction center, where the photosynthetic chemical reaction happens. A full understanding of EET dynamics may lead to high-performance solar cell and molecular electronic devices.

Porphyrin dimers are building blocks for more complicated multiporphyrin systems. We use the zinc-nickel porphyrin dimer with an ethynyl linker as an example.[2] The calculated one- and two-color SXRS signals (Zn/2p edge pump, Zn/2p edge probe, Zn2p/Zn2p; and Zn/2p edge pump, Ni/2p edge probe, Zn2p/Ni2p) are shown in Fig. (c). We see an almost 90 degree phase difference between these SXRS signals probed on different monomers, which indicates a back-and-forth motion of the electron density. Further natural orbital analysis of the doorway

and window wavepackets created by the X-ray pulses reveals that electron and hole move together, which confirms that we are detecting EET, not ET.[2]

3. Electron Transfer in Re-modified Azurin Detected by Stimulated X-ray Raman Spectroscopy and Transient X-ray Absorption Spectroscopy

Azurin is a small (128 residues for Re-modified azurin) type I blue copper protein (cupredoxin)[3] produced by several aerobic bacteria. Azurin transfers one electron between cytochrome c-551 and cyt oxidase, which helps Pseudomonas oxidase or Pseudomonas nitrite reductase to reduce O_2 to H_2O, or NO_2-to NO.

A Re complex was used to modify azurin by Harry Gary et al. to mimic the electron acceptors in living organisms, and acts as a trigger for the photoinduced long-distance electron transfer.[4] A tryptophan group along the path was suggested to play a key role in accelerating the long-range ET. The ET mechanism was described in Ref. [4]. First, a metal-to-ligand charge transfer (MLCT) state involving a hole on the Re center and an electron on the dmp ligand is created by a UV pulse. This singlet excited state is rapidly converted into a triplet state through intersystem crossing. After vibrational relaxation, this triplet is in equilibrium with a charge-separated state, where the hole migrates to the tryptophan group. Finally an electron from the Cu(I) center completes the long-distance electron transfer process. A kinetic model was suggested for the ET process.[4]

To make the tryptophan intermediate state detectable for X-ray experiment, we decorate the tryptophan with a chlorine atom. With the time-dependent population of each intermediate state in the ET process from the kinetic model, we can simulate the transient X-ray absorption and SXRS signals of the model system, which captures the essential physics of the long-range ET dynamics in azurin.

References

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