

# Probing Molecular Electronic and Nuclear Dynamics by Nonlinear Ultrafast X-Ray Spectroscopy

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## Abstract

The advent of ultra-short pulsed x-ray sources allows the measurement of photophysical and photochemical processes in electronically excited states. With this comes the need for theoretical approaches that can model transient snapshots of x-ray absorption spectra of transient species. The FEFF8.2 code is commonly used to calculate the XANES (X-ray Absorption Near Edge Spectra) of molecules initially in their ground state. The FEFF algorithm for producing the molecular charge distribution focuses on the ground state. By modifying this charge distribution to that of excited states using the quantum chemistry code GAUSSIAN94, we aim to simulate the x-ray absorption of the molecules in excited states. The relative and the translational motions of electron-hole pairs in conjugated molecules and nanostructures may be directly probed using x-ray signals which provide localized (atom-specific) probes of core excitations. Examples are shown for two systems: A piperidine ligated metalloporphyrin which ejects its ligands upon optical excitation, and ruthenium bipyridine which is optically excited to a metal to ligand charge transfer state.

In a piperidine solvent, nickel tetraphenyl porphyrin (NiTPP) bonds to two piperidine ligands axial to the porphyrin ring producing nickel

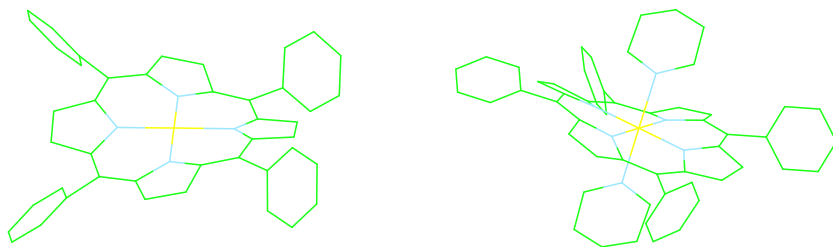


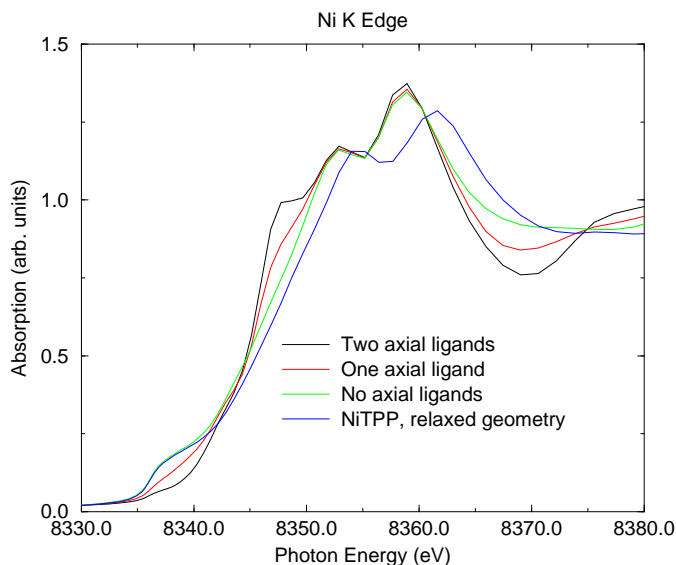
Figure 1: The geometry of NiTPP and NiTPP(Pip)<sub>2</sub>

tetraphenyl porphyrin dipiperidine (NiTPP(Pip)<sub>2</sub>). When photoexcited, both axial ligands are ejected, and within a few hundred picoseconds the NiTPP reaches its ground state. The recombination of the NiTPP with piperidines from the solvent occurs on a timescale of tens of nanoseconds. Within this time scale, NiTPP may be probed using transient x-ray absorption. This experiment has been carried out by Chen *et. al.* [3].

We simulated the x-ray absorption near edge spectrum (XANES) of NiTPP and NiTPP(Pip)<sub>2</sub> using the FEFF8.2 code. The ligands were selectively removed from the NiTPP(Pip)<sub>2</sub> molecule and the XANES calculated for these additional geometries. This allowed the separation of the ligand chemistry from the effects of the relaxation of geometry of the porphyrin after the ligand removal. These simulations explain the experimentally observed peaks [3] in terms of the orbitals involved in bonding the nickel to the piperidine and porphyrin nitrogens.

Ruthenium (II) tris-2,2'-bipyridine is a ligand/metal complex which is readily photoexcited to a long lived metal to ligand charge transfer state. In a non-polar solvent, the electron transferred to the ligands is delocalized over the three bipyridines. In a highly polar solvent, the electron becomes localized on one ligand. X-ray absorption spectroscopy offers a unique method of measuring the dynamics that occur immediately following the photoexcitation. Chemical shifts in XANES are sensitive to the local electronic structure of the ruthenium, while the extended x-ray absorption fine structure (EXAFS) can be inverted to obtain bond lengths and other geometrical details. Time resolved

## NiTPP and NiTPP(Pip)<sub>2</sub> Simulation



x-ray absorption can directly reveal the geometrical relaxation after excitation and the symmetry breaking of the charge localization. By combining molecular dynamics simulations with calculations of the x-ray absorption spectra in the excited state, we plan to simulate the time resolved x-ray spectra of this molecule as it undergoes relaxation and localization. Such experiments were recently performed by Saes *et. al.* [4].

The pump probe techniques used in the above simulations may be modeled as a sequential two step process, where the photoexcitation and x-ray probe are well separated. More generally, however, intense x-ray pulses can interact with each other or with optical pulses dynamically and non-linearly, leading to x-ray analogues of optical non-linear spectroscopies. Correlation function expressions of charge and current densities provide a unified treatment and classification of information content of the various coherent ultrafast x-ray techniques and connect them with their optical counterparts. Simulations of both pure x-ray and joint optical/x-ray techniques including pump probe, x-ray fluorescence, four wave mixing, coherent Raman time resolved EXAFS and diffraction measurements will be presented. Multidimensional x-ray spectroscopies may provide a wealth of novel structural and dynamical

information. The time-resolved sum frequency generation signal of an optical and x-ray pulse is calculated for a one-dimensional molecular chain. We show how the valence exciton motion induced by the first optical light pulse can be probed with atomic scale precision by tuning the x-ray frequency across a core excitation of a particular atom. Raman resonances in femtosecond x-ray four-wave mixing may be also used to probe exciton dynamics. Time-resolved coherent x-ray Raman signals of molecules are computed. Simulations performed on one-dimensional molecular chains demonstrate that Raman resonances provide a direct local probe for valence-excitation dynamics with high spatial and temporal resolutions.

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