Ultrafast intersystem crossing in nickel porphyrins

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We study the relaxation dynamics and intersystem-crossing to the metastable state in laser-pumped tetra and hexa-coordinated nickel porphyrins. We use a ligand-field model which takes into account the crystal field created by the porphyrin ring and axial ligands. By accounting for the energy redistribution of the lattice vibrations of the metal-ligand stretch mode we get an irreversible decay within the order of the hundreds of femtoseconds timescale. We show how non-equilibrium time-dependent x-ray absorption at the Ni K-edge measurements can elucidate the nature of the intermediate states involved in the decay. Understanding radiationless transitions in this system is of interest for their relevance in photocatalytic systems and photothermal sensitizers for cancer treatment.

I. INTRODUCTION

Photoinduced excited-state dynamics is a subject of current scientific interest. In pump-probe experiments, an optical pulse is used to excite a system in the ground state and a second spectroscopy pulse probes the excited states. Until recently, techniques like optical, Mössbauer or Raman spectroscopy were used to study the relaxation process.1,2 The recent advances in ultrafast pulsed x-ray sources now provide a powerful method for obtaining knowledge on these excited states processes.3,4

Metalloporphyrins have been the subject of intensive research.2 They have interest as model systems for biological processes like photosynthesis, electron transport, and radiationless transitions in this system. From the time-dependent x-ray absorption measurements we can elucidate the intermediate states participating in the decay. Understanding the decay of the photoexcited state is important for applications, such as the design of photocatalytic systems (fuel generation by sunlight), or photothermal sensitizers for cancer treatment, where a fast decay is necessary for converting photons into vibrational energy and killing tumor cells by heat.19–21

II. MODEL HAMILTONIAN

We consider a ligand-field Hamiltonian taking into account the Ni d-shell and the porphyrin ring π and π* orbitals. We use a full configuration-interaction approach that takes into account exactly the Coulomb interaction between the 3d electrons in the metal center. For the Slater integrals we use Hartree-Fock estimates22 scaled to 50% of their atomic values to account for the effect of hybridization. A crystal field of D4h symmetry splits the d-orbitals into different irreducible representations: a1g(dxz, y2z2), b1g(dxy, dz2−y2), e_g (dπ, i.e. dxz and dyz), and b2g(dxy). We take for the single-particle energies of
III. DECAY PATHWAY

The decay is described in terms of two steps of internal conversion that would recombine the hole in \( \pi \) and the electron in \( \pi^* \) with the metal \( d \)-shell and a step of intersystem crossing produced by spin-orbit coupling. The hybridization between the metal center orbitals and the porphyrin ring orbitals \( \pi \) and \( \pi^* \) allowed by a lowering of the \( D_{4h} \) symmetry is responsible for the internal conversion. The metal center state \((d_{xy}^2d_{x^2-y^2}^2d_{z^2})\) opens the door to intersystem crossing to the metastable state, since it is directly connected to it via spin-orbit coupling (SOC).

To calculate the dependence with time of the occupation of the different quantum states we use an effective probability-conserving dissipative Schrödinger equation (see refs. 16–18). To obtain an irreversible decay to the metastable state, we include in our model the exchange of energy of the metal-ligand system with a thermal bath. We approximate the nuclear wavefunction of the metal-ligand stretching mode as harmonic, and consider the electron-phonon coupling to be linear, i.e. the vibrational frequencies are the same for the different electronic states, only the equilibrium position of the harmonic oscillator changes as the result of an electronic transition.

The different electronic states couple to each other via spin-orbit coupling or hybridization. For the tetra-coordinated complex, the effective spin-orbit coupling that we obtain from Hartree-Fock is \( \zeta = 0.074 \) eV (we already take into account the possibility that there are 3 possible final states). In the case of the hybridization responsible of internal conversion steps in the decays we use the value \( V_\pi = V_\sigma = 0.05 \) eV.

For the energy dissipation we consider one totally symmetrical breathing mode, whose equilibrium distance would depend on the occupation of the metal center orbitals. In the square planar complex, we assume the bond-length would be proportional to the number of electrons in the \( xy \) plane (i.e. \( d_{xy} \), \( d_\pi \) and \( d_{x^2-y^2} \)). We assume a change in the occupation of one electron would produce a change in elastic energy of \( \epsilon = 0.4 \) eV in the square-planar complex and \( \epsilon = 0.6 \) eV in the hexa-coordinated. For the frequency of the Ni-N stretching mode we use the value \( \frac{\hbar \omega}{2} = 0.05 \) eV. The Huang-Rhys factors would be \( g = 8 \), and \( g = 12 \) phonons in the tetra and hexa-coordinated cases respectively. For the observed change in bond-length of \( \Delta Q \approx 0.1 \) Å, these changes in elastic energy \( \epsilon = \frac{1}{2} f \Delta Q^2 \) would correspond to a force constant \( f = 2.1 \times 10^5 \) dyn/cm (1.3 \times 10^3 eV/nm²) per Ni-N bond. For the environmental relaxation constant we use the value \( \Gamma^{-1} = 40 \) fs similarly to ref. 15.

The obtained time dependence of the probabilities of the four states involved in the radiationless relaxation of the tetra-coordinated complex is shown in Fig. ???. The change in bond-length from the \((\pi, \pi^*)\) excitation and the dissipation of the energy produced by the Ni-N bond-length oscillations suppresses the recurrence to the initial \( d_{xy}^2(\pi, \pi^*) \) state in less than 100 fs. The probability is transferred to the intermediate charge-transfer state, which is only occupied less than 200 fs, until the excitation is transferred to the metal center state \( d_{xy}^2d_{x^2-y^2}^2d_{z^2} \), connected by spin-orbit coupling to the metastable state \( d_{xy}^1d_{x^2-y^2}^1d_{z^2}^1 \). The system decays to the metastable state within 800 fs.

IV. TIME DEPENDENT X-RAY ABSORPTION

We now turn into the question of how time dependent x-ray absorption can elucidate which decay path to the metastable state the system is undergoing. We calculate the isotropic K-edge quadrupolar x-ray absorption using Fermi’s golden rule. For this, we exactly diagonalize the ligand-field hamiltonian for the initial state and for the final state with a core-hole in 1s. For the monopolar part of the Coulomb interaction between core and valence we assume it to be equal to the monopolar part of the valence coulomb interaction, i.e. \( U_{1s,3d} = U_{3d,3d} \). The pre-edge of the calculated spectra is adjusted such that the absorption features of the metastable state coincide with their position in the experimental measurements 24, 30. We use a core-hole lifetime lorentzian broadening of \( \Gamma = 0.7 \) eV. The calculated time evolution of the spectra were convolved with a 50 fs width gaussian to suppress the strong probability oscillations and account for a finite time resolution.

The calculated spectra for the different intermediate states for the tetra-coordinated complex are shown in Fig. ?? and the time evolution of the spectra is shown in Fig. ?? The spectra of the laser-pumped state \( d_{xy}^2(\pi, \pi^*) \) corresponds to a single feature at 8832.5 produced by transitions to the empty orbital \( d_{x^2-y^2} \). The metastable state \( d_{xy}^1d_{x^2-y^2}^1d_{z^2} \) and the metal-center intermediate state \( d_{xy}^1d_{x^2-y^2}^1d_{z^2} \) would both produce a similar absorption spectra with two features corresponding to the energies of the singly occupied orbitals.

V. CONCLUSIONS

We have studied the relaxation dynamics and the possible intersystem-crossing pathways to the
metastable state in photoexcited square-planar and hexacoordinated nickel-porphyrins. Our model gives a fast dissipation of the metal-ligand oscillation energy and an irreversible decay to the metastable state in a hundreds of femtoseconds timescale. Radiationless transitions in this system are of interest because of their relevance for applications, such as the design of catalytic systems, or photothermal sensitizers for cancer treatment, where a fast radiationless decay is desirable.

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4-coordinated Ni-P

FIG. 1: Energy level scheme and possible decay paths in square planar nickel-porphyrins. The system is initially in the ground state (G.S.) \(^1(d^9_z)\). The laser pump induces an excitation (\(\pi, \pi^*\)) in the porphyrin ring and the system decays to a metastable state. The different horizontal postions of the excited states correspond to the equilibrium position for each electronic configuration that we assume for the totally symmetrical breathing mode responsible for the energy dissipation. Possible transitions between states are marked with arrows. Transitions that change the equilibrium position of the breathing mode and involve energy dissipation are marked with a one direction arrow, while those that don’t change the phononic mode equilibrium position are marked with a double directional arrow.

FIG. 2: Isotropic K-edge x-ray absorption calculated for the different intermediate states involved in the radiationless decay of laser-pumped square-planar nickel-porphyrins.
FIG. 3: Time-dependent Ni K-edge isotropic x-ray absorption for laser-pumped square-planar nickel-porphyrins.