

Survival of Nuclear Coherences for a Series of Internal Conversions in Free Base Tetraphenylporphyrin

So Young Kim,¹ Sangkyu Kim,² and Taiha Joo^{1,*}

¹Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

²Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea
e-mail: thjoo@postech.ac.kr

Abstract: The stepwise internal conversions from B to Q_y and to Q_x states in free base tetraphenylporphyrin generate coherent nuclear wave packets in both Q states. The wave packets in each Q state are observed by highly time-resolved fluorescence, and they are quite distinct. Theory and experiment show that the observed vibrational wave packet motions involve out-of-plane vibration of the porphyrin ring that is strongly coupled to the internal conversions.

OCIS codes: (320.7130) Ultrafast processes in condensed matter; (300.6530) Spectroscopy, ultrafast

Porphyrins, including free base tetraphenylporphyrin (H_2TPP), comprise one of the most important group of molecules in nature, and have been under intense investigation [1-3]. Unlike the steady-state spectroscopy, however, the ultrafast relaxation dynamics from B to Q_y and Q_x states in H_2TPP have not been clearly revealed, although Baskin *et al.* reported the femtosecond time-resolved experimental results [1]. Because the excited-state dynamics of porphyrins often occur on a femtosecond time scale, the exact internal conversion rate as well as the nuclear coordinates responsible for the internal conversion are not clear.

Coherent nuclear wave packets in the excited states can be launched by an internal conversion process occurring faster than the vibrational period in an analogy to the Franck-Condon transition. Such a reaction-driven wave packet motion provides a valuable information on the reaction coordinate and electron-nuclear couplings along the relevant coordinates. The resulting nuclear wave packet motions can be measured most unambiguously by time-resolved fluorescence (TRF) with a resolution higher than the periods of vibrations [4]. In this work, we present the ultrafast internal conversion dynamics by TRF, which gives the signal from the excited state exclusively. The TRF of H_2TPP in toluene was measured by fluorescence up-conversion with 50 fs time resolution, which was high enough to resolve the wave packet oscillations up to 500 cm^{-1} .

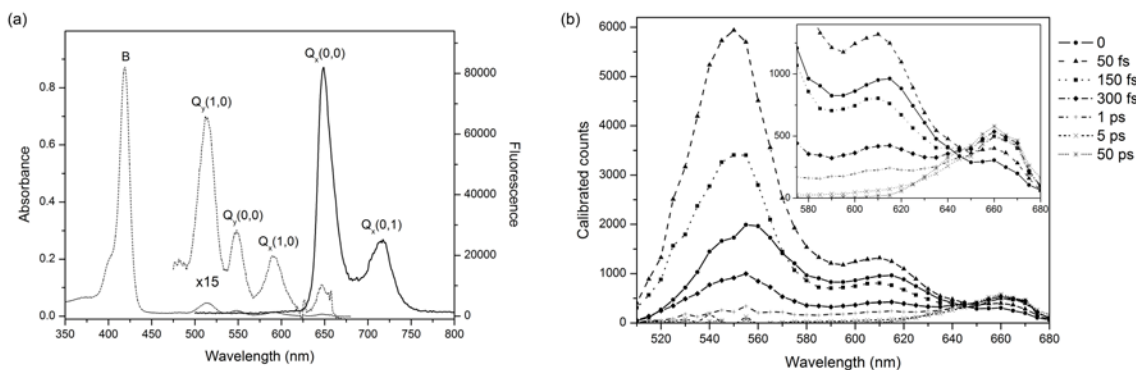


Fig. 1. (a) Steady-state absorption and emission spectra of H_2TPP in toluene. Only $Q_x(0,0)$ and $Q_x(0,1)$ bands appear in the emission spectrum after the B excitation, indicating the ultrafast internal conversion. (b) TRF spectra of H_2TPP in toluene. Excitation wavelength was 410 nm and time resolution for the TRF spectra measurement was 80 fs.

Fig. 1b shows the TRF spectra of H_2TPP over the Q emissions after the B excitation. Immediately after the photoexcitation, the TRF spectra show two peaks at 550 and 610 nm, which are absent in the steady-state spectra (Fig. 1a). The observed peaks can be assigned to the $Q_y(0,0)$ and $Q_y(0,1)$ bands, and both bands rise and decay within 100 fs in the same manner. Fig. 2 shows the TRF of H_2TPP measured at different Q bands after the excitation of the B band. The TRF in the Q_y band (610 nm, Fig. 2a) rises by 60 fs, which can be assigned to the $B \rightarrow Q_y$ internal conversion, and rapidly decays by 80 fs. On the other hand, the TRF in the Q_x band (650 nm, Fig. 2b) shows a delayed rise of 80 fs, which is the same as the fastest decay of the Q_y emission. These temporal features are well-matched with the TRF spectra, and they denote that the $Q_y \rightarrow Q_x$ internal conversion occurs in 80 fs.

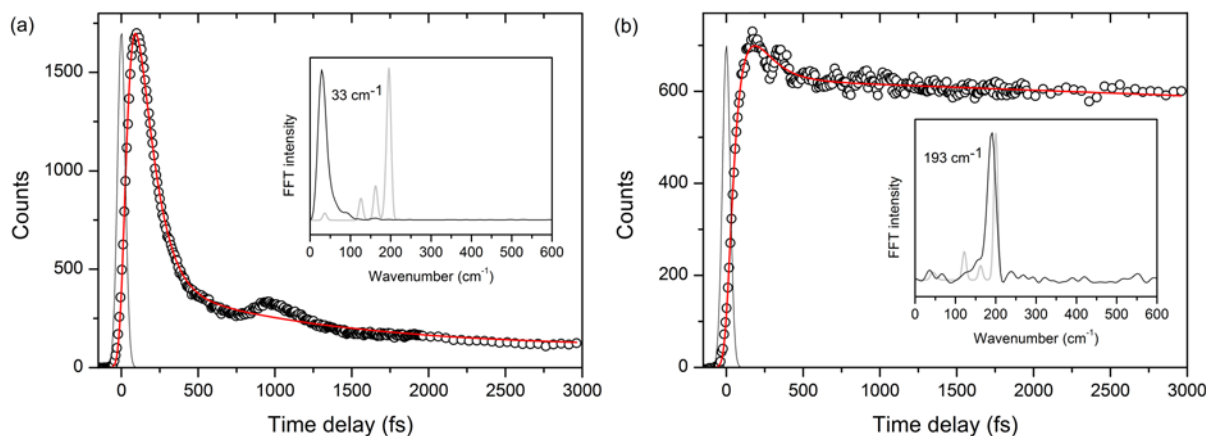


Fig. 2. TRFs of H_2TPP in toluene detected at (a) 610 nm and (b) 650 nm after the B excitation at 410 nm. Red solid lines represent the exponential fits and instrument responses are also shown. Insets show the frequency spectra obtained by Fourier transform (black) with the calculated frequency spectra (grey).

The most notable feature is the distinct oscillations in the TRF signals at each Q band. In the Q_y emission, a unique low-frequency oscillation at 33 cm^{-1} can be observed, while a higher frequency at 193 cm^{-1} is dominant in the Q_x emission. Since $B \rightarrow Q_y \rightarrow Q_x$ internal conversions occur ultrafast, each internal conversion can act as an impulsive excitation to generate the coherent nuclear wave packets in Q states. To identify this unusual distinct wave packet dynamics, quantum mechanical calculations were performed. Geometry optimizations and frequency calculations were carried out at the B3LYP/6-311G level for the first excited state (Q_x) and B3LYP/6-31G level for the second excited state (Q_y) by using the Gaussian 09 package. In an analogy to the Franck-Condon transition, vibrational modes with large displacements between the reactant and product states will be excited preferentially. We can define a general Huang-Rhys factor coupled to the electronic transition, and calculate the amplitudes of vibrational modes comprising the wave packet in each Q state by calculating the projection of the structural displacement onto the normal modes of the product state.

We have carried out the normal-mode-projection calculation for two different cases: ground $\rightarrow Q_x$ and ground $\rightarrow Q_y$. Here we assumed that the internal conversion from the B state is fast enough to regard the ground state as the reactant. For the first case, the vibrational mode at 200 cm^{-1} (ν_{22}) is dominant and matches well with the 193 cm^{-1} mode observed in the Q_x emission. This mode corresponds to the out-of-plane motion of the entire porphyrin ring with some rocking/scissoring motion of the phenyl groups. The second case turned out to be similar to the first case and the same out-of-plane mode at 196 cm^{-1} (ν_{22}) shows the largest displacement. This result is quite reasonable because the wave packets generated in the Q_y state quickly move to the Q_x state along the $Q_y \rightarrow Q_x$ internal conversion. Hence we can assign the calculated ν_{22} to the 193 cm^{-1} mode observed in the TRF, which has a half period of 86 fs that is nearly the same as the internal conversion time of 80 fs. We propose that this out-of-plane vibrational mode can be regarded as the reaction coordinate of $Q_y \rightarrow Q_x$ in H_2TPP leading to the ultrafast internal conversion.

Although most Q_y population transfers to the Q_x state, a small part of the population remains in the Q_y state and shows the low frequency oscillation in the TRF of Q_y emission. Interestingly, only the slow low frequency mode remains in the Q_y state, even though the internal conversion is ultrafast. For the second case (ground $\rightarrow Q_y$), there are about 10 vibrational modes in the low-frequency region, but only one vibrational mode at 37 cm^{-1} (ν_5) shows nonzero displacement. Thus, the 33 cm^{-1} mode observed in the Q_y emission can be assigned to ν_5 . However, the 33 cm^{-1} mode may not be directly related to the $B \rightarrow Q_y$ internal conversion, unlike the 193 cm^{-1} mode. These vibronic coherences in porphyrins may be related to the long-lived electronic coherences in light-harvesting complex and requires more investigation.

- [1] J. S. Baskin, H. Z. Yu, and A. H. Zewail, "Ultrafast Dynamics of Porphyrins in the Condensed Phase: I. Free Base Tetraphenylporphyrin," *J. Phys. Chem. A* **106**, 9837-9844 (2002).
- [2] K. Y. Yeon, D. Jeong and S. K. Kim, "Intrinsic Lifetimes of the Soret Bands of the Free-Base Tetraphenylporphyrine (H_2TPP) and Cu(II)TPP in the Condensed Phase," *Chem. Comm.* **46**, 5572-5574 (2010).
- [3] B. Białkowski, Y. Stepanenko, M. Nejbauer, C. Radzewicz, and J. Waluk, "The Dynamics and Origin of the Unrelaxed Fluorescence of Free-Base Tetraphenylporphyrin," *J. Photochem. Photobiol. A: Chemistry* **234**, 100-106 (2012).
- [4] C. H. Kim and T. Joo, "Coherent Excited State Intramolecular Proton Transfer Probed by Time-Resolved Fluorescence," *Phys. Chem. Chem. Phys.* **11**, 10266-10269 (2009).