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Broadband ultrafast transient absorption of iron (III) tetraphenylporphyrin chloride in the condensed phase

Aaron S. Rury [a,b], Roseanne J. Sension [a,b,c,*]

[a] Applied Physics Program, University of Michigan, Ann Arbor, MI 48109, United States
[b] Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States
[c] Department of Physics, University of Michigan, Ann Arbor, MI 48109, United States

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ABSTRACT

Ultrafast transient absorption of iron (III) tetraphenylporphyrin chloride [$Fe^{(III)}$TPPCl] is used to probe the excited state relaxation in room temperature solution. The ground state was excited either at 400 nm near the Soret resonance or at 520 nm in the Q resonance. Relaxation from the lowest lying porphyrin singlet (π, π^*) manifold results in formation of a LMCT (π, d_π) state on a time scale of 0.4–0.6 ps followed by a metal-to-ligand charge transfer transition from the iron to the porphyrin on a time scale of 1.8–2.3 ps, producing an excited ^{4}T intermediate spin state of $Fe^{(III)}$TPPCl. The system relaxes back to the high spin $^6A_1$ ground state on a time scale of 13–18 ps. The relatively slow electronic relaxation of the more symmetric $Fe^{(III)}$TPPCl compound is contrasted with the much faster subpicosecond ground state recovery observed for less symmetric biologically active heme systems at room temperature.

1. Introduction

Synthetic and natural metalloporphyrins have been studied extensively for over 50 years. The optical, photochemical, and electronic properties of these compound have led to their use in applications ranging from light harvesting and energy conversion to medical therapeutics and molecular electronics [1]. Since iron atoms display a variety of oxidation and spin states, Fe-centered porphyrins provide avenues to materials that couple optical, electronic and magnetic functions. Researchers have used basic Fe-porphyrin units to produce molecular structures for nanoscale reaction catalysis, spintronics, opto-electronic thin films and opto-magnetics [2–6]. Although much has been accomplished already, the ability to use synthetic, five-coordinate Fe-porphyrins in these emerging condensed phase technologies will be enhanced by a comprehensive understanding of their electronic dynamics and structure. This paper presents a careful study of the excited state dynamics of one such porphyrin, iron (III) tetraphenylporphyrin chloride ($Fe^{(III)}$TPPCl).

Ultrafast and steady state spectroscopies have been used extensively to study the excited state dynamics of metalloporphyrins. Fluorescence yield measurements have been used to investigate the mechanism for radiationless decay and the applicability of gap laws to account for excited state lifetimes [7–11]. Ultrafast transient absorption spectroscopy and time-resolved fluorescence have been used to study the excited state dynamics of many of these compounds more directly. Ultrafast measurements have been reported for free-base tetraphenylporphyrin (H_2TPP) [12], a variety of metalloporphyrins in the condensed phase [13–23], and gas phase [20,24], and a wide range of iron containing heme proteins including hemoglobin, myoglobin, and cytochrome c [13,23–35]. However, there remains a gap in the literature concerning the condensed phase ultrafast electronic dynamics of model synthetic Fe-porphyrins. The symmetry and planarity of the porphyrin ring can have a substantial influence on the excited state dynamics of metalloporphyrins. Thus the dynamics of synthetic Fe-porphyrins can differ significantly from those observed for protein bound hemes, and the need persists for careful studies of model Fe-porphyrin systems.

A recent study of the ultrafast (<1 ps) gas phase dynamics of several different metallo-tetraphenylporphyrins (MTPPs) and metallo-octaethylporphyrins (MOEPs) including $Fe^{(III)}$OEP provides important insight into the electronic dynamics of porphyrins [20,24]. These studies show two dominant relaxation processes corresponding to ligand-to-metal charge transfer (LMCT) from the excited porphyrin macrocycle to the Fe atom and retrodonation of a low lying metal *d*-electron to the highest occupied molecular orbital (HOMO) of the porphyrin ground state. A comparison of porphyrins ligated to metal atoms with unfilled *d*-orbitals to $Zn^{(II)}$-TPP where the *d*-orbitals are filled was used to assign the dominant relaxation pathways through the metal centers. However, since Soep et al. studied gas phase dynamics via mass spectrometry

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* Corresponding author. Address: 930 N University Ave., University of Michigan, Ann Arbor, MI 48109-1055, United States. Tel.: +1 734 763 6074; fax: +1 734 647 4865.

E-mail addresses: arury@umich.edu (A.S. Rury), rsension@umich.edu (R.J. Sension).

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and photoelectron emission, their investigations cannot account for possibly important effects related to coupling between excited state dynamics and environment, nor can they relate their results to previous studies of the absorption spectra of the excited states of metalloporphyrins [21,36].

In the work reported here we use broadband UV–visible transient absorption spectroscopy to study the excited state relaxation processes of the prototypical iron porphyrin, $\mathrm{Fe^{(III)}}$TPPCl. Unlike the study by Sorgues et al., we study the electronic dynamics excited either in the Soret band or the Q_v band providing us insight into the connection between different excited singlet states and orbitals of the central metal atom. Although this system was one of the first investigated by Hochstrasser et al. using picosecond transient absorption spectroscopy [37,38], it has not been revisited using femtosecond methods. The early measurements provided enough information to propose a simple, two-level model. A lifetime of ~100 fs was inferred for the first state based on the structure of the excited state absorption (ESA), but it could not be resolved with the >1 ps pulses available at the time. The second state has a lifetime on the order of 10's of ps and was assigned, somewhat tentatively, to the triplet of the porphyrin ring. The current state-of-the-art in broadband femtosecond transient absorption spectroscopy allows for a more precise analysis of the excited state dynamics.

The models proposed in early studies of iron-porphyrins and in the more recent gas phase ultrafast studies are based upon the four-orbital scheme of the porphyrin electronic states first developed by Goutermann [39]. In this scheme two nearly degenerate highest occupied molecular orbitals (HOMO's) of a_{1u} and a_{2u} symmetry, respectively, and a degenerate pair of lowest unoccupied molecular orbitals (LUMO's) of e_{1u} symmetry give rise to four electronic transitions. The strongly allowed electronic transitions are associated with near ultraviolet (UV) to high-energy visible absorption denoted as the Soret or B resonance. The weak or forbidden transitions are designated as the Q transitions.

A more sophisticated calculation of the $\mathrm{Fe^{(III)}}$TPPCl molecule reveals a more complicated electronic structure. In particular the open shell spin state of iron increases the total number of transitions in the spectrum. Paulat and Lehnert combined low temperature magnetic circular dichroism and room temperature absorption measurements with TD-DFT calculations to assign the electronic spectrum of $\mathrm{Fe^{(III)}}$TPPCl [40]. Their assignment is summarized in Fig. 1. The bands indicated in red are in-plane polarized (π, π^*) states arising primarily from the HOMO–LUMO transitions of Goutermann's four state model, with the band at 500 nm attributed to the vibronic component of the Q state transition. The vibrationless origin of the Q state transition carries little intensity and is located at lower energy.

With a more complete understanding of the electronic structure of this system and modern technology, we have undertaken the measurement of the transient excited state dynamics of $\mathrm{Fe^{(III)}}$TPPCl in three solvent environments at room temperature (toluene, CH_2Cl_2 and a 1:1 mixture of toluene and CH_2Cl_2). We find that a sequential model of internal conversion, charge transfer and retrodonation explains the measured dynamics of this system when excited on the Soret resonance. We compare this model with that proposed by Soep and coworkers based on their studies of the gas phase ultrafast dynamics of several different metalloporphyrin systems. This study is especially important in the context of the emerging literature on iron-porphyrin nanostructures and single-molecule electronics technologies that hope to take advantage of the unique optical, electronic and magnetic properties of synthetic Fe-porphyrin molecules. The dynamics uncovered in this study may provide essential insights into the use of porphyrins in a variety of important applications ranging from energy science to information technology to biophysics.

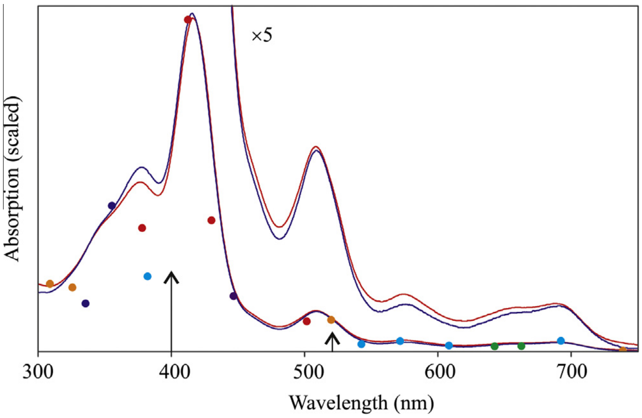

Fig. 1. The room temperature absorption spectrum of $\mathrm{Fe^{(III)}}$TPPCl in CH_2Cl_2 (blue line) and a mixture of toluene and CH_2Cl_2 (red line). The two arrows indicate the excitation wavelengths used in the transient absorption measurements reported here (400 nm, 520 nm). The color-coded circles represent the electronic state assignments from the calculations of Paulat and Lehnert [40]. The peaks indicated by blue circles are predominantly out-of-plane polarized charge transfer transitions. The very weak transitions indicated by green circles are in-plane transitions involving charge transfer and (π, π^*) character. The peak indicated with yellow is an in-plane and out-of-plane polarized mixture of charge transfer and (π, π^*) character. The bands indicated in red are in-plane polarized (π, π^*) states arising primarily from the HOMO–LUMO transitions of Goutermann's four state model. The peaks indicated by dark blue circles are higher in-plane polarized (π, π^*) transitions. The peaks indicated in orange are not well assigned. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Experimental setup

Room temperature transient absorption (TA) measurements were performed using two available amplified 1 kHz, 800 nm Ti:Sapphire laser systems. In each system the compressed output of the amplified laser was split into two arms with a 70/30 beamsplitter to produce the pump and probe pulses. The time delay between the pump and probe was provided by passing the probe pulse down a computer controlled variable delay stage.

A 400 nm excitation pulse was produced by frequency doubling the stronger arm in a β-barium borate (BBO) crystal. In measurements exciting the Q_v resonance the more powerful arm was used to pump a non-collinear optical parametric amplifier (NOPA). The NOPA was optimized to produce output pulses centered near 520 nm, close to the peak of the Q_v resonance. The spectrum of the 520 nm pump covered the entire Q_v resonance of the $\mathrm{Fe^{(III)}}$TPPCl ground state. The weaker arm from the amplified laser was used to generate a broadband continuum probe in a CaF_2 window. The window was continually translated vertically and horizontally to avoid damage. Both pump beams were focused to a spot between 100 and 200 μm in the sample. The cross correlation of the pump and probe beams varied between measurements, but was generally 0.15–0.25 ps. This was short enough to accurately characterize the 0.4–0.6 ps decay component described below, but cannot not rule out the possibility of an additional <100 fs decay component.

$\mathrm{Fe^{(III)}}$TPPCl was synthesized using literature techniques [41,42]. Purification was achieved by column chromatography on silica, eluted first with 100% CH_2Cl_2 to remove free H_2TPP and then +5% MeOH to elute $\mathrm{Fe^{(III)}}$TPPCl. Metallated bands were combined and then washed twice with 1 M HCl. The organic layer was dried with Na_2SO_4 and evaporated to dryness. The room temperature sample was dissolved in the desired solvent and flowed through a 1 mm path-length fused silica cell at a rate high enough to ensure that each pulse interrogated a fresh portion of the sample. Sample concentrations were prepared to provide between 0.3 and 0.5 O.D.