

Ultrafast Electronic Deactivation and Vibrational Dynamics of Photoexcited Uranium(IV) Porphyrin Sandwich Complexes

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The ground- and excited-state optical spectra of two U^{IV} bis(porphyrin) sandwich complexes reveal features characteristic of porphyrins held within van der Waals contact. The photoexcited complexes exhibit ultrafast (~1 ps) deactivation to the ground electronic state in a multistep process involving intersystem crossing into the triplet manifold and subsequent relaxation via ligand-field (f,f) excited state(s). This ultrafast and highly energetic electronic deactivation is followed by complex time-dependent spectral changes on the picosecond time scale that are ascribed to vibrational relaxation in the ground electronic state.

Introduction

Metalloporphyrins exhibit a wide range of photophysical behavior depending on the nature of the macrocycle, the central metal ion, and the axial ligands. Much recent effort has been devoted to the determination of the rates, pathways, and mechanisms by which nonluminescent porphyrins deactivate to the ground electronic state following photoexcitation. As predicted by early theoretical and spectroscopic investigations,¹ ultrafast laser studies have generally found that the lack of emission from certain metalloporphyrins can be associated with rapid deactivation of the (π, π^*) excited states of the macrocycle via ligand-field or metal \leftrightarrow ring charge-transfer (CT) excited states.² In such cases, the electronic nature of the metal ion is an important factor contributing to the establishment of nonemissive deactivation pathways. However, the interesting question of whether the deactivations proceed via the singlet or triplet manifold is often left unanswered.

Equally intriguing but much less explored is the role of the metal ion in the photophysical behavior of bis(porphyrin) sandwich complexes, in which an octacoordinate central metal ion (such as Zr, Hf, Ce, Th, or U) holds two porphyrins at a separation of ≤ 3.5 Å.³⁻⁶ The porphyrin sandwich compounds have a number of characteristic optical properties that are not exhibited by monomeric porphyrins or dimers having larger spacings between the rings.³⁻⁸ These properties are believed to arise from the strong electronic interactions between the porphyrin subunits. The strength of the interaction between the porphyrin subunits is inversely correlated with the distance between the subunits, which in turn is dictated in large measure by the ionic radius of the central metal ion. The metal ion also has a significant and perhaps more intimate influence on the excited-state dynamics. For example, the Th^{IV}, Hf^{IV}, and Zr^{IV} porphyrin sandwich complexes all fluoresce but have ¹(π, π^*) lifetimes ranging from about 10 ps to over 1 ns; these molecules all phosphoresce and have ³(π, π^*) lifetimes on the microsecond time scale.^{5b,8c-e} On the other hand, the analogous Ce^{IV} complexes are nonemissive and deactivate in a few picoseconds following excitation, most likely via a low-energy metal-to-ring CT excited state.^{3b,8a,b}

Here we present the results of time-resolved and steady-state optical studies on two U^{IV} porphyrin sandwich complexes. The ground- and excited-state absorption properties of these bis(porphyrin) complexes further establish the correlation between the optical characteristics and the distance between the subunits

and provide additional support for the molecular orbital/configuration interaction model recently proposed for the neutral sandwich complexes.^{8d,e} Additionally, these actinide bis(porphyrin)s reveal rich and complex spectral dynamics that involve ultrafast relaxation via the triplet manifold and low-energy ligand-field excited states followed by vibrational relaxation in the ground electronic state.

Experimental Methods

U(OEP)₂ and U(TPP)₂ were synthesized and purified as described previously, and their photophysical properties were studied in spectral grade toluene.^{8d,e} Ground electronic state absorption spectra were recorded on Perkin Elmer Lambda 3B and Model 330 spectrometers. Emission spectra were determined on a Spex Fluorolog spectrofluorometer equipped with either a Hamamatsu R928 photomultiplier tube and photon counting electronics or an RCA C30956E silicon avalanche photodiode and lock-in detection. Time-resolved absorption experiments on ~ 10 μ M samples were performed using a 150-fs, 582-nm, 75- μ J excitation laser pulse and a broad-band (380–1000 nm) probe pulse of comparable duration.¹¹

Results

The ground electronic state absorption spectra of U(OEP)₂ and U(TPP)₂ are qualitatively similar to those of other porphyrin sandwich complexes containing a tetravalent metal ion such as zirconium, hafnium, thorium, or cerium (Figure 1).³⁻⁸ In particular, the spectra show both "monoporphyrin-like" features (a strong near-UV Soret or B band and weaker visible Q bands) and new features designated^{8c-e} Q'' and Q' to the blue and red, respectively, of the Q bands.

Upon photoexcitation of both U(OEP)₂ and U(TPP)₂ at 582 nm, the absorption difference spectra show that relaxation back to the ground state does not follow simple single-exponential kinetics. Instead, there appear to be two relaxation processes: A subpicosecond phase followed by a complex phase on the picosecond time scale characterized by a detection wavelength-dependent time constant. Representative spectral and kinetic data for U(OEP)₂ are shown in Figures 2–5.

The absorption difference spectrum in the blue region at early times shows that the ground-state Soret band near 390 nm has bleached and that a broad absorption tailing to longer wavelengths has appeared (Figure 2A). The near-infrared spectrum of the initially observed transient state (400 fs in Figure 3) is charac-

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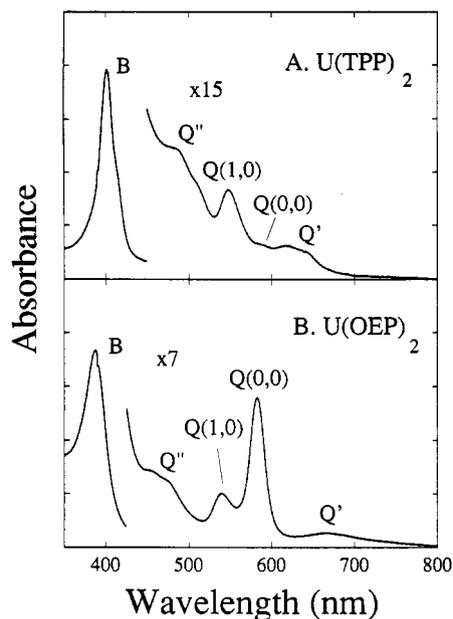


Figure 1. Electronic ground-state absorption spectra of (A) $U(TPP)_2$ and (B) $U(OEP)_2$. The Q'' and Q' bands are characteristic features of two porphyrins in very close proximity, whereas the B and Q bands are monomer-like features.

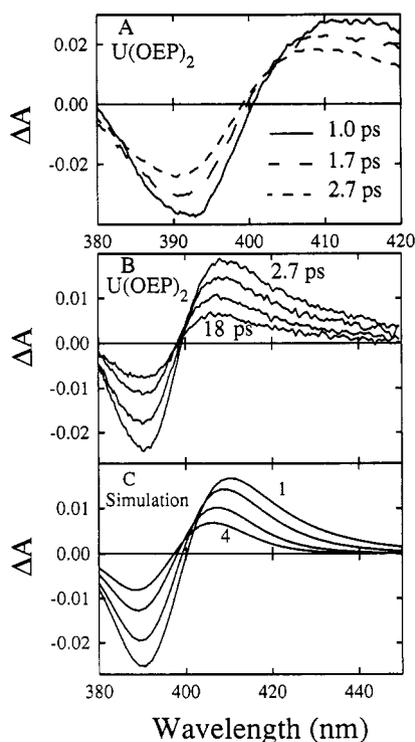


Figure 2. Time-resolved absorption difference spectra of $U(OEP)_2$ during the first several picoseconds (A) and at 2.7, 6.0, 11.3, and 18 ps (B) after excitation. Panel C shows simulations of the spectra at times corresponding to those in panel C using the distribution model described in the text. The spectra in panels A and B have not been corrected for group velocity dispersion in the probe pulse; the data on the extremes of the wavelength region shown differ by approximately 1.5 ps, which results in a slight distortion of the spectra at very early times. The times correspond to the data at 410 nm. Note that this does not affect the kinetic data, which are evaluated using the zero time corresponding to each wavelength.

terized by a prominent absorption band with a peak at a wavelength somewhat longer than 950 nm ($\log \epsilon \geq 4.7$) and considerably weaker features between 700 and 800 nm. These near-infrared absorption features decay with a time constant of 0.6 ± 0.1 ps to give a null spectrum in this region that is retained to the longest times investigated (~ 3 ns).

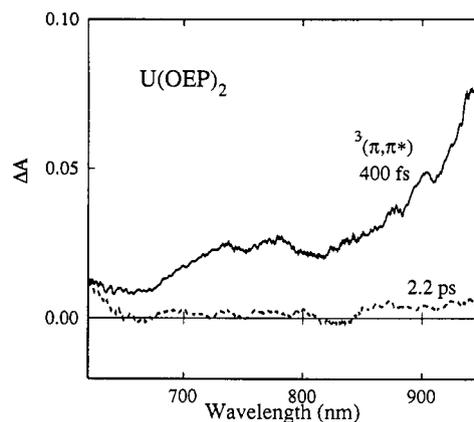


Figure 3. Time-resolved absorption difference spectra of $U(OEP)_2$ at two times after excitation. The spectra are not corrected for group velocity dispersion in the probe pulse, which is approximately 1 ps over the region shown. The times correspond to the data at 800 nm.

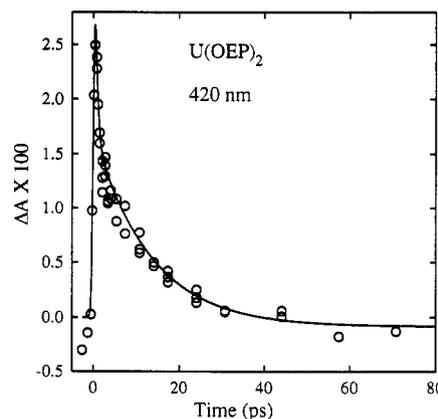


Figure 4. Representative dual-exponential decay of absorption change following excitation. This data corresponds to decay of the transient absorption at 420 nm. The solid curve is a fit to the data using a dual-exponential function giving time constants of 0.6 ± 0.1 and 13 ± 2 ps.

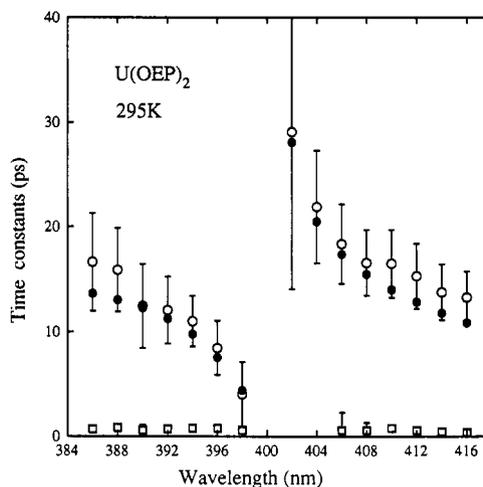


Figure 5. Results of the dual-exponential fits to the data across the region of the spectrum shown in Figure 2. The open squares show that there is a fast component having a time constant of about 0.6 ps, independent of wavelength. The open circles reveal a slower wavelength-dependent component with a time constant that ranges from about 5 to 25 ps. The wavelength-dependent time constant indicates that the data are, in fact, more complex than can be described by a simple dual-exponential kinetic model. The closed circles are the results of exponential fits to the simulations shown in panel 2C, which are based on the distribution model discussed in the text.

During this fast kinetic phase, an isosbestic point is maintained at 403 nm ($\Delta\Delta A = 0$ and $\Delta A \sim 0.015$ in Figure 2A). At shorter wavelengths, the ground-state Soret band near 390 nm begins to

recover its original intensity, while at longer wavelengths the transient absorption decays. This initial phase of the dual-exponential decay seen across the blue region has a time constant (0.6 ± 0.2 ps) that is essentially independent of the detection wavelength (squares in Figure 5) and that matches the time constant observed for decay of the near-infrared absorption.

After several picoseconds, the isosbestic behavior is lost, and the $\Delta A = 0$ point begins to shift to the blue with time (Figure 2B). This behavior is apparently due to a continuous blue-shifting and narrowing of the transient absorption and to the continuing recovery of the intensity of the ground-state Soret band near 390 nm. This complex spectral evolution is accompanied by a dramatic wavelength dependence of the apparent decay time constant, which varies from ~ 5 to ~ 25 ps over the 380–420-nm region (open circles in Figure 5).

Discussion

Ground-State Absorption Spectra. The ground electronic state absorption spectra of $U(OEP)_2$ and $U(TPP)_2$ exhibit the characteristic features found in the spectra of the corresponding Th^{IV} , Ce^{IV} , Hf^{IV} , and Zr^{IV} complexes.^{3–8} Notable are the Q'' band at higher energy and the Q' band at lower energy than the monoporphyrin-like Q bands. The Q' and Q'' bands are not observed in the spectra of mono(porphyrin) complexes or of porphyrin dimers having large (>3 Å) spacings between the macrocycles.

Recently, we proposed a molecular orbital/configuration interaction model that accounts for all the major optical characteristics of bis(porphyrin) sandwich complexes of tetravalent central metal ions.^{8d,e} (A supermolecule MO approach has also been used successfully to describe the properties of the oxidized sandwich complexes.^{7a}) A key feature of this model is that there are strong electronic interactions between the two porphyrin subunits and that the molecular orbitals are delocalized over the entire sandwich complex. In other words, the frontier molecular orbitals of the dimer are comprised of bonding and antibonding linear combinations of the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ HOMOs and the $e_g(\pi^*)$ LUMOs of the four-orbital model that describes the electronic states of monomeric porphyrins.¹² Mixing of the configurations resulting from the appropriate HOMO \rightarrow LUMO configurations defines the electronic states of the bis(porphyrin)s. Of particular importance is the finding that the excited states responsible for the Q'' and Q' bands have substantial charge resonance character (i.e., significant contributions from the two CT configurations A^+B^- and A^-B^+). The positions of the Q' and Q'' bands are thus expected to depend strongly on the distance between the subunits, in agreement with observation.

The ground-state absorption spectra of $U(OEP)_2$ and $U(TPP)_2$ correlate well with the spectra of the other bis(porphyrin) complexes and provide additional support for the model. For example, among the $M^{IV}(TPP)_2$ compounds, the approximate position of the broad Q' band and the ionic radius of the metal ion vary as follows: Hf (690 nm, 0.78 Å), Zr (690 nm, 0.79 Å), Ce (630 nm, 0.92 Å), U (620 nm, 0.97 Å), and Th (615 nm, 1.02 Å). Among the $M^{IV}(OEP)_2$ complexes, the approximate position of the Q' band for the same sequence of central metal ions is 750, 750, 660, 663, and 635 nm. Hence, as predicted, the Q' bands for the U^{IV} complexes lie at longer wavelengths than those for the compounds containing the larger Th^{IV} ion and at a much shorter wavelength than for the Zr^{IV} and Hf^{IV} complexes.

Subpicosecond Formation of the Lowest $^3(\pi, \pi^*)$ Excited State. The near-infrared spectrum observed at 400 fs following excitation of $U(OEP)_2$ is representative of the absorption changes found immediately after a 150-fs excitation flash (Figure 3). The prominent absorption with a peak in the vicinity of 1000 nm and the weaker features between 700 and 800 nm are similar to the features found previously in the near-infrared spectrum of the

phosphorescent $^3T'(\pi, \pi^*)$ excited states of the Th^{IV} , Hf^{IV} , and Zr^{IV} porphyrin sandwich complexes.^{8c–e,13} The strong near-infrared band is assigned to the $^3T'(\pi, \pi^*) \rightarrow ^3T''(\pi, \pi^*)$ transition and is expected to move to higher energy as the macrocycles are brought closer together, which is consistent with observation. The analogous $^1Q'(\pi, \pi^*) \rightarrow ^1Q''(\pi, \pi^*)$ transition in the excited singlet spectrum is expected to occur at a much longer wavelength (~ 1300 nm) than the 1000-nm absorption seen in the 400-fs triplet spectrum in Figure 3.^{8c–e} The transient absorption data thus suggest that, following excitation of the $^1Q(\pi, \pi^*)$ state with a 582-nm flash, ultrafast (<200 fs) radiationless decay to the $^3T'(\pi, \pi^*)$ state occurs, most likely via the $^1Q'(\pi, \pi^*)$ excited state.

The ultrafast formation of the $^3T'(\pi, \pi^*)$ state can be attributed to nonnegligible exchange integrals involving the frontier MOs of the porphyrin system and the partially filled metal f orbitals. Such interactions are known to lead to substantially reduced fluorescence yields in transition metal and lanthanide monoporphyrins with nonzero metal spin.^{1a,2,14} For example, intersystem crossing from the initially excited singlet manifold to the triplet manifold in <350 fs has been observed for Cu^{II} porphyrins.¹⁵ Thus, there is precedent for the subpicosecond formation of the $^3T'(\pi, \pi^*)$ excited state in the U^{IV} porphyrin sandwich complexes. The reduced energetic separation between the $^1Q'(\pi, \pi^*)$ and $^3T'(\pi, \pi^*)$ states in the sandwich complexes relative to the $^1Q(\pi, \pi^*)$ / $^3T(\pi, \pi^*)$ spacing in monoporphyrins, and the common mixed exciton/charge resonance character of the $^1Q'(\pi, \pi^*)$ and $^3T'(\pi, \pi^*)$ states, may also facilitate such rapid intersystem crossing following excitation of $U(OEP)_2$ and $U(TPP)_2$.

Ultrafast Decay of the $^3T(\pi, \pi^*)$ State. The prominent near-infrared absorption observed at 400 fs assigned to the $^3T'(\pi, \pi^*)$ excited state decays with a 600-fs time constant. This kinetic phase is accompanied by partial decay of the transient absorption in the blue region and of the recovery of the intensity of the ground-state Soret band near 390 nm (Figure 2A and squares in Figure 5). This correlation suggests that the decay of the $^3T'(\pi, \pi^*)$ state is accompanied by substantial conversion to the ground state. In fact, it is likely that repopulation of the ground electronic state is largely complete in the first few picoseconds after excitation and that vibrational equilibration of the S_0 state contributes substantially to the wavelength-dependent kinetics on the ~ 5 to ~ 25 ps time scale (Figure 2B and open circles in Figure 5). Two aspects of this scenario that need to be addressed are the mechanism of the ultrafast deactivation of $^3T'(\pi, \pi^*)$ and the nature of the vibrational equilibration process.

Although we have argued that intersystem crossing from the excited singlet manifold to the $^3T'(\pi, \pi^*)$ state is extremely fast, we do not believe that deactivation of $^3T'(\pi, \pi^*)$ to the singlet ground state occurs by *direct* intersystem crossing. The latter process would be much more exoergic than the former and would be characterized by a greatly reduced Franck–Condon factor. Additionally, the $^3T'(\pi, \pi^*)$ excited states of the Th^{IV} , Hf^{IV} , and Zr^{IV} porphyrin sandwich complexes exhibit substantial phosphorescence and decay on the microsecond time scale.^{8c–e,13} Therefore, some feature unique to the U^{IV} but not characteristic of Zr^{IV} , Hf^{IV} , or Th^{IV} must be responsible for the fast decay of the $^3T'(\pi, \pi^*)$ excited state. In view of these considerations, we believe that at least one low-energy excited electronic state participates in the deactivation of $^3T'(\pi, \pi^*)$.

Along these lines, a similar ultrafast and complex deactivation has been observed for the Ce^{IV} porphyrin sandwich complexes and has been proposed to occur via a ring-to-metal (π, f) CT excited state.^{8a,b,16} On the basis of redox potentials, such a CT excited state is expected to lie at low energy for the Ce^{IV} complexes; this is because Ce^{IV} is rather easily oxidized to Ce^{III} .^{3a,b} However, the U^{IV} ion is very difficult to reduce to U^{III} or oxidize to U^V , and thus metal \leftrightarrow ring CT excited states probably lie at higher energy than the lowest (π, π^*) states in the U^{IV} complexes. This is evidenced by both qualitative and quantitative similarity of the

cyclic voltammogram of U(OEP)₂ with that of Th(OEP)₂, which suggests that the first two oxidations and reductions primarily involve the porphyrin π -system and not the metal.^{4,9} Thus, we can rule out the involvement of CT excited states in the deactivation of the ³T'(π, π^*) states of the uranium bis(porphyrin) complexes.

Since the central metal ion in U(OEP)₂ and U(TPP)₂ has two unpaired f electrons, a more likely scenario is that one or more low-energy (f,f) excited states play a key role in the rapid radiationless decay in these molecules. We expect the absorption difference spectrum of the (f,f) excited states to be generally similar to the spectra described and analyzed previously for metalloporphyrin (d,d) excited states. In particular, the (d,d) excited states have absorption bands (i.e., Soret and Q bands) that are similar to those of the ground electronic state but shifted due to the metal perturbation, with negligible absorption in the near-infrared region (where the ground state also does not absorb).^{15,17,18a} Hence, metalloporphyrin (f,f) excited states are expected to have essentially null spectra to the red of about 650 nm. Accordingly, the wavelength independence of the 600-fs decay time for the complete disappearance of the prominent ³T'(π, π^*) band near 1000 nm (Figure 3) and for the substantial return of intensity of the ground-state Soret band (Figure 2A) suggests that the intervening (f,f) excited state(s) have <600-fs lifetime(s) and are transiently populated to only a very small degree. However, due to the complexity of the absorption changes and the kinetics in the blue region, it is difficult to rule out a small contribution of the (f,f) state(s) to the data during the first few picoseconds after excitation.

Vibrational Relaxation in the Ground Electronic State. Following the initial 600-fs kinetic phase assigned to deactivation of ³T'(π, π^*) to the ground state via the (f,f) state(s), there is a slower wavelength-dependent evolution of the absorption difference spectrum in the Soret region. The variation of the observed time constant from ~ 5 to ~ 25 ps (open circles in Figure 5) and the lack of a constant $\Delta A = 0$ point during this time (Figure 2B) clearly show that the underlying photophysics are much more complex than the simple evolution of one state to another. Similar complex behavior on this time scale has been observed for a variety of metalloporphyrin systems following excitation and rapid radiationless deactivations. Among these are the Ce^{IV} porphyrin sandwich dimers, four- and six-coordinate Ni^{II} porphyrins, and porphyrin-quinone complexes.^{8b,18} Wavelength-dependent transient absorption decays have also been observed following photoisomerization of *cis*-stilbene and proton transfer in the benzotriazole complex.¹⁹ This wavelength-dependent kinetic behavior has generally been attributed to vibrational relaxation, although other mechanisms have been considered.^{8b,18-20} For the Ni porphyrins and Ce sandwich complexes, the behavior was found to be largely independent of solvent and temperature. These findings indicate that solvent reorientation dynamics do not contribute substantially to the observed behavior.

A change in structure as a function of time could also lead to wavelength-dependent kinetics.^{18,20} For the sandwich complexes we expect that formation of the ¹Q'(π, π^*) and ³T'(π, π^*) excited states will result in a decrease in the separation between the two porphyrin subunits due to the increased π - π bonding interactions (since these states are derived from electron promotion from antibonding HOMOs to bonding LUMOs). However, to a first approximation, one might expect that this structural change, as well as the subsequent increase in the interporphyrin distance upon return to the ground electronic state, should occur in less than 1 ps. Furthermore, the observation of similar wavelength-dependent kinetics in a variety of porphyrin systems is difficult to reconcile simply with structural dynamics and suggests that a more universal mechanism such as vibrational relaxation is operable.^{18d} In other words, we believe that although a change in structure may accompany the passage of one electronic state

to another, the presence and the dissipation of excess vibrational energy are largely responsible for the spectral dynamics. The finding of similar relaxation behavior in a number of solvents and at low temperature also is consistent with the dissipation of excess vibrational energy into the medium and the flow of that energy away from the porphyrin.^{18a,d,21f} These considerations lead us to propose that the complex spectral evolution extending from a few picoseconds to about 25 ps after excitation of the U^{IV} porphyrin sandwich complexes largely reflects vibrational equilibration in the ground electronic state.

The overall vibrational equilibration process undoubtedly involves both internal vibrational energy redistribution/equilibration and also subsequent intermolecular relaxation wherein the excess internal vibrational energy is given up to the solvent (vibrational "cooling").^{18a,d,21} Following previous work on the Ni porphyrins,^{18a} and studies on other organic molecules,^{19a,21a} the absorption changes in the Soret region for vibrationally-excited U(OEP)₂ can be simulated (or fit) using a phenomenological distribution model. In this model, the transient absorption in the Soret region of Figure 2B is considered to arise from a distribution of vibrational levels of the ground electronic state, where the distribution is described by a normalized, asymmetric exponential distribution function of the form

$$f(v) = \theta \exp[-\theta(v - v_0)] \quad \text{for } v \leq v_0 \quad (1a)$$

$$f(v) = 0 \quad \text{for } v > v_0 \quad (1b)$$

where v_0 is the frequency of the ground-state Soret maximum and θ is the distribution width. It is assumed that the spectrum of each vibrational level is described by a Gaussian function of width σ . Convolution of the spectral and distribution functions gives an analytic expression for the absorption at frequency ν

$$A(\nu, v_0, \theta, \sigma) = \frac{1}{2}\theta \exp[\theta(\nu - v_0) + \frac{1}{2}\theta^2\sigma^2] \{1 + \text{erf}[-(\nu - v_0)/(2^{1/2}\sigma) - \sigma\theta/2^{1/2}]\} \quad (2)$$

Thus, the absorption difference spectrum for the vibrationally excited ground electronic state is given by

$$\Delta A = A(\nu, v_0, \theta, \sigma) - A(\nu, v_0, \theta_{\text{gnd}}, \sigma) \quad (3)$$

with θ and θ_{gnd} representing the distribution width of the vibrationally excited and equilibrated electronic ground state, respectively. The time dependence of the absorption difference spectrum is introduced by allowing θ to vary with time such that

$$\theta^{-1} = \theta^{-1}(t) = \theta^{-1}(\infty) + (\theta^{-1}(0) - \theta^{-1}(\infty)) \exp[-t/\tau] \quad (4)$$

where $\theta(0)$ and $\theta(\infty) = \theta_{\text{gnd}}$ denote the initial and steady-state values of θ .

The results of simulations of the Soret region spectra at several values of θ are shown in Figure 2C. These spectra were generated by holding the other parameters constant ($v_0 = 25\,640\text{ cm}^{-1}$, $\sigma = 320\text{ cm}^{-1}$, $\theta_{\text{gnd}}^{-1} = 200\text{ cm}^{-1}$) at values that reproduced the main features of the transient absorption spectra in Figure 2B. The simulations reproduce all the key aspects of the time evolution of the absorption difference spectra, including the absence of an isosbestic point as $\theta \rightarrow \theta_{\text{gnd}}$ and the continuous shifting of the $\Delta A = 0$ point as the spectrum decays. The wavelength dependence of the slow kinetic phase in the Soret region (open circles in Figure 5) can also be simulated well using the same parameters. The solid circles in Figure 5 show the time constants obtained by letting $\tau = 12.5$ ps for the evolution of the distribution width, substituting θ of eq 4 into eq 3, and then fitting the resulting ΔA vs time plot to a single-exponential function at the corresponding wavelengths across the spectrum. It should be noted, however, that the wavelength dependence of the observed kinetics as well as the simulations based on a distribution of vibrational levels indicates that the time evolution of the absorption at each wavelength is rigorously more complex than single exponential.²²

Thus, the complicated spectral changes and dynamics of U(OEP)₂ are well reproduced by variation of a single parameter, namely, the distribution width.

Although the simple asymmetric distribution model is excellent at reproducing the experimental results, it does have shortcomings. For example, the general formulation does not explicitly include details of the mechanism of vibrational relaxation or of the molecular changes in the porphyrin or solvent associated with the presence and dissipation of the excess vibrational energy. Along these lines, it is tempting to associate the distribution width parameter θ with $1/kT$, thus yielding a Boltzmann distribution model from which one could estimate a vibrational temperature for the "hot" porphyrin. Although reasonable photoinduced temperature increases have been obtained from such analyses for some dye molecules,^{21a} stilbenes,^{19a} and monomeric Ni porphyrins,^{18a} the estimated temperature increase of ~ 1000 K at $t \sim 0$ for U(OEP)₂ is about a factor of 2 larger than expected for distribution of the energy of a 582-nm excitation photon over the vibrational modes of a porphyrin dimer. Of course, there are several possible reasons for such a discrepancy. First, assigning a thermodynamic temperature at a particular time after excitation requires that the internal vibrational equilibration of the porphyrin is complete on a shorter time scale. (The subsequent time evolution then reflects only dissipation of the excess energy within the porphyrin into the solvent and away from the porphyrin.) Most studies on dyes, heme proteins, and other large organic molecules generally have been interpreted in terms of a substantial separation of time scales for the two processes: internal equilibration in several hundred femtoseconds followed by vibrational cooling in a few to tens of picoseconds depending on the amount of excess energy present.²¹ However, we have argued previously that intramolecular vibrational relaxation in porphyrins likely extends into the picosecond time scale,^{18a,d} which would preclude a simple estimate of the vibrational temperature, especially at early times. A "slow" internal vibrational energy redistribution rate and a higher temperature increase than expected at early times may reflect a preference of the molecule to populate for some time a subset of the porphyrin modes. However, at the present time there is no clear evidence for such bottleneck modes in these systems. Additionally, as discussed above, we cannot exclude some contribution of the (f,f) states or other (conformational or solvent) dynamics during the first few picoseconds after excitation.

Finally, the simple distribution model described here in essence assumes that (i) the ground and excited electronic states have harmonic potentials, (ii) transitions initiated from all the vibrational states of the ground electronic state have equal Franck-Condon factors, and (iii) the only parameter that changes as the excess energy is dissipated into the solvent is the population of the excited vibrational levels of the ground electronic state. In other words, a simple "hot-band" picture for the absorption spectrum of the vibrationally excited porphyrin is assumed. Although this model accounts well for the enhanced absorption and faster relaxation times observed on the red side of the Soret band (Figures 2B and 5), it cannot account for the fact that red shifted emission has been observed from vibrationally excited porphyrins.^{18d} (The simple hot-band model predicts that the emission from a vibrationally excited upper electronic state will be blue-shifted from the position in the vibrationally relaxed molecule.) Accordingly, it is likely that the presence of excess vibrational energy in such porphyrin complexes induces additional effects such as anharmonic expansion, a change in vibronic coupling between the Soret and Q states, and/or alterations in the interactions between the porphyrin and the solvent.^{18d} Such molecular details ultimately will need to be incorporated into a more rigorous distribution model. However, the fact that the simple, generalized asymmetric distribution model does so well in describing the complex early-time dynamics of the U^{IV} sandwich

complexes and other porphyrin systems supports the idea that relaxation of a vibrationally excited electronic state underlies the complex ultrafast photophysics.

Summary

The ground- and excited-state electronic spectra of the uranium bis(porphyrin) sandwich complexes exhibit features characteristic of strong electronic interactions between the two porphyrin subunits. The complexes relax to the electronic ground state within 1 ps following photoexcitation. This multistep process involves intersystem crossing from the lowest ¹(π,π^*) state of the coupled macrocycles to the lowest ³(π,π^*) state within 200 fs followed by relaxation via one or more low-energy (f,f) excited states. The electronic ground state thus produced is highly vibrationally excited. The dissipation of the excess internal vibrational energy into the solvent requires up to 25 ps and is accompanied by a complex spectral evolution that can be modeled with a distribution function whose width decreases with time. The results obtained from these bis(porphyrin)s further elucidate the vibrational relaxation time scale and how excess vibrational energy affects electronic spectra in porphyrinic systems.

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