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Excited-State Transient of Vanadyl Uroporphyrin I Detected by Resonance Raman Spectroscopy

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Transient Raman spectroscopy has been used to investigate excited states of vanadyl uroporphyrin I (VOUroP) in both monomeric and dimeric forms. Uroporphyrins are water-soluble porphyrins with propionic and acetic acid groups substituted at the β -pyrrole carbon positions. In solution, the metal uroporphyrins form π - π dimers at high ionic strength. Monomeric VOUroP in aqueous solution is known to be six-coordinate with a ligand trans to the oxo ligand. Upon dimerization, the sixth ligand site is inaccessible, and a five-coordinate species is observed. At high laser fluence, an excited-state transient is formed in the monomeric species. Raman spectra of this species are most consistent with an $^2A_{1u}(a_{1u}(\pi) \rightarrow d_{xy})$ charge-transfer state. In contrast, dimeric VOUroP shows little evidence of an excited state in the transient Raman spectra during a 10-ns laser pulse.

Introduction

The photodynamics of heme proteins have been studied intensely in an attempt to understand the mechanisms of these complex systems.^{1,2} Vanadyl porphyrins provide a structural analogue of heme proteins including those that activate molecular oxygen. The intermediates of cytochrome P450, horseradish peroxidase, and cytochrome *c* peroxidase are believed to contain a ferryl heme (Fe=O) in analogy to the V=O multiple bond of vanadyl porphyrins.³⁻⁶ The chemistry of vanadium porphyrins is also important because of their occurrence in petroleum and source rocks. VO porphyrins are useful molecular fossils for the diagenesis of petroleum deposits. Their coordination chemistry plays a role in catalyst deactivation in hydrotreating processes.^{7a} Vanadyl porphyrins also serve as the photoactive components in electrophotography applications.^{7b}

Uroporphyrins are water soluble porphyrins that possess alternating propionic and acetic acid substituent groups at the β -pyrrole carbons of the macrocycle. They have been shown to photosensitize redox reactions, such as the reduction of methylviologen.⁸⁻¹⁰ In order to better understand the intermolecular processes involved in these electron-transfer systems, it is useful to determine the intramolecular excited states that may be involved in redox photochemistry for porphyrins containing various metals. In this study, the photodynamics of monomeric and dimeric vanadyl uroporphyrin I (VOUroP) are probed on a 10-ns time scale by using transient resonance Raman spectroscopy. The monomer and π - π dimer differ in their photochemistry as a result of complexation and the loss of the axial sixth ligand.

Materials and Methods

VOUroP was purchased from Porphyrin Products and used without further purification. The samples were dissolved in 0.1 M KOH typically at concentrations of 300 μ M. The absorption spectra of the samples were checked both before and after laser irradiation with an HP Model 8452A spectrophotometer. Neither the monomeric nor dimeric forms of vanadyl uroporphyrin show any indication of photodegradation during laser irradiation. However, other studies have found that other vanadyl porphyrins, such as VOOEP, readily photodegrade upon laser irradiation.¹⁴

Raman spectra of the monomeric and dimeric forms of VOUroP were obtained at laser excitation wavelengths coincident with the maxima of the porphyrin Soret transition via protocols explained in detail elsewhere.¹¹ Excitation wavelengths of 406, 410, 420, 430, 435, and 445 nm (obtained from a Moletron

N₂-pumped dye laser) were used to irradiate the samples. The temporal resolution of the transient spectra was limited by the \sim 10-ns laser pulse width. A backscattering geometry was utilized. The scattered radiation was focused into a SPEX Industries 1403 scanning double monochromator and detected by a Hamamatsu R928 photomultiplier tube in a cooled housing. The laser fluences were varied by using cylindrical or spherical lenses and neutral-density filters. Peak positions are considered accurate to ± 2 cm⁻¹.

Results and Discussion

Previous studies have demonstrated that, in alkaline solution, VOUroP has absorption and Raman spectra quite distinct from those of other vanadyl porphyrins in noncoordinating organic solvents.¹² In noncoordinating solvents, such as chloroform and benzene, vanadyl porphyrins are known to be in a five-coordinate out-of-plane vanadium(IV) configuration.^{13,14} The spectrum of VOUroP at high pH is thought to be the result of coordination of a sixth ligand, either a water molecule or a hydroxyl group.¹² Under conditions where the sixth coordination site of VOUroP is sterically blocked, a five coordinate species results. This includes salt- and concentration-induced dimerization^{12,15-17} as well as

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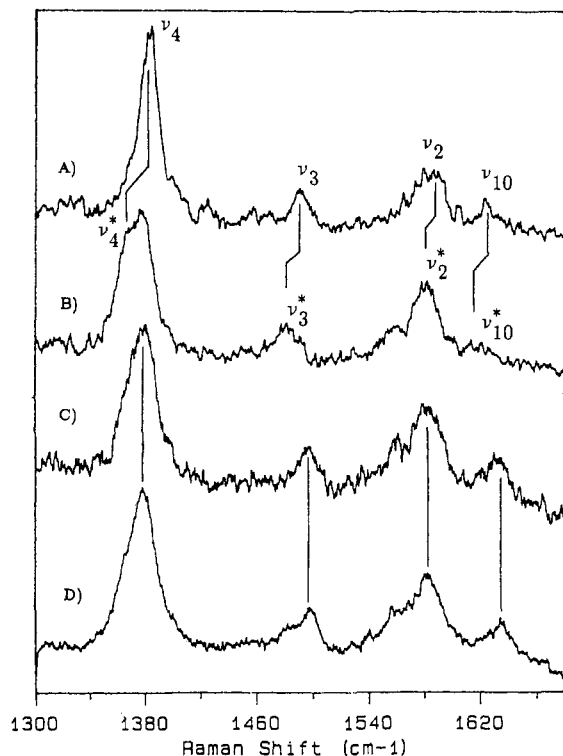


Figure 1. High-frequency portion of the resonance Raman spectra under 10-ns 435-nm excitation pulses of (A) monomeric VO(OH)UroP at low laser fluence ($\sim 10^6$ W/cm²), (B) monomeric VO(OH)UroP at high laser fluence ($\sim 10^8$ W/cm²), (C) dimeric VOUroP at low laser fluence ($\sim 10^6$ W/cm²), and (D) dimeric VOUroP at high laser fluence ($\sim 10^8$ W/cm²). Samples were ~ 300 μ M VOUroP in 0.1 M KOH. Dimeric species were prepared by saturating the solution with KCl. Spectra were obtained at ~ 5 cm⁻¹ spectral band-pass and are the unsmoothed sums of 3–4 scans at 15 cm⁻¹/min.

complexation with methylviologen¹⁶ and phenanthroline.¹² Interestingly, the dimerization of VOUroP substantially alters its photodynamics.

Figure 1 shows transient Raman spectra of VO(OH)UroP, which were obtained with 435-nm excitation at low (A) and high (B) laser fluences. The modes ν_4 , ν_3 , ν_2 , and ν_{10} are at 1382, 1490, 1585, and 1623 cm⁻¹ for the six-coordinate ground-state species of VO(OH)UroP observed at low power density. At higher laser fluences, a transient species is observed within the 10-ns laser pulses that exhibits lower frequencies for all of these modes. These bands are assigned to an excited state of VO(OH)UroP (see discussion below). This phototransient species has modes at 1375, 1481, 1581, and 1617 cm⁻¹, which are assigned to ν_4^* , ν_3^* , ν_2^* , and ν_{10}^* , respectively. It should be noted that the quoted positions of these modes in some cases are not the frequencies of the excited state but rather the convolution of the phototransient and the residual ground-state spectra. The formation of the transient excited state is entirely reversible since spectra obtained at low power density, after observation of the excited state at high power, are identical with the initial low-power spectrum (see Figure 2).

Dimerization of VO(OH)UroP to form the five-coordinate species induces large shifts in ν_3 , ν_2 , and ν_{10} to 1498, 1590, and 1635 cm⁻¹, respectively (see Figure 1). However, ν_4 shifts by only 1 cm⁻¹, but broadens considerably. These shifts were shown previously to result from a dimerization-induced change from the six-coordinate VO(OH)UroP to the five-coordinate out-of-plane VOUroP.¹² Comparison of spectra obtained at low (C) and high (D) laser fluence yields little evidence of an excited state in VOUroP dimers on a 10-ns time scale.

In order to ascertain the effects of the excited state in VO(OH)UroP on axial ligand–metal interactions, the V=O stretching

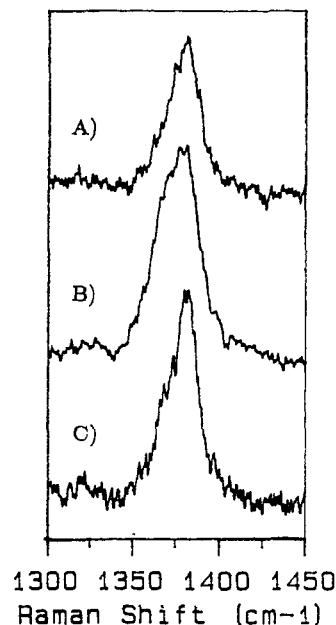


Figure 2. Reversible behavior of ν_4 of monomeric VO(OH)UroP as a function of laser fluence: (A) $\sim 10^6$ W/cm², (B) $\sim 10^8$ W/cm², and (C) $\sim 10^6$ W/cm² obtained immediately after (B). Conditions were the same as Figure 1.

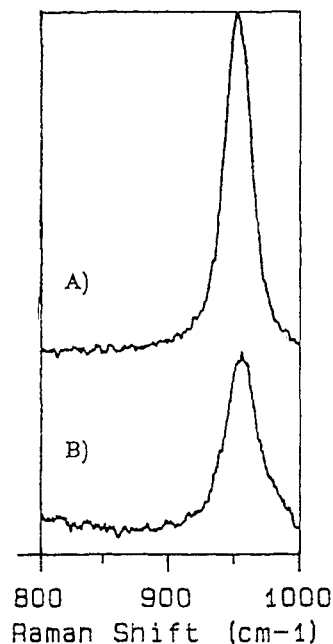


Figure 3. Transient Raman spectra of the ν_{VO} region under 10 ns 435 nm excitation pulses of (A) monomeric VO(OH)UroP at low laser fluence ($\sim 10^6$ W/cm²) and (B) high laser fluence ($\sim 10^8$ W/cm²). Other conditions were the same as Figure 1.

frequency (ν_{VO}) at 950 cm⁻¹ for VO(OH)UroP in 0.1 M KOH was monitored as a function of laser flux. Figure 3 shows transient Raman spectra in the region of ν_{VO} at low (A) and high (B) laser fluences. The small (~ 4 cm⁻¹) shift and line-shape change in ν_{VO} at high flux indicates a strengthening of VO bonding interactions in the excited state.

The photolability of the OH⁻ ligand can also be determined from the transient spectra. In this case, ν_{VO} is not particularly informative since a comparison of the V=O stretching frequencies of the ground states of the monomeric and dimeric forms reveals that ν_{VO} is at ~ 950 cm⁻¹ in both species (data not shown). However, if the hydroxyl group photodissociated from VO(OH)UroP, the modes ν_3 , ν_2 , and ν_{10} would presumably shift to higher frequency based upon the ground-state spectra of the six-coordinate monomer and the dimerized five-coordinate species (Figure 1). Instead, all of the high-frequency modes of VO-

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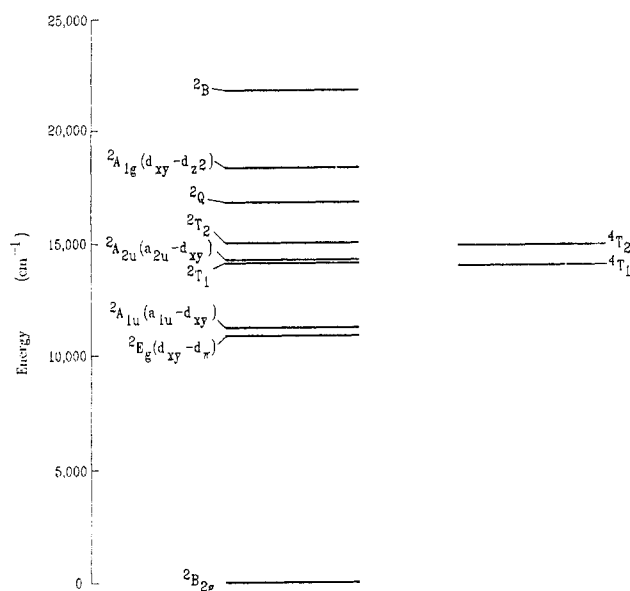


Figure 4. State diagram of vanadyl porphyrin based upon extended Hückel calculations¹⁴ and luminescence studies.¹⁸

(OH)UroP shift to lower frequency upon photoexcitation. This result precludes the possibility of ligand photoejection in the transient six-coordinate species. Thus, the transient vibrational spectra of the VO(OH)UroP suggest minimal alterations in the axial bonding properties of the excited state and strongly argue for the participation of nonbonding metal orbitals in the excited-state dynamics.

A number of excited states are candidates for the observed behavior. Figure 4 is a diagram of the electronic states of vanadyl porphyrins (five-coordinate) predicted by calculations performed by Zerner and Gouterman.¹⁸ There is likely to be little direct quantitative correspondence between these extended Hückel calculations and various condensed-phase species of VOuroP. Nonetheless, these studies provide a useful qualitative description of the low-lying excited states that might participate in VOuroP photodynamics. One of the lowest excited states in the doublet manifold is the $^2A_{1u}$ state, which is approximately 11 000 cm^{-1} above the $^2B_{2g}$ ground state. The $^2A_{1u}$ state results from a net charge transfer from the $a_{1u}(\pi)$ orbital of the porphyrin to the d_{xy} nonbonding orbital of the metal. This produces a cationic porphyrin species with the hole in the $a_{1u}(\pi)$ orbital. A net d-d state (designated 2E_g) resulting from a net electron promotion from the $d_{xy}(b_{2g})$ to a $d_{\pi}(e_g)$ orbital of vanadium is nearly degenerate with the A_{1u} charge-transfer state. A final possibility is deactivation directly from triplet states. Low-temperature luminescence studies^{19,20} assigned the long-lived (microseconds) excited state observed in a number of vanadyl porphyrins as a 4T_1 state in thermal equilibrium with the 2T_1 state. However, the lifetime of the 4T_1 state was found to be extremely temperature dependent.¹⁹ Similar phenomena are observed for d^9 (copper porphyrins) and d^1 (molybdenum porphyrins)²¹ analogues. For example, the lifetime of the 4T_1 state in CuOEP at 77 K is 1000 μs , while at room temperature the lifetime is 13 ns.²²⁻²⁴ No room temperature luminescence data are currently available for the vanadyl system. Previous studies^{19,20} have suggested that, within the doublet manifold (see Figure 4), an activation barrier exists that prevents radiationless decay from the 2T_1 state to lower states at low temperatures in the doublet manifold of the vanadyl system. Interestingly, these lower states do not exist in the four-coordinate

copper (d^9) systems. This necessitates decay directly from the 2T_1 - 4T_1 equilibrium at any temperature in the copper system.

The structural content of the transient Raman data can be used to discriminate among these possible bottleneck states. The current results are consistent with the electronic changes anticipated for the $^2A_{1u}$ state. Since the d_{xy} orbital of the vanadyl system is a nonbonding orbital directed between the pyrrole nitrogens, addition of substantial electron density to this orbital would have a minimal effect on the interaction between the vanadium and the oxo ligand. Also, since the $a_{1u}(\pi)$ orbital has a node through the pyrrole nitrogens, it interacts little with the metal. Thus, the hole in the $a_{1u}(\pi)$ orbital would have a small effect on ν_{VO} . In other words, little or no shift in ν_{VO} would be anticipated by the charge transfer to the d_{xy} orbital. In addition, the generation of a cationic species on the macrocycle would perturb significantly the π -electron density and concomitantly alter the force constants of the macrocycle. This might result in relatively large changes in the modes sensitive to core size,^{25,26} such as ν_3 , ν_2 , and ν_{10} , as well as modes sensitive to the electron density of the macrocycle, such as ν_4 .²⁵

The other possibilities for the observed excited state of VO-(OH)UroP are the 2E_g and the 2T_1 - 4T_1 states. While the 2E_g state has been calculated to be at comparable energy to the $^2A_{1u}$ state for five-coordinate species, it is expected to produce spectral changes that do not correlate with our experimental data. The electron density of the porphyrin π -system would be affected by the promotion of an electron within the d-orbitals of the central metal since they are coupled to the porphyrin π -system. Consequently, the d-d state would be expected to produce changes in the high-frequency Raman lines of the porphyrin. However, substantial changes ($\geq 30 \text{ cm}^{-1}$) in ν_{VO} to lower frequency would be apparent because occupation of the $d_{\pi}(e_g^*)$ orbital, which is involved in the axial ligand bond, should result in severe weakening of the VO bond strength, using a simple bond order argument. The triplet states of vanadyl porphyrins result from a π - π transition into the $e_g(\pi^*)$ orbitals of the macrocycle. Studies have suggested that the d_{π} orbitals of the vanadyl system are nearly degenerate with the $e_g(\pi^*)$ orbitals of the macrocycle, resulting in strong mixing of these orbitals. Consequently, both the 4T_1 and 2T_1 states should have significant d_{π} character. We anticipate that population of the 2T_1 - 4T_1 states would also weaken the V=O bond through partial occupation of the d_{π} antibonding orbitals of the metal.

Additional studies are required to probe the ligand specificity of the excited state. Because of the near degeneracy of the $^2A_{1u}$ and 2E_g states, the relative energetics of these states could change significantly, depending on the nature of the sixth ligand. The 2E_g state would be especially sensitive to the interaction with the sixth ligand. Small changes in the ligand field splittings of the vanadium could switch the ordering of the lowest states in the doublet manifold or destabilize them sufficiently to make the 2T_1 state the lowest state in the manifold.

Dimerization of VOuroP at high salt concentration has been shown to generate five-coordinate species.¹² Interestingly, the photodynamics of the monomeric form of VOuroP are markedly different from those of the dimeric species. In addition to the changes in axial ligation, more subtle electronic changes produced by π - π interactions between the macrocycles may contribute to the faster decay kinetics of the porphyrin. Thus, the lack of an observable excited-state transient on a 10-ns time scale in the VOuroP dimeric species may result, in part, from an increase in the density of states through intermolecular electronic coupling or shifts in the relative energies of the excited states. In any event, excited-state lifetimes decrease significantly when uroporphyrins aggregate.^{8,15,27}

This study demonstrates that dimerization of VOuroP dramatically affects its photodynamics. The dominant effect of dimerization appears to be a change in axial ligation which, in

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turn, modulates the relative energies of VOUroP charge transfer and d-d states. On the basis of the transient Raman data presented in this study and the theoretical work of Zerner et al.,¹⁸ the photochemically generated bottleneck state of the monomer is the 2E_g , the $^2A_{1u}$, or the 2T_1 - 4T_1 thermal equilibrium. The $^2A_{1u}$ state, however, is favored by the Raman data of this study.

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Femtosecond-Picosecond Laser Photolysis Studies on the Photoinduced Charge Separation and Charge Recombination of a Produced Ion Pair State of Some Typical Intramolecular Exciplex Compounds in Alkanenitrile Solvents

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Femtosecond and picosecond laser photolysis and time-resolved absorption spectral studies have been made to observe directly the photoinduced charge separation (CS) and charge recombination (CR) of a produced CS state of aromatic amine (D) and aromatic hydrocarbon (A) combined systems: p -(CH₃)₂N-Ph-(CH₂)_{*n*}-(1-pyrenyl) (P_{*n*}, *n* = 1, 2, 3) and p -(CH₃)₂N-Ph-(CH₂)_{*n*}-(9-anthryl) (A_{*n*}, *n* = 0, 1, 2, 3), in alkanenitrile solvents. The time constants τ_{CS} of the photoinduced CS of these systems are considerably longer than the solvent dielectric relaxation time τ_L as well as the solvation time τ_S (determined from the time-dependent Stokes shift of fluorescent probe) except that τ_{CS} of A₁ is close to τ_S . In the case of A₀ where D and A groups are more strongly interacting than in A₁, the photoinduced CS is much slower than that of A₁, which cannot be interpreted simply by usual electron-transfer theories. The time constants τ_{CR} of the CR decay of the produced CS state have been confirmed to be more than 2-3 orders of magnitude longer than τ_{CS} and to become shorter with increase of chain number *n* contrary to the case of τ_{CS} . These results are discussed on the basis of the solvent dynamics and/or solvation, the magnitude of the D-A electronic interaction, structural rearrangements, and the energy gap dependence of electron transfer.

Introduction

It is believed in general that the rate of the photoinduced CS and that of the CR of the produced ion pair (IP) state are regulated by the magnitude of the electronic interaction responsible for the electron transfer (ET) between D and A groups, the Franck-Condon (FC) factor which is related to the energy gap for the ET reaction, and the reorganization energies of D and A as well as the surrounding solvent and solute-solvent interactions and the solvent orientation dynamics in the course of ET in polar solvent.¹

When the electronic interaction between D and A is very weak, the ET process is considered to be nonadiabatic (a). When the interaction becomes fairly strong, the reaction will become adiabatic (b). If the electronic interaction becomes sufficiently strong in case b and the energy gap relations are also favorable, the ET process will become barrierless (c). In such a case, it is believed that the ET process is governed mainly by the orientational motions of polar solvent molecules or polar groups in the environment surrounding D and A, and the longitudinal dielectric relaxation time τ_L will be important as a factor controlling the ET rate.² In a limit of strong interaction between D and A groups combined by rigid spacer or single bond, its excited singlet state can be regarded as a very polar single molecule and we can observe a large fluorescence Stokes shift due to the solvation in polar solvents (d), for which the first theoretical formula was given by

one of the present authors³ and Lippert⁴ and has been extended recently by Bagchi et al.⁵ and others to take into account its dynamical aspects.

For the elucidation of the above mechanisms, especially the interactions of D and A with polar solvent including its dynamical effects on the ET process, which are believed to be controlling the ET reaction, systematic femtosecond-picosecond laser photolysis studies on various combined D,A systems with different degrees of electronic interaction between them are of crucial importance. However, results of such experimental investigations on the D,A combined systems which seem to be appropriate for such purpose are very few. The discrimination among the above cases a-d does not seem to be very clear in some systems examined until now.⁶ Although these problems have been investigated mainly by means of time-resolved fluorescence measurements, time-resolved transient absorption spectral measurements are also very important for the elucidation of the ET mechanisms. The latter method gives direct information on the electronic structures of the system undergoing ET, which is extremely helpful for discriminating various cases of ET mechanisms.

From the above viewpoints, we have examined the following systems with different degrees of electronic interactions between combined D,A groups by femtosecond and picosecond laser photolysis and time-resolved transient absorption spectral measurements: p -(CH₃)₂N-Ph-(CH₂)_{*n*}-(1-pyrenyl) (P_{*n*}, *n* = 1, 2, 3) and p -(CH₃)₂N-Ph-(CH₂)_{*n*}-(9-anthryl) (A_{*n*}, *n* = 1, 2, 3) in alkanenitrile solvents. Some results of picosecond laser photolysis

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