

# SPECTROSCOPIC INVESTIGATIONS ON THE LOWEST EXCITED STATE OF OXO-VANADYL(IV) PORPHYRINS

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The excited-state relaxation dynamics and pathways of oxo-vanadyl(IV) porphyrins have been investigated by the emission and transient absorption and resonance Raman spectroscopies. At room temperature, the emission spectrum has a single broad feature centered near 790 nm in noncoordinating solvent such as toluene and benzene and 814 nm in THF, whereas at 77 K the emission bands exhibit blue-shift to 745 and 784 nm, respectively. Furthermore, the emission decay time in benzene increases from 40 to 60 ns with decreasing temperature from 323 to 268 K. However, the decay time in THF is ca. 10 ns, which is almost independent of temperature. The activation energy between  $^2T(\pi, \pi^*)$  and  $^4T(\pi, \pi^*)$  under the proposed relaxation scheme of photoexcited OVIVTPP has been estimated to be ca.  $500\text{ cm}^{-1}$  in noncoordinating solvents such as benzene and toluene. All the spectroscopic results including the transient Raman spectrum led us to conclude that the nature of the lowest excited state should be  $^4T(\pi, \pi^*)$ . The decay times for both the photoinduced absorption and bleaching signals are equal to each other and also in good accordance with that of the emission decay time as far as temperature and solvent are the same. The time-resolved emission spectra and wavelength dependent decay kinetics reveal that the observed emission spectra apparently originate from three different emitting species. These observations are discussed in terms of postulating a quenching state, which is thermally accessible from  $^2T(p,p^*)$  of  $OV^{IV}TPP$ .