

VIBRATIONAL ENERGY RELAXATION IN THE (d, d) EXCITED STATE OF NICKEL OCTAETHYLPORPHYRIN

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The formation of a hot photoproduct of nickel octaethylporphyrin (NiOEP) upon $\pi\pi^*$ excitation and its subsequent vibrational energy relaxation were monitored by picosecond time-resolved resonance Raman spectroscopy. Resonance Raman bands due to the photoproduct instantaneously appeared upon the photoexcitation. Their intensities decayed with a time constant of 330 ± 20 ps, which indicates electronic relaxation from the (d,d) excited state (B_{1g}) to the ground state (A_{1g}). Anti-Stokes ν_4 band of the hot (d, d) excited state of NiOEP appeared immediately after the excitation and decayed with time constants of 11 ± 2 and 330 ± 40 ps. In contrast, the rise of anti-Stokes ν_7 intensity was not instantaneous but delayed by 2.6 ± 0.5 ps, which suggests that IVR has not been completed in a subpicosecond time regime.

Keywords: Picosecond time-resolved resonance Raman spectroscopy; vibrational energy relaxation; metalloporphyrin

Internal conversion processes following optical excitation invariably will leave the molecules with excess energy. Subsequent energy redistribution and relaxation in large molecules in solution phases are of fundamental importance for understanding ultrafast chemical dynamics. In this study, we investigated the formation of a hot photoproduct of nickel octaethylporphyrin (NiOEP) upon $\pi\pi^*$ excitation and vibrational energy redistribution with picosecond time-resolved resonance Raman spectroscopy.

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Stokes resonance Raman bands due to the photoproduct instantaneously appeared upon the photoexcitation. Their intensities decayed with a time constant of 330 ± 20 ps, which indicates electronic relaxation from the (d,d) excited state (B_{1g}) to the ground state (A_{1g}). This is consistent with the results of transient absorption measurements by Rodriguez *et al.* [1]. The core-size marker bands of the photoproduct are shifted to a lower frequency side of those of the parent molecule, suggesting core expansion upon the (d,d) excitation.

Anti-Stokes ν_4 intensity in the hot (d,d) excited state of NiOEP appeared also promptly and decayed with time constants of 11 ± 2 and 330 ± 40 ps (Fig. 1(a)). The former and latter components are assignable to vibrational and electronic relaxations, respectively. The anti-Stokes ν_7 band also showed intensity decay of which time constants are almost the same with those for the anti-Stokes ν_4 intensity. In contrast to the ν_4 intensity, however, the rise of anti-Stokes ν_7 intensity was not instantaneous but delayed by 2.6 ± 0.5 ps (Fig. 1(b)). This difference in the rise of anti-Stokes intensities suggests that IVR has not been completed in a subpicosecond time regime.

The peak positions of the ν_4 and ν_7 bands shifted by nearly 10 cm^{-1} between 0 and 50 ps. The time constant for the shift of the ν_4 band was

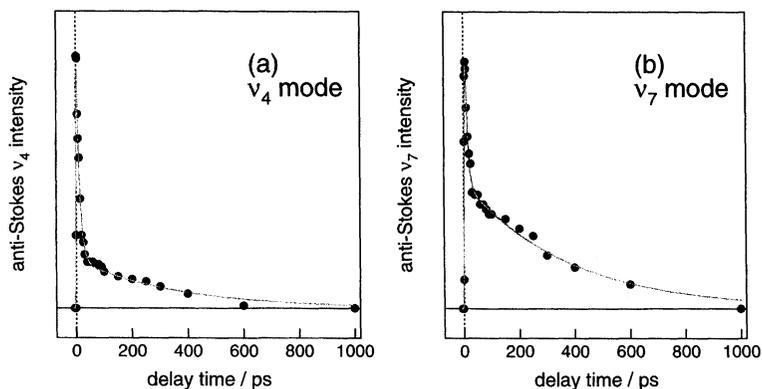


FIGURE 1 (a) Anti-stokes ν_4 intensity as a function of delay time. Solid circles indicate the observed band intensity. Solid line indicates a fit with biexponential decays (fast component, 11 ± 2 ps; slow component, 330 ± 40 ps). (b) Anti-stokes ν_7 intensity as a function of delay time. Solid circles indicate the observed band intensity. Solid line indicates a fit with biexponential decays (fast component, 10 ± 2 ps; slow component, 350 ± 40 ps) and monoexponential rise (2.6 ± 0.5 ps).

9.1 ± 3.3 ps, which was close to that for the fast component of intensity decay. The bandwidth of the ν_4 band got narrower as the delay time increased. These temporal change in band shape can be ascribed to intramolecular anharmonic coupling of the ν_4 mode to thermally populated low frequency modes [2].

References

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- [2] Shelby, R. M., Harris, C. B. and Cornelius, P. A. (1979). *J. Chem. Phys.*, **70**, 34.