

PROBING THE WAVELENGTH-DEPENDENT EXCITED-STATE DYNAMICS OF A PHOTOCROMIC MOLECULAR SWITCH USING RESONANCE RAMAN SPECTROSCOPY

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Diarylethene (DAE) derivatives are an important class of photochromic molecular switches that undergo ring-opening and ring-closing reactions following excitation with visible or UV light, respectively. Here, we use resonance Raman spectroscopy to examine the wavelength-dependence of the cycloreversion (ring-opening) reaction following excitation into the two lowest electronic absorption bands of a common DAE derivative. Resonance Raman spectroscopy reveals the initial dynamics on the excited-state potential energy surface based on mode-specific enhancements of the vibrational spectrum that depend on the electronic resonance condition. Although the vibrational frequencies report on the ground-state structure of the molecule, the relative intensities of the Raman transitions reflect the initial motion immediately following excitation to the upper electronic state. Specifically, we report stimulated resonance Raman spectra and Raman gain profiles for excitation into two separate absorption bands centered near 560 nm and 370 nm. Although excitation into either band results in the cycloreversion reaction with similar $\sim 2\%$ quantum yield, the resonance Raman spectra indicate that the initial dynamics are different for the two excited states. Excitation into the lower energy absorption band reveals resonance enhancement of a 986 cm^{-1} mode that corresponds to a ring breathing mode of the central cyclohexadiene ring, and likely represents motion directly along the ring-opening reaction coordinate. In contrast, excitation into the higher energy absorption band results in resonance enhancement for 1400 cm^{-1} and 1600 cm^{-1} modes that represent ethylenic stretching along the conjugated backbone of the molecule and of the peripheral phenyl rings, respectively, and probably do not map directly onto the reaction coordinate. These observations provide key information for understanding the reactivity of DAE derivatives following excitation in the visible and near-UV.