

COHERENT MOTION OF LOW FREQUENCY VIBRATIONS IN ULTRAFAST EXCITED STATE PROTON TRANSFER

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Photoexcitation of internal proton transfer in the tinuvin molecule causes the excitation of some low frequency vibrational modes which oscillate with high amplitudes in a coherent manner over 700 fs. Such effect is observed for the first time applying two color pump/probe measurement with 25 fs pulses. Based on resonance Raman spectra a normal coordinate analysis of the modes is performed. It is shown that the nuclear movement given by the normal vibration of one of the modes serves to open up a barrierfree proton transfer path.

Keywords: Proton transfer; ultrafast time resolved spectra; Raman spectra-molecules; excited state-molecules; potential energy surface

Photoexcitation into the 350 nm-band of the 2-(2'-hydroxy-5'-methyl-phenyl) benzotriazol molecule (TIN) induces internal proton transfer proceeding in a time of 60–80 fs. Spectrally resolved two color pump/probe experiments with 25 fs pulses reveal an oscillation in the induced transmittance caused by coherent oscillations in some low frequency vibrational modes [1]. This coherent oscillation as observed for the first time pertains up to 700 fs which is approximately 10 times longer than the time for the transfer from the enol- to the keto-form of the molecule in the excited electronic state (Fig. 1). Fourier decomposition of the oscillations reveals two strongly excited modes at 250 and

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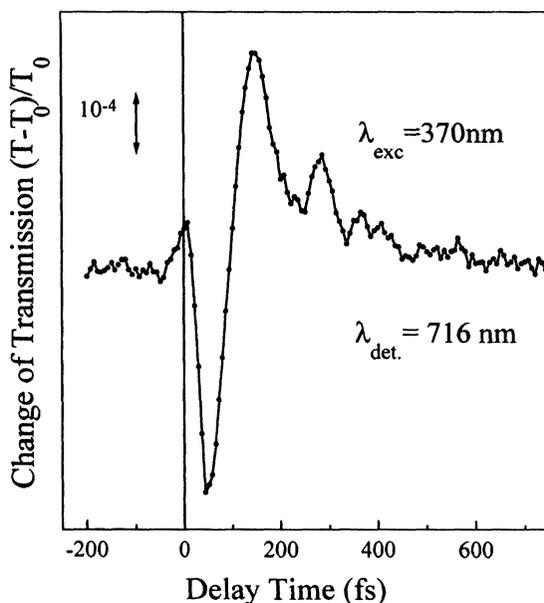


FIGURE 1 Spectrally resolved transient absorption and emission of TIN.

470 cm^{-1} in the excited state keto-product. They are close in frequency to two strong Raman modes being at 299 and 469 cm^{-1} in the enol-ground state of the molecule. Both enol-modes are in-plane skeleton vibrations. From the resonance Raman spectra for them a relatively high vibronic coupling strength is derived. The resonance Raman spectrum shows characteristic features in the range of combination tones $1600\text{--}3000\text{ cm}^{-1}$ closely related to the PT process. This range is built by groupings of relatively strong lines which originate as combinations of one of the oscillating modes (469 cm^{-1}) with further strong fundamentals (Fig. 2). Deuteration effects upon the 1422 cm^{-1} mode allow to identify the $\nu_{1422} + n\nu_{469}$ combinations up to the order $n = 4$. From the intensity distribution and its spectral dispersion (visible in Fig. 2 for two excitations at 363.8 and 351.2 nm) a strong anharmonicity and shift of the potential minimum in the excited electronic state is derived for the 469 cm^{-1} mode [2]. This origin shift represents a shortening of the distance between proton-donor and-acceptor (O...N) which reflects the geometrical change in the excited

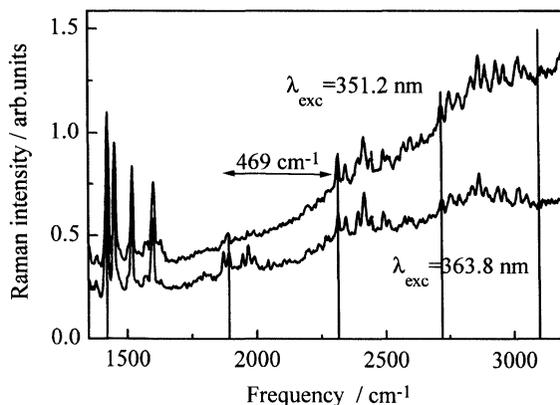


FIGURE 2 Combination tones in the Raman spectrum of TIN.

keto-state in the same manner as derived from quantum chemical estimates.

The experimental results of the fs-measurements and of resonance Raman spectroscopy suggest the 469 cm^{-1} mode to be of functional importance for the transfer dynamics. Confining to a two-dimensional subspace on the excited state potential hypersurface we propose a phenomenological model for the transfer [3] in which the excitation of the 469 cm^{-1} -deformation mode in the initial phase of the process leads to a nuclear reorganisation corresponding to the 469-origin shift. By this way a barrierless reaction channel is formed on the potential hypersurface along which the PT path proceeds.

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