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Revealing the Excited State Dynamics of Betaine-30 using Two-dimensional Electronic-Vibrational Spectroscopy

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Abstract: Two-dimensional electronic-vibrational spectroscopy was used to investigate the ultrafast photoinduced dynamics of betaine-30 in methanol-d₄ solution. Our study reveals three vibrational modes (1330, 1350 and 1370 cm⁻¹) are strongly coupled to the back charge transfer process.

OCIS codes: (300.0300) Spectroscopy (300.6530) Spectroscopy, ultrafast

1. Introduction

The ultrafast excited state dynamics of betaine-30 represent a tractable model system to study fundamental charge transfer processes [1-5]. Previous studies by Walker *et al.* [1] proposed that the high frequency vibrational modes in the molecule serve an important role in mediating the reverse charge transfer process.

Two-dimensional electronic-vibrational spectroscopy (2DEV) is emerging as a useful technique to investigate the correlation between electronic and nuclear motion on photoexcited states [6-10]. In this study we have investigated the photoinduced ultrafast dynamics of betaine-30 in methanol-d₄ using 2DEV spectroscopy, allowing us to elucidate the vibrations active in the back charge-transfer reaction.

2. Experimental Methods

The details of the 2DEV spectroscopy experiment have been described elsewhere [6-10]. Briefly, a commercial 1 kHz regenerative amplifier pumped a visible non-collinear optical parametric amplifier (NOPA) and a near-IR optical parametric amplifier (OPA). The output of the NOPA (centered at 580nm, 50nm FWHM) was compressed to 20fs using an acousto-optic programmable dispersive filter (AOPDF, Dazzler, Fastlite). The AOPDF was also used to generate the pump pulse pair (k_1 and k_2), and control the relative phase and time delay (t_1). The mid-IR probe pulse (k_3 , 7400nm) was generated by difference frequency generation of the signal and idler outputs of the near-IR OPA. The time delay between the visible pump pair and the IR probe pulse (t_2) was controlled by a mechanical delay stage, and the two beams were focused into the sample in a pump-probe geometry. After passing through the sample, the IR probe pulse was imaged onto a 64-channel HgCdTe IR detector. A small portion of the mid-IR output was used as a reference to normalize fluctuations in the IR light intensity. A 4×1×1 phase cycling scheme was used to retrieve the ω_1 - ω_3 correlation 2DEV spectra at each specific t_2 waiting time. The betaine-30 sample was dissolved in methanol-d₄ and circulated in a demountable CaF₂ flow cell with an optical path length of 250μm. Samples were continuously flowed throughout experiments to mitigate photo-bleaching.

3. Results and Discussion

Figure 1(a) shows the visible pump, mid-IR probe transient spectra of betaine-30 in methanol-d₄. The positive feature at 1330 cm⁻¹ corresponds to the bleach of a ground electronic state vibration and the two main negative signals at 1350 and 1370 cm⁻¹ can be attributed to vibrational transitions on the excited electronic states. (TD-)DFT calculations using the B3LYP functional and 6-31G** basis set with a polarized continuum solvent model were performed to calculate the S₀ and S₁ minimum energy structures of betaine-30. The optimized S₀ and S₁ geometries of betaine-30 are displayed in figure 1(b). The main vibrational bands in the pump-probe spectra were assigned

Figure 1. (a) Vis-IR pump probe spectra of betaine-30 in methanol-d₄ (b) Calculated optimized S₀ and S₁ geometries of betaine-30 (c) 2DEV spectra of betaine-30 in methanol-d₄ for the three displayed waiting times. (d) Time trace of peak intensity, central vibrational and excitation frequencies of 1330, 1350, 1370 cm⁻¹ features extracted from 2DEV spectra

using (TD-) DFT vibrational normal mode calculations. The S₀ 1330 cm⁻¹ feature is assigned to a stretching mode along the C–N axis between phenolate and pyridinium rings. The 1350 and 1370 cm⁻¹ bands correspond to two different phenolate ring breathing modes coupled to the peripheral benzene rings.

The lifetime of the different vibrations varies between 0.1–2 ps for rapid time scale and 4–8 ps for longer time scale [2]. These correspond to the time scale of the intramolecular charge transfer and back charge transfer, respectively [1–3, 5], indicating that these vibrational modes do indeed couple with the back charge transfer process as previously suggested [1].

Figure 1(c) shows 2DEV spectra of betaine-30 in methanol-d₄ for t₂ = 0, 1 and 5 ps. The major features in the 2DEV spectra correspond to the bands found in the transient IR absorption spectra. Tracking the peak position of each

vibrational mode in the 2DEV spectra, we extracted the dynamics of three parameters: $\Delta T/T$ intensity, IR and VIS central frequencies. Figure 1 (d) displays the time traces of these three parameters for each of the vibrational modes. The band at 1330cm^{-1} exhibits a slight red shift (1333cm^{-1} at 0ps, 1331cm^{-1} at 0.5ps, 1329cm^{-1} at 10ps) of the vibrational frequency with increasing t_2 , while keeping the same VIS center frequency. The apparent shift in the IR frequency can be explained by the overlap between ground state bleach signal and a very weak excited state absorption signal coming from a slightly different vibrational frequency (1333cm^{-1} in the S_0 state and 1335cm^{-1} in the S_1 state from TDDFT calculation). This type of structure has previously been observed in transient IR absorption [11]. This red shift provides information concerning the change of the vibrational frequency in the S_1 state. The 1350cm^{-1} mode shows a slow red-shift after 5ps, from 1348 to 1342cm^{-1} . The 1370cm^{-1} mode shows blue-shift within 0.5ps from 1366cm^{-1} to 1368cm^{-1} . The 1350cm^{-1} and 1370cm^{-1} modes show blue-shifts in the VIS center frequency. The 1350cm^{-1} mode is initially at 17136cm^{-1} and relaxes to 17265cm^{-1} and the 1370cm^{-1} mode relaxes from 17116cm^{-1} to 17782cm^{-1} . These apparent blue-shifts could be explained by inhomogeneity in the relaxation dynamics with the red side of the spectral band relaxing more quickly than the blue side.

The shifts in vibrational frequencies allow us to follow the structural evolution of betaine-30 molecules from the vertical Franck-Condon region to the bottom of the S_1 potential. A recent femtosecond stimulated Raman spectroscopy study observed similar time dependent shifts in vibrational frequencies [5]. The correlated spectral shifts along the electronic excitation axis could provide information about the proximity of different molecular conformations to the surface crossing between the S_1 and S_0 surfaces.

4. Conclusions

We have observed coupled electronic-nuclear motion of betaine-30 molecules in methanol- d_4 solution, using 2DEV spectroscopy. The simultaneous frequency dependence of electronic excitation and vibrational detection tells us the coupled electronic-nuclear motion more drastically than previous studies [1-5]. These spectra reveal a simultaneous red-shifting of the excited vibrational frequencies on a similar timescale to the blue-shift observed along the electronic excitation axis. These spectral dynamics can be understood as being related to the structural relaxation from Franck-Condon region to the minimum of potential energy surface in the S_1 state, and to the back charge transfer process that returns the molecule to the ground state.

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