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### Authors

Teramoto, Takahiro  
Lewis, Nicholas H  
Oliver, Thomas  
et al.

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

Takahiro Teramoto<sup>1</sup>, Nicholas H.C. Lewis<sup>2,3,4</sup>, Thomas A.A. Oliver<sup>5</sup>,  
Akihito Ishizaki<sup>6</sup>, and Graham R. Fleming<sup>2,3,4</sup>

<sup>1</sup>College of Science & Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga, 525-8577, JAPAN

<sup>2</sup>Department of Chemistry, University of California, Berkeley, CA 94720, USA

<sup>3</sup>Molecular Biophysics and Integrated Bioimaging Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

<sup>4</sup>Kavli Energy Nanoscience Institute at Berkeley, Berkeley, California 94720, USA

<sup>5</sup>School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

<sup>6</sup>Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki, 444-8585, JAPAN

tteramo@fc.ritsume.ac.jp

**Abstract:** Two-dimensional electronic-vibrational spectroscopy was used to investigate the ultrafast photoinduced dynamics of betaine-30 in methanol-d<sub>4</sub> solution. Our study reveals three vibrational modes (1330, 1350 and 1370 cm<sup>-1</sup>) 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-d<sub>4</sub> 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  $4 \times 1 \times 1$  phase cycling scheme was used to retrieve the  $\omega_1$ - $\omega_3$  correlation 2DEV spectra at each specific  $t_2$  waiting time. The betaine-30 sample was dissolved in methanol-d<sub>4</sub> and circulated in a demountable CaF<sub>2</sub> flow cell with an optical path length of 250 $\mu$ m. 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-d<sub>4</sub>. The positive feature at 1330 cm<sup>-1</sup> corresponds to the bleach of a ground electronic state vibration and the two main negative signals at 1350 and 1370 cm<sup>-1</sup> 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 S<sub>0</sub> and S<sub>1</sub> minimum energy structures of betaine-30. The optimized S<sub>0</sub> and S<sub>1</sub> geometries of betaine-30 are displayed in figure 1(b). The main vibrational bands in the pump-probe spectra were assigned

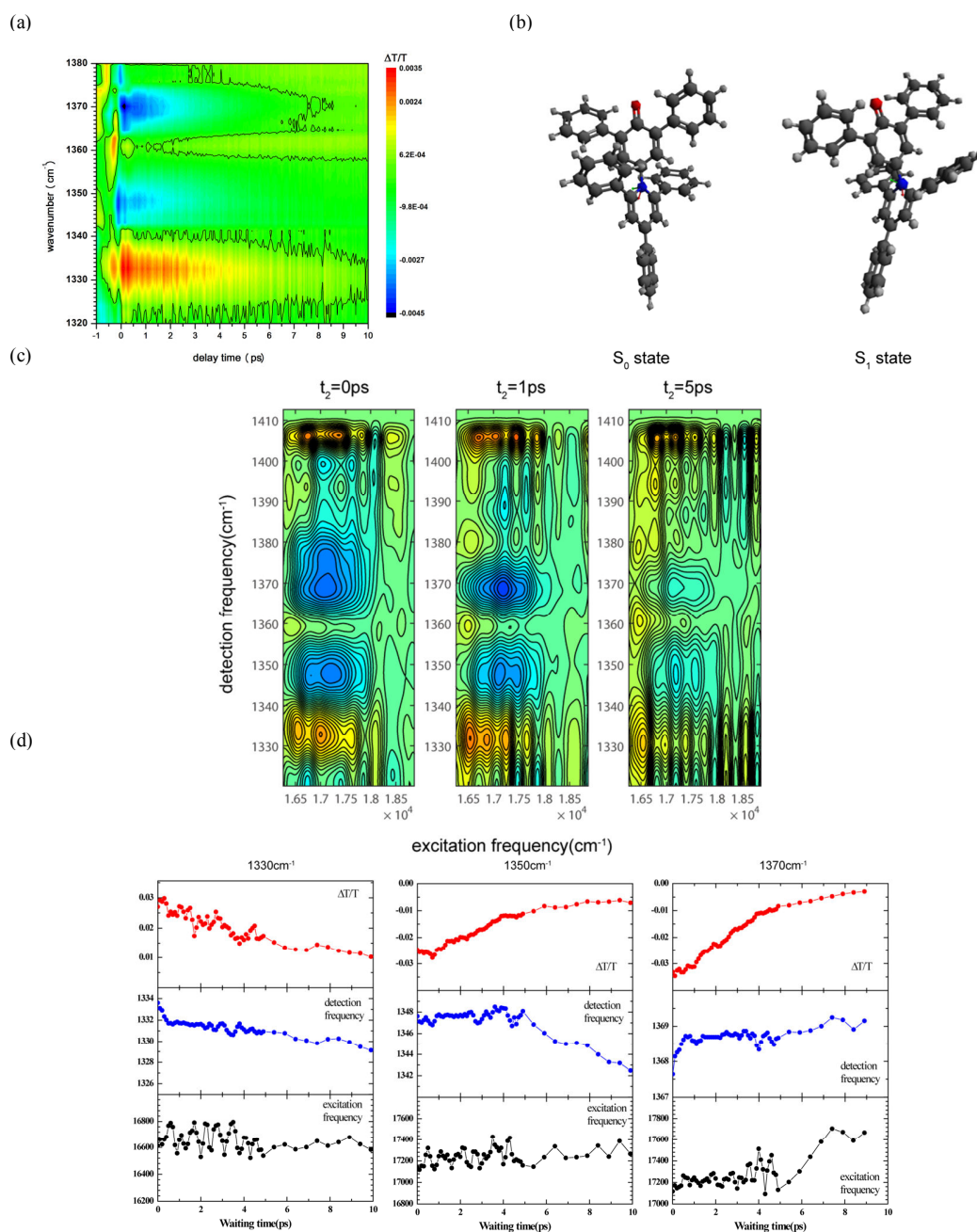


Figure 1. (a) Vis-IR pump probe spectra of betaine-30 in methanol- $d_4$  (b) Calculated optimized  $S_0$  and  $S_1$  geometries of betaine-30 (c) 2DEV spectra of betaine-30 in methanol- $d_4$  for the three displayed waiting times. (d) Time trace of peak intensity, central vibrational and excitation frequencies of 1330, 1350, 1370 $\text{cm}^{-1}$  features extracted from 2DEV spectra

using (TD-) DFT vibrational normal mode calculations. The  $S_0$  1330 $\text{cm}^{-1}$  feature is assigned to a stretching mode along the C–N axis between phenolate and pyridinium rings. The 1350 and 1370 $\text{cm}^{-1}$  bands correspond to two different phenolate ring breathing modes coupled to the peripheral benzene rings.

The lifetime of the different vibrations varies between 0.1-2ps for rapid time scale and 4-8ps 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- $d_4$  for  $t_2 = 0, 1$  and 5ps. 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  $1330\text{cm}^{-1}$  exhibits a slight red shift ( $1333\text{cm}^{-1}$  at 0ps,  $1331\text{cm}^{-1}$  at 0.5ps,  $1329\text{cm}^{-1}$  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 ( $1333\text{cm}^{-1}$  in the  $S_0$  state and  $1335\text{cm}^{-1}$  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  $1350\text{cm}^{-1}$  mode shows a slow red-shift after 5ps, from  $1348$  to  $1342\text{cm}^{-1}$ . The  $1370\text{cm}^{-1}$  mode shows blue-shift within 0.5ps from  $1366\text{cm}^{-1}$  to  $1368\text{cm}^{-1}$ . The  $1350\text{cm}^{-1}$  and  $1370\text{cm}^{-1}$  modes show blue-shifts in the VIS center frequency. The  $1350\text{cm}^{-1}$  mode is initially at  $17136\text{cm}^{-1}$  and relaxes to  $17265\text{cm}^{-1}$  and the  $1370\text{cm}^{-1}$  mode relaxes from  $17116\text{cm}^{-1}$  to  $17782\text{cm}^{-1}$ . 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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