

Coherent Wavepacket Motion in Ultrafast Intermolecular Electron Transfer in Electron-Donating Solvent

Yusuke Yoneda¹, Shohei Nambu¹, Eisuke Takeuchi¹, Yutaka Nagasawa¹⁻³, Hiroshi Miyasaka^{1,2}

¹Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama Toyonaka 560-8531 Japan

²Center for Quantum Science and Technology under Extreme Conditions, Osaka University, Japan

³PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012 Japan

author e-mail address: yoneda@laser.chem.es.osaka-u.ac.jp

Abstract: Coherent wavepacket motion in an ultrafast electron transfer (ET) system consisting of electron accepting solute, 5,12-bis(phenylethynyl)-naphthacene and donating solvent, N,N-dimethylaniline was investigated by means of femtosecond transient absorption spectroscopy and excitation wavelength dependence was investigated.

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

1. Introduction

Photoinduced electron transfer (ET) is one of the most important fundamental chemical processes and its relation with the solvation dynamics has been studied extensively by time-resolved spectroscopy[1]. In polar solvent, solvation is the main driving force because it is capable of stabilizing the produced charge or electric dipole moment. While intramolecular nuclear reorganization is also considered important for ultrafast ET, its understanding is still insufficient and further investigation is necessary. In the Marcus inverted region and near the top of the bell-shaped energy gap dependence of ET, it becomes possible for the reactant to access the intramolecular vibrational levels of the product state and ultrafast ET can manifest without much solvation[2]. Higher vibrational levels in the excited state of a reactant are also accessible by photoexcitation with excess energy. It could be possible to accelerate the reaction by selecting particular vibrational level with the strongest electronic coupling with the product state.

By employing femtosecond ultrafast spectroscopies that can induce and monitor coherent intramolecular wavepacket motions, dynamical aspects of the molecular vibrations in ET systems can be investigated. We have monitored wavepacket motions in a photoinduced ultrafast ET system consisting of electron accepting solute, 5,12-bis(phenylethynyl)-naphthacene (Naph) and donating solvent, N,N-dimethylaniline (DMA) by means of femtosecond white-light supercontinuum transient absorption spectroscopy. The absorption spectrum of Naph exhibits clear vibrational structure as can be seen from Fig. 1a, thus selective photoexcitation to a particular vibrational level is possible for this molecule.

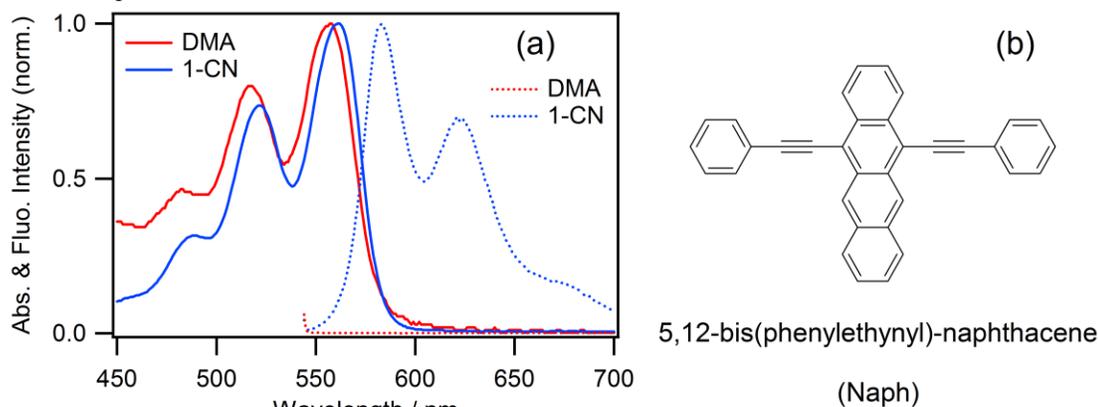


Fig. 1. (a) Absorption (red and blue solid curves) and fluorescence spectra (red and blue dotted curves) of bis(phenylethynyl)-naphthacene (Naph) in N,N-dimethylaniline (DMA) and in 1-chloronaphthalene (1-CN), respectively. (b) Molecular structure of Naph.

2. Experimental methods

The laser system used in this work has been described in detail previously[3] although the laser system was replaced by a pair of non-collinear optical parametric amplifiers (TOPAS-White, Light Conversion) pumped by regenerative amplified Ti: sapphire laser (Solstice, Spectra Physics). The pulse centered at a wavelength of ca. 560 nm generated from one of the TOPAS-White was used as the pump pulse. White-light supercontinuum was generated from a 1 mm thick CaF plate by focusing the beam centered at ca. 1000 nm generated from the other TOPAS-White. The

concentration of Naph was adjusted to obtain absorbance of ca. 1.0 at ca. 560 nm in a rotating cell with a thickness of 0.1 mm. The pulse duration of the pump beam was measured by self-diffraction in a sapphire plate and fwhm was optimized to be 20-25 fs at the sample position by a pair of fused silica Brewster prisms. The signal and the reference pulses were detected with multichannel diode array systems and sent to a personal computer for further analysis. Spectra were calibrated numerically for group velocity dispersion based on an optical Kerr measurement between the pump pulse and the white-light continuum.

3. Results and discussion

Fig. 1a shows absorption and emission spectra of Naph in DMA and also in 1-chloronaphthalene (1-CN) which is an inert solvent with polarity similar to that of DMA and often used as a reference solution for DMA. Naph is a sufficient fluorophore that strongly fluoresce in 1-CN, although emission in DMA is unobservable due to the solvent→solute ET. Although femtosecond TA spectrum was measured with white-light supercontinuum that covers the entire visible range, only those in the range of 520-660 nm with characteristic features are shown in Fig. 2.

The strong negative band at 560-580 nm (Fig. 2a) is a mixture of ground state bleach and stimulated emission of Naph in 1-CN and the oscillation with frequency of ca. 307 cm^{-1} observed in this band can be wavepacket motion in either ground or excited state. Time dependence of the second vibrational structure at 620 nm in the stimulated emission is shown in Fig. 2b which is free of the ground state bleach. Thus, the oscillation with frequency of 304 cm^{-1} in this band is safely assigned to the excited state wavepacket. The mirror symmetry between absorption and emission spectra (Fig. 1) indicates similarity of the molecular structure in the ground and excited states, thus similar vibrational frequencies are also expected. The band shows a slight red-shift in the subpicosecond range which could be due to an ultrafast solvation but not to structural relaxation, because oscillation persists longer than the shift.

In DMA, the intensity of the negative band at 560-580 nm rapidly reduces (Fig. 2c) because of the reduction of the stimulated emission by ET. The reduction of the stimulated emission is more dramatic at 620 nm (Fig. 2d) and the vibrational decay time of the oscillation at this wavelength is reduced to ca, 300 fs from 900 fs of that in 1-CN, indicating a subpicosecond ET. Because the vibrational decay and the red-shift of the emission occurs in a similar time scale, the ET may be induced by the ultrafast solvation component which is due to the small angle inertial rotational motion of the adjacent solvent molecules surrounding the solute. The result of excitation wavelength dependence with the wavelength tuned to 520 nm will be also presented at the conference.

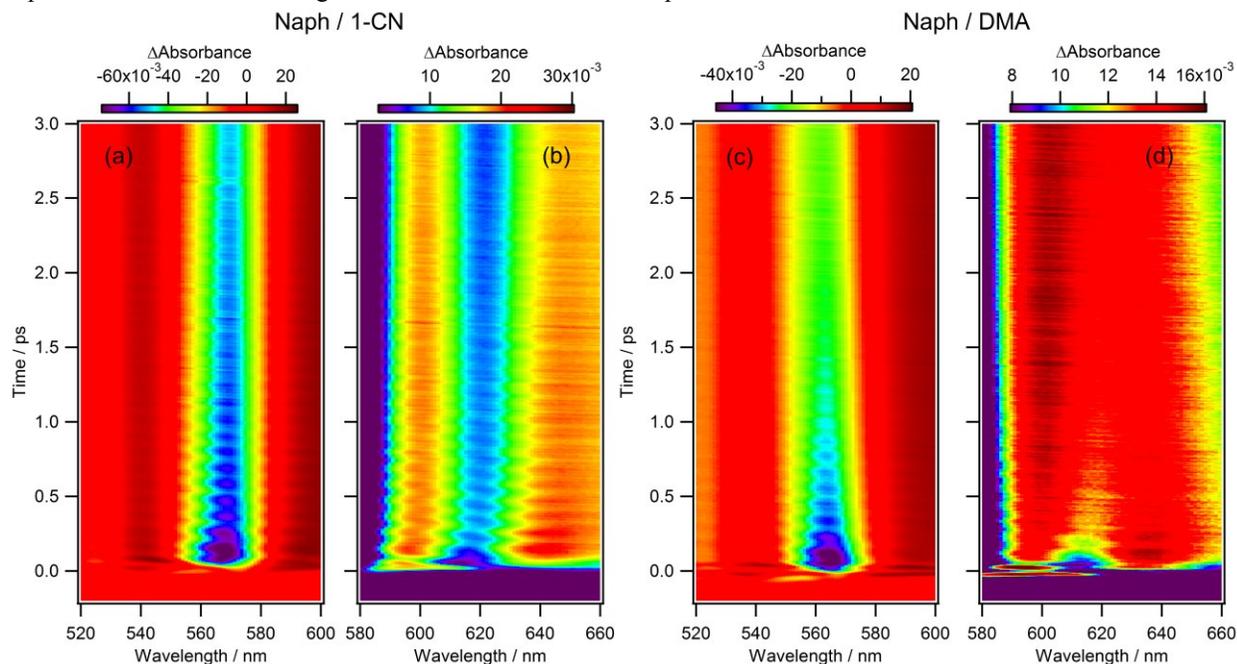


Fig. 2. Transient absorption (TA) spectrum of Naph in 1-CN (a and b) and DMA (c and d). The presented wavelength ranges are 520-600 nm for (a) and (c) and 580-660 nm for (b) and (d).

4. References

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