Vibrational Coherences in Photoinduced Charge Transfer Systems

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We have been studying the relation between nuclear wavepacket motion (coherent molecular vibration) and charge transfer (CT) reaction. Certain molecular motions, such as vibration and torsion, are considered to be coupled to chemical reactions, the simplest example of which is the photodissociation of a diatomic molecule. When sodium iodine, NaI, is photoexcited, stretching vibration is induced in the excited state and the molecule dissociates into atomic Na and I with some probability when the molecule is fully stretched.^[1] CT reaction is also an important fundamental chemical process which is extensively studied on the basis of the theoretical model of Marcus. In biological photosynthesis, solar energy is harvested by the antenna protein complexes, transferred to the reaction center (RC), and primary CT takes place which initiates a long chain of chemical reaction that produces sugar and oxygen from water and carbon dioxide. Recently, it was suggested that efficient and ultrafast CT in the RC is strongly correlated with the degree of electronic coherence, which is maintained by vibrational modes (electronic–vibrational resonance).^[2]

By applying femtosecond laser pulses with durations shorter than half the period of the oscillation, one can coherently generate molecular vibrations. Our strategy is to monitor wavepacket motions associated with ultrafast CT in the inverted region of the bell-shaped energy gap dependence of Marcus theory. In the inverted region, CT can occur not necessarily along the solvation (solvent polarization) coordinate but through higher vibrational levels of the product state (CT state). Thus we expected that wavepacket motions coupled to CT is observable in such systems. We have mainly studied on two systems: (i) CT between electron donating solvent and accepting solute molecules and (ii) intramolecular charge separation (CS) in an ionic liquid (IL).

For system (i), we have carried out femtosecond transient absorption (TA) spectroscopy for a fluorescent dye molecule, 5,12-bis(phenylethynyl)-naphthacene (BPEN), in an electron donating solvent, N,N-dimethyaniline (DMA), and compared to that in an inert solvent, 1-chloronaphthalene (1-CN).^[3] Periodic modulation of the stimulated emission (SE) was observed in both solvents, which is attributed to the wavepacket motion in the excited state. The CT occurred biexponentially in DMA with time constants of 910±40 fs and 7.6±0.3 ps with ratio of 0.37:0.63 and the behaviour of the wavepacket in DMA was different from that in 1-CN. 3D trajectory of differential absorbance at the second maximum of the SE spectra of BPEN plotted against wavenumber and time are shown in Figure 1. In 1-CN, it can be seen

that the wavenumber of the SE maximum is modulated by the wavepacket motion and also the SE intensity becomes stronger at shorter wavelengths, indicating that the radiative rate constant is the largest near the Frank-Condon region. In DMA, the wavenumber of the maximum is still modulated, although the SE intensity is no longer modulated by the wavepacket motion. These results indicates that, in DMA, the excited state potential energy surface of BPEN is modified by the strong coupling with the CT state and the radiative rate constant is no longer dependent on the position of the wavepacket.



Figure 1. 3D trajectory of differential absorbance at the second maximum of the SE spectra of BPEN plotted against wavenumber and time (a) in 1-CN and (b) in DMA.

For system (ii), intramolecular CS of 10-cyano-9,9'-bianthryl (CBA) was compared to that of 9,9'-bianthryl (BA) in IL. Due to the electron-withdrawing cyano group, CS of CBA is expected to be faster than that of BA, because of the larger energy gap and the presolvated nature of the ground state of CBA compared to that of nonpolar BA. Femtosecond TA spectroscopy revealed that the CS reaction of CBA takes place in a time range of ≤ 100 fs while minor increase of the electric dipole moment was observed in the slower time range as a slight reduction of the emission intensity due to the solvation of IL in the CS state.^[3] The radiative rate constant was estimated to be ~36 times larger for the locally excited (LE) state $(6.4 \times 107/s)$ compared to that for the CS state (1.8 × 106/s). For CBA in IL, wavepacket motion with a frequency of 682 cm⁻¹ was observed which lasted longer than the CS reaction. i.e., for a few picoseconds. Interestingly, wavepacket motion in nonpolar solvent, *n*-hexane, had a different frequency of 377 cm⁻¹, indicating that the oscillation observed in the IL is induced in the CS state. Because the emission intensity is significantly weaker in the CS state compared to that in the LE state, the wavepacket motion along the reaction coordinate can modulate both the frequency and the intensity of the emission. Details of the experiments will be presented at the conference.

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