Oscillatory Fluorescence Decay of an Electron Donor−Acceptor Complex

Igor V. Rubtsov[†,‡] **and Keitaro Yoshihara***[,†]

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-12, Japan

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We report an oscillatory fluorescence decay of an electron donor−acceptor complex of hexamethylbenzene and tetracyanoethylene in CCl_4 at room temperature. A fast spontaneous fluorescence decay with a characteristic time of 105 ± 20 fs is observed. An underdamped oscillation of fluorescence is overlapped with this fast decay. The period of the oscillation is 209 ± 4 fs, which corresponds to a frequency of 159 ± 3 cm^{-1} and is tentatively assigned to the intermolecular vibration in the excited state. The damping time of the oscillation is 280 ± 30 fs.

Introduction

The study of the excited-state dynamics of molecules in solution is important for the understanding of the mechanism of photoinduced chemical reactions. We have been studying an ultrafast intermolecular electron transfer (ET) faster than the diffusive solvation dynamics.[1] One of the main questions is the role of molecular motions on ET rate. In other words, how do inter- and intramolecular vibrational motions of reagents modulate the reaction rate, and what kind of vibrational modes are most important for the reaction?

With improvements in femtosecond lasers, low-frequency vibrations up to several hundred wavenumbers could be excited coherently. Observation of this coherence gives direct information about roles of these vibrations in photophysical processes. Recently vibrational quantum beats in photodynamic processes have been observed rather commonly.[2−13] In condensed media, the coherent vibrations in the ground electronic state were observed by the time-resolved coherent anti-Stokes Raman technique[3] and pump−probe method.[4−9] The coherent motion in the excited state was observed in the bacterial photosynthetic reaction center.[6] Recently, a wave packet motion in a nitric oxide complex of myoglobin was observed.[7] We know only a few examples of the vibrational oscillation observed in spontaneous emission. These are oscillations in oxazine dye molecules,[10] in sodium dimer molecules,[11] in light-harvesting antenna of purple bacteria mutants,[12] and in the reaction center of purple bacteria.[13]

In this paper we present results of the investigation of an electron donor−acceptor (EDA) complex of hexamethylbenzene (HMB) and tetracyanoethylene (TCNE) in CCl_4. We report the first time-resolved fluorescence measurements of an EDA complex at an ultrafast time scale. Oscillatory behavior in spontaneous fluorescence decay is clearly observed. The relaxation of high-frequency vibrational modes and back ET are also considered.

The systematic studies of EDA complexes were started more than 50 years ago by Mulliken.[14] A new absorption band appears when two molecules form a complex and is called a charge transfer (CT) band. The optical transition to the CT state causes a charge separation. The heat of formation of the HMB−TCNE complex in the ground state is about 6.3 kcal mol^{-1}.[15] It gives a very broad absorption band with the maximum at ~530 nm and an extinction coefficient of ~4600 cm^{-1} M^{-1} in CCl_4.[15,16] This CT band is far from absorption band of each component molecule, so one can selectively excite only the CT band. By the resonance Raman technique, Myers and co-workers have measured all high-frequency vibrations (greater than ~80 cm^{-1}) which are coupled with the optical transition.[15,17] They tentatively assigned the lowest vibrational band at 167 cm^{-1} to the intermolecular vibration in the EDA complex in the ground state.[18] They measured the steady-state fluorescence spectrum of this complex. The peak-to-peak separation between absorption (535 nm) and fluorescence (910 nm) maxima in CCl_4 is about 7700 cm^{-1}. The lifetime of the CT state of this complex was measured to be about 10 ps by the pump−probe transient absorption technique, and this gives a rate of electron back transfer.[8] In this work we present the first time-resolved fluorescence measurements of an EDA complex at an ultrafast time scale.

Experimental Section

In order to measure an ultrafast fluorescence decay we used a femtosecond up-conversion setup as described elsewhere in detail.[19] Briefly, the second harmonic of a chromium-forsterite femtosecond laser (pulse width of 40 fs at 635 nm) was used for excitation of the complex. The collected fluorescence was focused onto an up-conversion crystal (β-barium borate) and mixed with the fundamental of the laser (1270 nm) pulse, which served as a gate pulse. The light at the mixed frequency was collected through a monochromator and measured with a photon-counting photomultiplier. By changing the delay between excitation pulse and gate pulse, the time profile of fluorescence intensity was measured. The width of the cross-correlation function was 80 fs (fwhm), which corresponded to the time resolution of about 30 fs. The polarization of fluorescence was parallel to the polarization of excitation light. The experiment was made at 23 °C.

The mixture of HMB ~5×10^{-2} M, TCNE ~6×10^{-3} M gives a concentration of the 1 to 1 complex of ~4×10^{-3} M. The concentration of 1 to 2 complex (TCNE-HMB_2) was estimated by using the equilibrium constants $K_1 = 160$ M^{-1} and $K_2 = 7.3$ M^{-1} [16,20,21] and was around 25% in our experiments.

Results and Discussion

We excited the complex at the "red" tail of the CT band at 635 nm, but the excess vibrational energy above the 0−0 transition is rather large, namely ~1850 cm^{-1}. We measured the fluorescence decays at different wavelengths at 746, 777, 811, and 895 nm, which were in the bluer slope to the center

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[†] Present address: Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-12, Japan.

[‡] Permanent address: Department of Ultrafast Processes, Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russian Federation.

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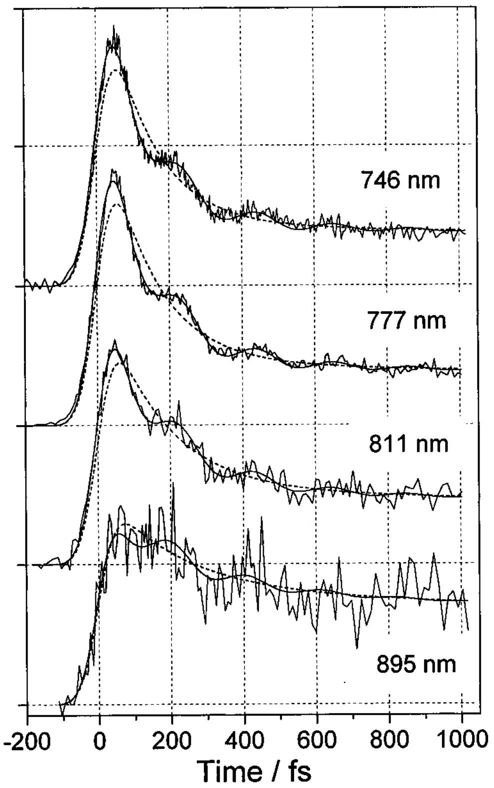

Figure 1. Fluorescence decays observed at four wavelengths: 746, 777, 811, and 895 nm (fluorescence intensity in arbitrary units). The best fit of convolution of *f(t)* (eq 1) with a cross-correlation function is shown. The dashed line without oscillations is the convolution with cross-correlation of *f(t)* where $a_3 = 0$ (without sinusoidal part).

of the static fluorescence spectrum. The fluorescence dynamics for four wavelengths are shown in Figure 1. The decays are approximated by two exponentials with very different characteristic times. The long one is on the picosecond time scale (~10 ps) and is in good agreement with the value in the previous study.[8] The fast component is about 100 fs and was observed for the first time. In addition clear underdamped oscillations in the fluorescence decay were observed for all wavelengths studied.

To separate the oscillatory part we treated our data with a biexponential decay superimposed with a single oscillation and an exponential damping.

$$f(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + a_3 \sin(\omega t + \varphi) \exp(-t/\tau_3) \quad (1)$$

The best fit of *f(t)* convoluted with an instrumental response function is shown in Figure 1. The convolution of a biexponential function without oscillations is also shown. The oscillatory part is emphasized in Figure 2. The period of observed oscillations of 209 ± 4 fs corresponds to a frequency of 159 ± 3 cm^{-1}. These are the same for all measured wavelengths with an accuracy better than 3%, so we used the same frequency for fitting all data. The damping time seems also not to be dependent on the observed wavelength (with an accuracy of 15%), and again we use the same value for all experiments. Only three parameters are wavelength dependent, *i.e.*, the contribution and characteristic time of the fast exponential component and the phase of oscillation.

Let us consider the fast exponential component. A fast decay at the blue edge of the fluorescence spectrum and a fast rise at the red part are often observed for the dynamic Stokes shift due to solvation.[22] In our case the polarity of the solvent CCl_4 is very small ($\epsilon = 2.3$). The solvation dynamics of CCl_4 probably could not explain a large amplitude of the effect. Another candidate is a vibrational relaxation in the excited state, which is usually on the time scale of hundreds of femtosecond.[9,23] Because of a relatively large vibrational excess energy (~1800 cm^{-1}) we could expect a large spectral diffusion. The characteristic time of the vibrational relaxation was estimated as a decay time at a blue part of the fluorescence spectrum. An extrapolation to ~710 nm gives a value of 105 ± 20 fs. More exact value can be obtained from the time dependence of fluorescence spectrum, namely, the spectral shift correlation function.[22]

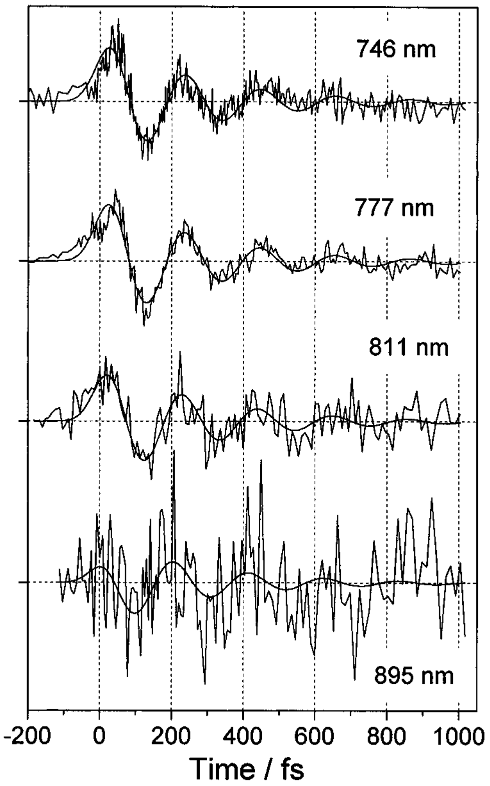

Figure 2. Difference between experimental data and fit with *f(t)* where $a_3 = 0$. The smooth line is the difference between the best fit with *f(t)* and the best fit with *f(t)* where $a_3 = 0$.

An underdamped oscillation is observed at all measured wavelengths. The amplitude of the oscillating component (a_3) is about 20%. The damping time is similar for all wavelengths measured and equals 280 ± 30 fs. It seems that only the phase of oscillations depends on wavelength.

The equilibrium intermolecular distance in an EDA complex in the excited state is shorter than that in the ground state because of the Coulombic attraction between D^+ and A^-.[14] The CT interaction in the excited state increases the force constant, and a resultant frequency of intermolecular vibrational mode should be higher than that in the ground state. The wave-packet motion changes the optical coupling between the excited and ground states through the Franck−Condon factor. As a result the mean wavelength of fluorescence oscillates with the frequency of wave-packet motion. In a single wavelength experiment the oscillations are observed. The oscillations seem not to be affected by the relaxation processes of the high-frequency intramolecular modes. In other words, this underdamped oscillation could be considered to be weakly coupled or orthogonal to intramolecular vibrations (Figure 3).

In the present experiment we observed two kinds of fast relaxations, namely, the ultrafast decay and low-frequency oscillation of fluorescence. The question is how to assign the underdamped mode. In general it is possible to coherently excite intramolecular and/or intermolecular vibrations. In large mol-

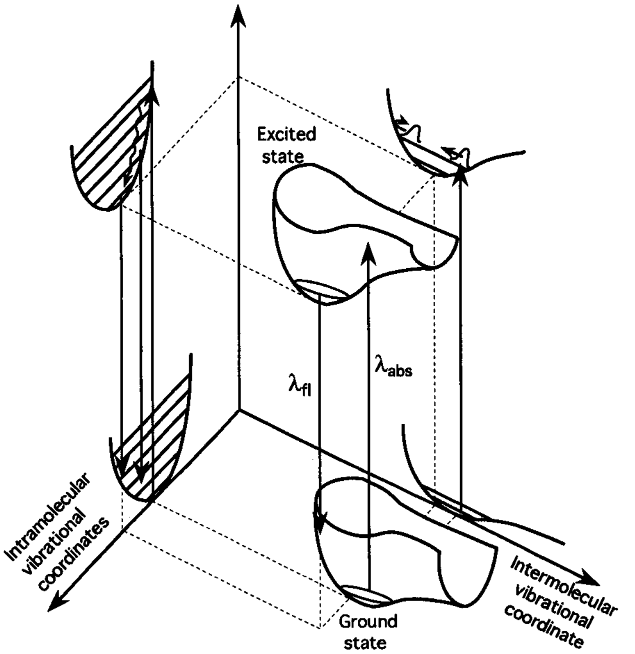

Figure 3. Schematic potential energy diagram. The *X*-axis represents the projection of the multidimensional potential surface to the intermolecular vibrational coordinate; the *Y*-axis represents the projection to the intramolecular vibrational coordinate. The optical transitions (absorption and fluorescence) are represented by vertical arrows in multidimensional space and in each projection.

ecules the anharmonicity of vibrational modes is large and causes a large coupling between different vibrational modes and makes the intramolecular vibrational redistribution (IVR) processes very fast. If the underdamped oscillation were of intramolecular nature, the fast vibrational energy redistribution and relaxation would suppress the coherence in this mode. In this case the damping time should not be longer than the relaxation time of high-frequency vibrations. In the present experiment the damping time is approximately three times longer than the relaxation time of high-frequency vibrational modes. The intermolecular vibrational modes are usually less coupled with intramolecular modes. This allows us to assume that the observed underdamped oscillation corresponds to an intermolecular vibration in the EDA complex.

There is some probability that observed underdamped oscillation is intramolecular vibration that is weakly coupled with other vibrational modes. Even with rapid vibrational energy relaxation and redistribution there could be retention of the vibrational phase of some modes, which was recently shown theoretically.[24] Another possibility is observing a difference-frequency beating between two high-frequency modes.[3]

Our result of the oscillation frequency (159 ± 3 cm^{-1}) is different from the resonance Raman data (165 ± 2 cm^{-1}) of this complex.[15, 17,18, 25−27] The vibrational mode observed in the present experiment corresponds to the excited-state vibration of the complex, whereas the Raman data corresponds to that of the ground state. If our assignment of the observed oscillations to the excited-state intermolecular vibrations is correct, then the ground state frequency is probably smaller[14] than 100 cm^{-1}. In a series of papers[17, 18, 27] it was suggested that a frequency of 165 cm^{-1} observed in resonance Raman experiments could be assigned to scissors-like vibration of TCNE in the ground state,[28] which could enhance its Raman activity for TCNE molecules in the complex.[25]

Dynamics of the pyrene−TCNE complex has been studied by the transient absorption technique.[9] The frequencies of oscillations observed in bleach recovery and stimulated emission were identical within the experimental accuracy (170 ± 9 cm^{-1}). The observed oscillations were assigned to a complicated intermolecular vibration, which has the same frequencies in the ground and excited states of the complex. In our work, the observed frequency definitely corresponds to the excited-state vibrational coherence, since it is from spontaneous fluorescence. The ultrafast decay is mainly due to the intramolecular vibrational relaxation in the excited state. How large the coherent effect is in back electron transfer is still a question. The damping time of the oscillations corresponds probably to dephasing rather than to relaxation. In this case we could not expect strong relation between damping time and back electron transfer rate. Further experiments are underway to make this point clearer.

In conclusion, the ultrafast vibrational relaxation is observed with a characteristic time of 105 ± 20 fs. A clear oscillation is observed on top of this ultrafast fluorescence decay and is tentatively assigned to an intermolecular vibration in the excited state of the complex. The period of 209 fs corresponds to the vibrational frequency of 159 cm^{-1}. The observed intermolecular oscillations in the excited state of the EDA complex opened a route to study directly intermolecular interactions in the liquid phase, particularly various types of relaxation processes such as intermolecular vibrational relaxation, high-frequency intramolecular vibrational relaxation, dephasing of vibrational relaxation, electron transfer reaction, and solvation.

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