Rate Limitation of Photothermal Effect in Solution

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The energy transfer rate from the photoexcited molecule to solvent molecule is investigated in solution phase using the acoustic peak delay method in picosecond time scale. The thermalization time of betaine-30 was strongly enhanced by the hydrogen bonding between the solute and the solvent. On the other hand, the rate is not sensitive to the hydrogen bonding for Malachite Green, but it is found that the rate depends on the concentration of MG. This fact may suggest that the electric interaction is important for the thermalization process of this molecule.

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When molecules in condensed phase are photoexcited, most of the absorbed energy ultimately flows into the thermal mode in many cases. As the consequence, the temperature of the sample increases, thermal expansion takes place, pressure wave is created, and many related phenomena, such as ablation, occurs. These phenomena are called the photothermal effect. The initial stage of this photothermal effect is the energy transfer process from the photoexcited molecules to the matrices. How fast is the electronic energy of photoexcited molecules converted into the thermal energy? Traditional photothermal techniques, such as the thermal grating, thermal lens, photoacoustic, and beam deflection methods, cannot be used to answer this question because of the temporal limitation of these methods. In order to improve the temporal response of the photothermal methods, one of the authors have developed several new techniques: temperature grating,1 temperature lens,2 acoustic peak shift,3,4 molecular heater-molecular thermometer methods.5 Here, we present our recent studies on the initial stage of the thermalization process in solution by using the acoustic peak delay method. We used betaine-30 (B30) and Malachite Green (MG) as the heat source after the photoexcitation. These molecules are known to have very short lived excited states. Monitoring the rate of the thermalization of these molecules in various solvents, we could determine the rate limitation of the photothermal effect in solution. We found that the thermalization rate depends on the intermolecular interaction between the photoexcited molecule and the solvent molecules.

Principle and method

When two laser beams are crossed at one spot within the coherence time, an optical interference pattern is created. The spatial modulated of the refractive index or absorption induced by the interference pattern can be detected as the diffraction of another probe light (transient grating (TG) signal).6 After the photoexcitation under the TG condition, the energy is deposited into the matrix by the nonradiative relaxation, and the medium will expand periodically, which leads the sinusoidally modulated refractive index change. If the thermalization is slow, it will change the shape of the acoustic signal, which becomes apparent as a temporal delay of the signal. By a curve fitting of the acoustic signal, the rate of the temperature increase and the amount of the thermal energy may be extracted as reported for a variety of systems so far.7 However, if the rate is very fast, the difference in the acoustic temporal shape for different thermalization time (τ_{temp}) is very subtle and it is almost impossible to determine the rate with a ps accuracy only from the temporal shape.

Because of the convolution effect of the acoustic signal with the thermalization process, the acoustic oscillation shifts continuously with increasing the lifetime, and naturally the peak of the oscillation shifts with it. Experimentally, to determine the time at the peak is rather easy with a good accuracy and it is expected that we can obtain τ_{temp} with a high time resolution only from the acoustic peak time. Therefore, by monitoring the acoustic peak time, we can determine τ_{temp} within a few ps accuracy. When the acoustic damping is neglected, the acoustic peak delay time (Δτ_{pd}) is almost the same as the thermalization time.7 This is a principle of the acoustic delay method. With increasing the attenuation constant, the peak delay decreases. When there are two heat releasing processes with different lifetimes of τ_f and τ_s (τ_f<τ_s), the temporal profile of the acoustic signal should depend on these time constants as well as the releasing energy from these processes. If we calculate the peak delay as a function of Q_f/Q_{tot} (Q_c: thermal energy from the slower process, Q_{tot}=Q_f+Q_s; total thermal energy), the acoustic peak shifts linearly with Q_f/Q_{tot} from Δτ_{pd} for Q_{tot}=Q_s to Δτ_{pd} for Q_{tot}=Q_f. If there are several thermalization processes, Δτ_{pd} provides the energy weighted average thermalization time.3,4 For example, if there are two thermalization processes with lifetimes of τ_f and τ_s, Δτ_{pd} is given by

\[ Δτ_{pd}=\left(Q_f/(Q_f+Q_s)\right)τ_f+\left(Q_s/(Q_f+Q_s)\right)τ_s \]  

(1)

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Molecular structures of Betaine-30 (left) and malachite green (right)
where $Q_i$ and $Q_s$ are thermal energies associated with the $\tau_i$ and $\tau_s$ processes, respectively.

The experimental setup was reported previously. We measured the first ($\tau_1$) and the second ($\tau_2$) acoustic peaks. The temporal separation between the first and the second peaks ($\Delta t = \tau_2 - \tau_1$) gives an acoustic frequency $\omega = 2\pi / \Delta t$ in that solution as long as $\tau_s$ varies in a fast rate region ($\tau_s < 60$ ps under this experimental condition). Next, $\Delta t_{\omega}$ was calculated by a relation of $\Delta t_{\omega} = \tau_1 - \Delta t / 2$.

**Results and Discussion**

**(a) Acoustic peak delay**

After the photoexcitation of B30 or MG, a weak TG signal generally appears in a fast time scale (0~40 ps range). The fast response signal is due to the population grating (PG), which reflects the population of the excited. In general, the signal can be fitted by a bi-exponential function;

$$I_{ac}(t) = A(t - \tau_1) + C_2 \exp(-t/\tau_s)^2$$

(2)

where $\tau_1$ and $\tau_2$ are lifetimes and $C_i$ ($i=1,2$) is the relative intensity of these components.

The acoustic signal rises gradually after the PG signal (Fig.1). Although the acoustic part could be fitted by the thermodynamical equation presented before, a reliable fit is almost impossible because of so many parameters in the equation. Instead, the peak position was determined by the fitting of only the top of the oscillation with a function of $a(t - \tau_i) + b$, where $a$ and $b$ are constants related with the sensitivity and $\tau_i$ is the time of the first ($i=1$) and the second ($i=2$) acoustic peaks (Fig.2). From $\tau_1$ and $\tau_2$, the acoustic frequency $\omega$ and the peak delay time $\Delta t_{\omega}$ are calculated.

**(b) Betaine-30**

First, the thermalization of B30 is described. These lifetimes of the PG signal are 2 ps and 20 ps for B30 in methanol. The peak delay $\Delta t_{\omega}$ is 8.4 ps in methanol. The observed $\Delta t_{\omega}$ should be interpreted by the energetic dynamics ($S_1 \rightarrow S_0$) as well as the lifetime of the $S_1$ state. In order to evaluate $\tau_{\text{comp}}$, the effect of the finite lifetime of the $S_1$ state should be corrected from $\Delta t_{\omega}$. The energy averaged thermalization time in methanol was determined to be 6.1 ps.

It is interesting to note that the PG signal as well as the transient absorption signals indicate the presence of the slower dynamics. For example, the PG signal in methanol shows $\tau_s = 20$ ps dynamics, which is assigned to the vibrational cooling process. If we assume that the whole energy is transferred to solvent with 20 ps rate, the observed peak delay should be 20 ps, which is quite longer than observed one (6.1 ps). Hence we conclude that a faster thermalization process should exist besides the 20 ps process. For simplicity, if we assume that the rate of the faster energy transfer process to solvent is less than our time resolution (< 3 ps), the relative energy for each process can be calculated from eq.(1) and $\tau_{\text{comp}}$. For methanol case, the energy coming out from the slower process ($E_{\text{slow}}$) is calculated as $E_{\text{slow}} = h\nu/20 \text{ ps} = 9500 \text{ cm}^{-1}$. Hence, about one third of the photon energy is transferred to solvent slowly (20 ps).

Plotting $\tau_{\text{comp}}$ against $N_{\text{OH}}$ ($10^2$ mole number of OH group/cm$^3$), which is a number of hydroxy group per unit volume, we found that the plot shows surprisingly good correlation between $\tau_{\text{comp}}$ and $N_{\text{OH}}$. This fact may indicate that the hydrogen bonding between the solvents and/or between solute-solvent enhances the rate of the temperature increase after the nonradiative transition.

The hydrogen bonding may affect the thermalization process in two ways; increasing the intermolecular interaction between the solute and solvent and enhancing the density of low frequency modes. The strong intermolecular interaction could be an efficient pathway of the solute energy to the solvent. The low frequency modes will effectively couple with the translational mode of the solvent and the coupling will enhance the thermalization rate. Here, in this report, we have shown that the rate of the temperature rise; i.e., vibrational relaxation of many vibrational modes, is enhanced by the hydrogen bonding.

**(c) Malachite green**

A similar acoustic signal was observed after the photoexcitation of MG. The excited state dynamics of MG has been extensively studied by the transient absorption and photobleach techniques. The lifetime of the $S_1$ state depends on the viscosity of the solvent and is in a range of 0.3 ps-0.8 ps in the solvents we examined. Hence the observed peak delay time should be equal to $\tau_{\text{comp}}$ within the experimental uncertainty. This acoustic peak delay was measured in several solvents at various concentrations. Interestingly, we found that $\tau_{\text{comp}}$ depends on the concentration of MG (Fig.3). The rate increases with the concentration of MG in all solvents we examined. For example, $\Delta t_{\omega}$ is 7.9 ps at 0.75 mM in methanol, but it becomes 2.7 ps at 8.1 mM. $\Delta t_{\omega}$ at low concentration region are listed in Table. In contrast with B30, this values are not sensitive to solvents.

The rate of the energy transfer to the matrix depends on the
solute-matrix interaction as shown above. Therefore, if the photoexcited MG collides with other MG during the cooling time, the energy could be efficiently transferred to the matrix through another MG. In this case, the thermalization rate may be expected to depend on the concentration. However, the average distance between MG is calculated to be around 5.5 nm even at 10 mM and it will take 15 ns between each collision by the translational diffusion. This period is sufficiently longer than the observed $\Delta t_{pd}$. Hence it is unlikely that collision of two MG molecules changes the thermalization rate. The most simple explanation of the concentration dependence is the aggregate formation of MG at the high concentrations. However, we could not observe absorption spectrum change with increasing the concentration. Hence the aggregate formation is less plausible. The origin of the concentration dependence is not clear at present. However, considering the ionic character of MG, we speculate that the counter ion (oxalic ion) tends to gather around MG at high concentrations and the presence affects the energy relaxation of MG. In order to investigate this possibility, we measured $\Delta t_{pd}$ for samples with additional oxalic acid in the solution. When oxalic acid was added to the solution (28 mM), $\Delta t_{pd}$ decreases to 2.4 ps. This salt effect may support the above suggestion: the thermalization rate is enhanced by the electric interaction between the photoexcited MG and the counter ion.

**Table**  The thermalization time of MG in various solvents at low concentration region.

<table>
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<tr>
<th>solvent</th>
<th>methanol</th>
<th>ethanol</th>
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<th>acetone</th>
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<td>7.2</td>
<td>5.4</td>
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**References**