

## High Temporally and Spatially Resolved Thermal Energy Detection after Nonradiative Transition in Solution Using a Molecular Heater–Molecular Thermometer Integrated System

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Received February 3, 1999

Revised Manuscript Received March 19, 1999

After photoexcitation of a molecule, the energy of the photoexcited state is dissipated into matrix by nonradiative transition as thermal energy. This energy conversion process is the most commonly observed phenomenon after photoexcitation in the condensed phase and is closely related to the vibrational relaxation process, which has been studied extensively during the last two decades.<sup>1</sup> It may be reasonably speculated that the energy launched from the solute initially heats only several solvents around the solute to make a local hot spot and propagates in the matrix, and then the hot spot area is expanded to eventually achieve a uniform temperature distribution in the photoilluminated region. After several 10–100 ps from the energy release, the energy propagation should be described by the macroscopic thermal diffusion equation, which can be detected by many photothermal techniques.<sup>2</sup> On the contrary, the temporal and spatial region between the energy release from the excited molecule and the macroscopic heat transport regime is unexplored and will be a next interesting target in the chemistry and physics of intermolecular energy conversion processes. Recently, Terazima and co-workers have developed new photothermal techniques and have observed ultrafast temperature rise (within a few ps) after the nonradiative transition.<sup>3–8</sup> The temperature within a few ps should be interpreted by a localized hot spot picture. However, since these techniques and other spectroscopic techniques used thus far do not have any spatial resolution, the heat transport process has been less clear. For extending this research, we have constructed a new molecular heater–molecular thermometer integrated system that generates thermal energy very fast, and we detect it with high temporal and spatial resolution. The heat flow at several distances from the solute can be monitored by changing the length of the bridge between molecular heater and thermometer. A preliminary attempt to achieve the high temporally and spatially resolved thermal energy study is reported.

For a heater molecule, it is preferable that the photoexcited state relax quickly to generate large excess energy instantaneously in the lower state. We chose azulene for the heater because the lifetime of the  $S_1$  state is as short as 1 ps<sup>9</sup> and the vibrational relaxation in the ground state has been extensively studied

already.<sup>10–20</sup> The thermalization process in the liquid phase was measured by monitoring the hot band of the  $S_0 \rightarrow S_1$  absorption edge<sup>14,15</sup> and  $S_0 \rightarrow S_3$  absorption edge.<sup>16</sup> For example, the vibrational cooling of azulene occurs with 11–13 ps in *n*-alkanes, 9 ps in ethanol, 3.3 ps in 3:1 mixture of water and methanol, and 25.9 ps in  $C_2Cl_3F_3$ .<sup>16</sup> We can compare the temporal change of the solvent temperature with that of azulene itself, and will be able to obtain a deeper understanding of the energy-releasing processes.

The temperature change at a specific spatial point after the thermal energy launched from azulene was detected by another probe molecule; a molecular thermometer. This molecule should possess several properties to be used as a thermometer in this system. (1) The absorption band should not overlap with that of azulene. (2) The energy of the  $S_1$  state of the thermometer should be higher than that of azulene to prevent direct electronic energy transfer from azulene to thermometer. (3) To be a thermometer, the absorption spectrum should be sensitive to (local) temperature. One of molecules which satisfies these demands is coumarin 151 (C151).

The center-to-center distance between azulene and the C151 moiety of this molecular integrated system (Az–CH<sub>2</sub>–C151) is estimated to be 0.65 nm from the optimized geometry calculated by a semiempirical molecular orbital method.<sup>21</sup> Hence, the temperature of the thermometer (C151) should be elevated by the temperature of the solvent molecule in the first solvent shell, because the radius of azulene is 0.33 nm<sup>15</sup> and the diameter of ethanol (one of solvents) is 0.43 nm.<sup>22</sup> The “temperature” of the thermometer was measured via the change of the hot band absorption of C151.

Figure 1 shows the absorption spectrum of Az–CH<sub>2</sub>–C151<sup>23</sup> in ethanol, which is almost identical to the sum of the absorption spectra of azulene and of C151 except for slight red shifts (~10 nm). Hence, the intermolecular interaction between azulene and C151 in the ground state appears to be weak.

The experimental set up for the transient absorption measurement was reported previously.<sup>24</sup> After the photoexcitation of

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(23) Details of the synthesis will be published elsewhere.<sup>8</sup> Briefly, a mixture of C151, 1-azulenecarboxaldehyde, *p*-toluenesulfonic acid, and toluene was heated to reflux in an oil bath under nitrogen with stirring for 2 days. Produced solid material was washed twice with benzene and dried in vacuo to give Az–CH=C151 (yield 70%). It was dissolved in ethanol, and sodium borohydride was added to the solution. The solution was stirred for 2 days at room temperature under nitrogen. Water was added to the reaction mixture, allowed to stand for ~5 min, and evaporated. The crude product was dissolved in benzene and was chromatographed first on alumina with 1% methanol/benzene (v/v) and then on size-exclusion column with benzene. The first green fraction was collected and evaporated, to yield Az–CH<sub>2</sub>–C151 (yield 22%).

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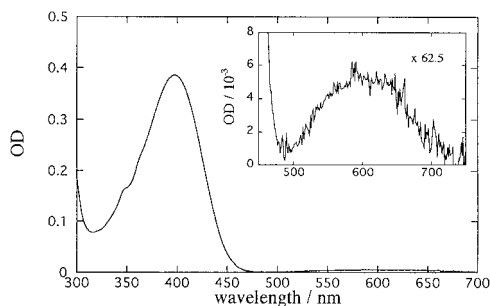
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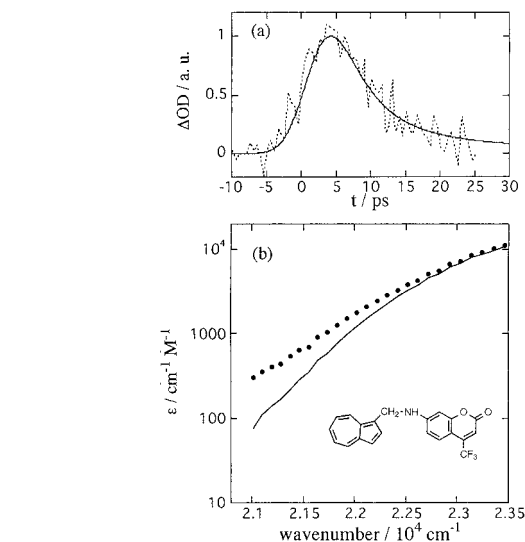


**Figure 1.** The absorption spectra of Az-CH<sub>2</sub>-C151 in ethanol.

azulene, the enhanced transient absorption at the red edge of the C151 band was observed, and the time evolution of the transient absorption signal is shown in Figure 2a. The observed absorption is attributed to the hot band absorption of C151 for the following reasons. First, since we did not observe any signals from a sample which contains only azulene or C151 under the same conditions, they are not due to any absorption from isolated molecules. Second, when we converted the observed OD to the molar extinction coefficient ( $\epsilon$ ) and plotted with the absorption spectrum of C151, the spectrum shows a characteristic feature of the hot band (Figure 2b).

A simple interpretation of this profile is that the rise of the absorption reflects the temperature rise of C151 due to the thermal energy dissipation from azulene. Therefore, the rate of the increase of this signal is determined by the thermalization rate of azulene as well as the heat conduction from azulene to C151 through the solvents. The decay rate must represent the cooling rate of C151 by the heat dissipation process to the outer solvents.

However, the interpretation may not be so simple. The hot band absorption appears because the vibrational levels of the thermometer is thermally excited and it requires certain delay after the heating. The rise part, therefore, should include the thermally vibrational excitation process of the thermometer, too. Taking into account these rates, we calculated the time profile of the transient temperature by using a thermalization model.<sup>7,25</sup> To reproduce the observed transient temperature profile, the energy-transfer rate from azulene to solvent is found to be less than 2 ps. The calculated temperature profile agrees well with the observed one (solid line in Figure 2a). The thermalization time observed here (<2 ps) is much shorter than the vibrational relaxation time of azulene obtained by monitoring the vibrational temperature of azulene itself.<sup>14–16</sup> A similar short thermalization time was observed also in the other solvents, and the time constant



**Figure 2.** (a) The time profile of the transient absorption signal probed at 450 nm. (b) The absorption coefficient of the red edge of C151 moiety. The solid line shows the absorption spectrum at room temperature and the solid circle the absorption coefficient at 4 ps after photoexcitation of azulene moiety.

depends on the solvents (<2 ps in 2-propanol, <5 ps in acetone and <3 ps in benzene). The difference between the thermalization times determined here and those reported previously should be further explored in a forthcoming paper.<sup>8</sup>

Another possibility we should examine is the through-bond vibrational energy transfer from the heater to the thermometer.<sup>26</sup> We think this direct energy transfer possibility is low, based on several reasons. First, if the intermolecular energy transfer can be explained by the through-bond mechanism, the rate constant of the energy transfer strongly depends on the number of intervening  $\sigma$ -bonds. We measured the transient absorption signal of the azulene-C151 combined with three  $\sigma$ -bonds (Az-(CH<sub>2</sub>)<sub>3</sub>-C151), but we did not observe such a delay.<sup>8</sup> (This fact could be explained by a closer distance between azulene and C151 of Az-(CH<sub>2</sub>)<sub>3</sub>-C151 than expected from the stretched structure, which is caused by the flexibility of the propyl chain.) Second, the transient temperature monitored by the thermometer was calculated to be  $\Delta T \approx 66$  K from the hot band analysis.<sup>8</sup> If the energy is directly transferred to the thermometer, the elevation of the temperature should be much higher. Third, the temporal profile of the temperature depends on the solvents. This solvent dependence may not be expected from the direct energy-transfer mechanism. Fourth, the time profile can be reproduced well by the thermalization model as described above.

There are several points we should further take into account for the analysis; the role of the chemical bond between the heater and the thermometer, the role of the molecular configuration of the chromophores, and the solvent effect. These points will be discussed elsewhere.<sup>8</sup>

In summary, the thermalization process of azulene was monitored via the hot band detection of the molecular thermometer which is placed in the vicinity of azulene. The observed thermalization was described well by the energy transfer from the solute to solvent and the thermal diffusion among the outer solvents. The rate was faster than the reported vibrational relaxation rate previously. This is the first attempt to use the molecular heater-molecular thermometer integrated system for investigating the thermalization process from the solvent side.

**Acknowledgment.** The authors thank Dr. Y. Kimura (Kyoto University) for his kind help of the transient absorption measurement. T.O. wishes to thank the Japan Society for the Promotion of Science.

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(25) In this thermalization model, the excess energy of photoexcited azulene is first transferred to several solvent molecules that are effectively coupled to the solute (the directly energy accepting (DEA) solvents). The rate is assumed to be proportional to the intermolecular interaction and the temperature difference between the solute and the solvent. The energy of the solute increases with two steps; S<sub>1</sub>\* → S<sub>1</sub> (S<sub>1</sub>\*: the Franck-Condon state from the ground state) and S<sub>1</sub> → S<sub>0</sub> processes (1 ps). The thermal energy of the DEA solvent diffuses to the outer solvents (which is assumed to be continuous) by the thermal diffusion. The response function of the thermometer is determined by assuming that the thermal activation time from the DEA solvent and the heat-releasing time to the outer solvents are identical. The time profile of the transient temperature is calculated by convoluting the temperature of the DEA solvent with the response function of the thermometer. The thermalization time of azulene and the thermal excitation (or deactivation) time of C151 cannot be independently determined under our signal-to-noise ratio. Hence, only the upper limit of the thermalization time of azulene was obtained.

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