Ultrafast Detection of Temperature Rise after Photoexcitation in Solution

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Photo-calorimetric spectroscopies have been frequently used as powerful tools for elucidating photophysical processes of molecules after photoexcitation. The most notable merit of these methods is the capability of detecting nonradiative transition as well as various energy transfer processes (e.g., electronic-electronic, vibrational-translation, etc.) with very high sensitivity. These methods do not require any luminescent processes or transient absorption. However, when one tries to detect energy transfer processes in a fast time scale with these methods, a relatively low time resolution limits the applicability. Here we will show two attempts to detect the heat evolution in pico- or femto-second time range; the transient grating (TG) and transient lens (TrL) methods.

1. Transient grating (TG)

In the TG experiment, the interference pattern induced by two excitation laser beams are used for the photo excitation of molecules. Photoexcited states are created in the bright region but not in the dark region, and the resultant sinusoidal heat pattern in the sample acts as a grating to diffract a probe beam.[1] If one monitor the diffracted probe beam as a function of delay time between the pump and probe pulses, the time evolution of the heat releasing processes can be detected. We used the second harmonic of a subpico-second dye laser pulse to create the grating. In such a short pulse case, acoustic signal dominates in a fast time scale. Then the fringe spacing of the grating determines the time resolution of the TG signal. For example, the period of the acoustic oscillation can be about 500 ps in benzene (excitation wavelength =320 nm). Heat evolution as fast as 50 ps can be separated from instantaneously respond component by analyzing the first oscillation.

2.Transient lens (TrL)

When the spatial shape of the excitation beam has a Gaussian form, the non-uniform temperature distribution is created in the sample. The temperature change induces the change of the refractive index, and the created Gaussian type distribution of the refractive index acts as a "lens", which focuses or defocuses another probe beam. Traditionally this type of experiment for detection of heat is called the thermal lens method. Until very recently one has not expected to be able to observe this thermal lens signal in a fast time scale, because of the "slow response" character of the signal. This expectation is true as long as the refractive index change is induced by the density change after the heating. However we found that there is another type of signal, which can respond immediately after the heating without accompanying any density change. This component is called the temperature lens.[2] This method will provide a very fast heat detection technique even faster than pico-second time scale.

References

1. M.Terazima and N.Hirota, J.Chem.Phys.,95,6490(1991).
2. M.Terazima, Chem.Phys.Lett.,230,87(1994)., Chem.Phys.,189,793(1994).