Photothermal Dynamics at the Surface of Copper Phthalocyanine Solid Revealed by Time-resolved Regular Reflection Spectroscopy

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Flat surfaces of compressed pellets made of copper phthalocyanine powders were excited by nanosecond laser pulses and their time-resolved extinction coefficients were obtained by using regular reflection spectroscopy independent of Kramers-Kronig transformation. The results showed transient depletion at the peaks of the ground state absorption spectra, which is due to a change in thermal population in vibrational states. The decay of the transient depletion was well described with the temperature dependency of extinction coefficient based on Sulzer-Wieland approximation and one-dimensional thermal diffusion towards the deep parts of the pellet samples.

Laser-chemistry and laser-physics of organic solids like dye crystals and pigments are of growing importance in the field of laser-functional material science. It is, however, difficult to measure a correct transient absorption spectrum of a solid sample having a high absorption coefficient by using conventional laser photolysis technique with transmittance configuration. The high absorption coefficient requires the preparation of a thin sample, and also causes considerable regular reflection at its surface which results in an apparent reduction of transmitted probe light intensity. To overcome this difficulty, we have recently developed time-resolved regular reflection spectroscopy and studied photochemical primary processes of copper phthalocyanine (CuPc) pellets employing Kramers-Kronig transformation.[1-3] Although this transformation has been widely used to obtain an extinction coefficient spectrum from a reflection spectrum, the application of the transformation is based on both the measurement of absolute reflectivity of the surface over a certain spectral range and the assumption that the measured spectral range involves all the necessary information for the transformation. These conditions may not always hold for a sample with the rough surface having a broad spectral band in UV-visible region. In this paper, we report the experimental method to measure transient extinction coefficient without using Kramers-Kronig transformation, and show that a change in extinction coefficient of CuPc solid after nanosecond laser excitation can be ascribed to a populational change in vibrational levels.

The β-form of CuPc was purified as usual.[4,5] The polymorph of the material was confirmed by its X-ray diffraction patterns.[6] Cylindrical pellets of 13 mm diameter and 3 mm thickness with smooth surface were prepared by compressing ground powders of CuPc at a pressure of 6 - 6.4 x 10^3 kg/cm^2. Figure 1 shows the schematic diagram of the time-resolved regular reflection spectroscopy system. A pulsed Xe lamp (Hamamatsu 2188, fwhm 1 μs), a polarizer, and other optical components were aligned on a rotatable arm for illuminating a sample surface with various angles. The sample is so placed at a rotatable stage as to reflect the monitor light to the direction of the entrance slit of a polychromator equipped with multi-channel photodiode array (MCPD, Otsuka Electronics). An excimer laser (Lambda Physik EMG101MSC, XeF, 351 nm, fwhm 18 ns) was employed for excitation of the sample surface.

The principle of the reflectance measurement is based on the method of Avery[7] except for laser excitation. The method has been known to be useful for obtaining extinction coefficients (k_0) and refractive indices (n) of compressed pellets of organic powders which can not give absolute flat surfaces without scattering of the incident light.[8,9] Namely, reflectance coefficients r_s and r_p for incident monitor light polarized perpendicular and parallel, respectively, to the plane of incidence are measured experimentally. From the two values of the ratio $R = r_p / r_s$ measured at the different angles of incidence (θ_1 , θ_2), one can obtain the values of n and k_0 by approximation calculation using a computer. The value of k_0 is represented by a molar absorption coefficient (ε) obtained from a transmittance configuration, the wavelength of the detection light in vacuum (λ_0), and molar concentration (C) as $k_0 = 2.303\varepsilon\lambda_0 C/4\pi$. Therefore, a change in concentration of photo-absorptive species can be analyzed by using k_0 values. In this paper, we have applied this method for the first time to obtain time-resolved spectra of n and k_0 after laser excitation. When a surface is excited by laser light, a change in the angle of incidence of the laser beam results in a change of the laser intensity at the sample surface. To avoid this problem, we irradiate the surface at an angle $\phi = (\theta_1 + \theta_2)/2$ from the optical axis of the polychromator. This means that the angle of incidence of the laser beam to the sample surface is set at $\pm|\theta_1 - \theta_2|$ for both the angles of incidence of the monitor light.

The obtained k_0 spectrum for the pellet of β-CuPc without laser excitation was quite similar to the absorption spectrum of its thin film,[6] which indicates that this measurement system is

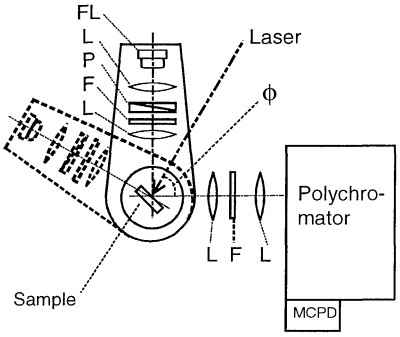

Figure 1. Schematic diagram of the time-resolved regular reflection spectroscopy system; FL: flash lamp, L: lens, P: polarizer, F: filter, MCPD: multi-channel photodiode array.

reliable. When the surfaces were excited by the laser light a few μs before irradiation of the monitor lamp, marked changes in both k_0 and n were observed. Figure 2 shows time-resolved spectra of extinction coefficient changes (Δk_0) and of refractive index changes (Δn) for β-CuPc. The spectral shape of Δk_0 is identical to the difference spectrum obtained by subtracting its k_0 spectrum at 297 K from that at 335 K.[1] It is also quite similar to those at the delay time after 100 ps obtained by the Kramers-Kronig transfrmation.[1] Therefore, we confirm that the previously reported method can give correct time-resolved spectra and the main component after 100 ps can be ascribed to hot molecules in the electronic ground state. The region from 530 nm to 720 nm in the Δk_0 spectra is mostly negative, representing the depletion of the vibrationally ground states caused by changes in thermal population.

Spectral changes due to vibrational excitation have been analyzed in many reports. Amongst them the simplest approximation for representing the depletion of absorption peaks is based on the Sulzer-Wieland formalism.[10] Assuming the Frank-Condon factors for the optical transitions from the ground state to the electronic excited states are dominated only by a single vibrational mode (ν_0), the absorption coefficient at a peak of an absorption spectrum is given by:

$$\varepsilon^{P}(T) = \varepsilon^{P}_0\,[\tanh(h\nu_0/2kT)]^{1/2} \qquad (1)$$

where T is temperature and ε^{P}_0 the absorption coefficient at 0 K. Thus we can explain that the depletion of peaks of the ground state absorption by vibrational excitation is significant when ε_0 is large. Namely, the ratio of two absorption peak intensities about 620 nm and 720 nm of solid CuPc are known to depend on its polymorph structure,[6] and the observed transient depletion clearly corresponds to the ground state absorption of β-CuPc.

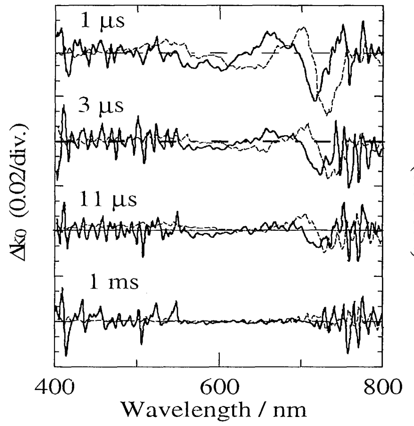

Figure 2. Time-resolved extinction coefficient (Δk_0, solid line) and refractive index (Δn, dotted line) changes for β-CuPc.

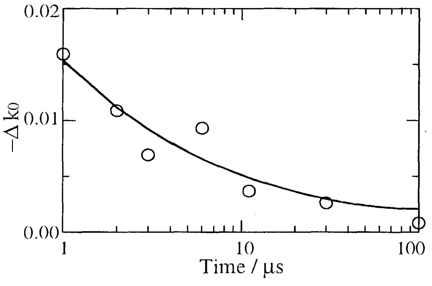

Figure 3. The decay of extinction coefficient changes ($-\Delta k_0$) around 600 nm (O) for β-CuPc and a simulated curve (solid line).

The initial temperature distribution in a pellet sample is a function of the depth (z) from the surface when the Beer's law holds during the laser excitation as follows:

$$T(z, t{=}0) = [\varepsilon_L C(1-R)I_L / \rho C_p]\,\exp(-\varepsilon_L C z) \qquad (2)$$

where R is the reflectivity of the surface at the laser wavelength, I_L the laser intensity, ρ the density of the sample, and C_p its specific heat capacity. Since the laser-irradiated area at the surface was larger than the monitored area, heat flow is considered to be one dimensional to the direction of z. Then the time dependence of temperature can be represented by:

$$\partial T(z, t)/\partial t = (\kappa/\rho C_p)\,\partial^2 T(z, t)\,/\,\partial z^2 \qquad (3)$$

where κ denotes the thermal conductivity. Eqs (2) and (3) can be combined and integrated numerically by using the forward difference approximation.[11] Values used in this calculation were $\varepsilon_L = 1.64 \times 10^5\ \mathrm{M^{-1}\,cm^{-1}}$,[6] $C = 2.8$ M,[12] $R = 0.3$, $I_L = 2.5\ \mathrm{mJ/cm^2}$, $\rho = 1.4\ \mathrm{g/cm^3}$, $C_p = 1.03\ \mathrm{Jg^{-1}K^{-1}}$,[13] and $\kappa/\rho C_p = 2\times10^{-4}\ \mathrm{cm^2/s}$.[14] This analysis is essentially similar to that used in photothermal laser ablation of a polymer film.[15] From the obtained temperature decay at the surface, we can simulate the decay of the depletion of $\varepsilon(T)$ by using Eq (1). Figure 3 shows the result of the best fitting by the Simplex method, assuming the surface layer of 50 nm is monitored by the regular reflection spectroscopy. Here, the value of the optically active vibration (ν_0) was obtained to be 420 cm^{-1}. This is a reasonable value since the absorption spectra of several hot polyatomic molecules were analyzed well with a single vibrational mode from 170 to 840 cm^{-1} for each molecule.[16]

Thus, we have shown that transient changes in the extinction coefficient of solid CuPc in this time scale are due to rises of its canonical temperature caused by laser-induced surface heating.

References and Notes

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