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LASER FOURIER IMAGING OF CHEMICAL REACTION. OBSERVATION OF THE DIFFUSION PROCESS OF HEAT EMITTED FROM DYE MOLECULES BY STRIPED LASER EXCITATION

Shozo ISHIZAKA,† Toshiyuki URANO,* and Katsumi TOKUMARU

Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

† *Institute of Biologival Sciences, The University of Tsukuba, Sakura-mura, Ibaraki 305*

Excitation of Eosin Y in ethanol solution with irradiated stripes of chopped argon ion laser beam gives thermal fringes which diffract helium-neon laser beam; the resulting diffraction fringes correspond to the Fourier transformation of the thermal fringes. By following the growth and decay of the transient diffraction signals the diffusivity of heat evolved by the photoexcitation in the solution was determined.

In the recent application of UV and visible laser technique to the investigation of chemical phenomena, the short pulsed, monochromatic and high intensity properties of laser have been most well employed for the spectroscopic observation of the transient species in photochemical reactions,[1] and several attempts have been done to utilize high intensity and monochromatic properties to induce highly selective reactions.[1] However, attempts to use coherent properties of laser are scarce except in a few works.[2,3] In the present investigation, chopped laser beams are irradiated stripedly on a cell containing a solution of Eosin Y, a photosensitive compound, to induce physical and chemical changes at the irradiated region of the cell making fringes with electric susceptibility fluctuated from the unirradiated region, which subsequently decay rapidly. These phenomena are investigated by a laser Fourier transformation technique,[4,5] and the decay of the fringe is reasonably attributed to the diffusion of heat evolved from the deactivation of the excited state of the dye or interaction of the resulting reactive species as described below. To our knowledge, this seems to be the first attempt to investigate the behavior of solution by the laser Fourier transformation technique.

It is known that Eosin Y is photobleached in alcoholic solution with a quantum yield lower than 10^{-3}.[6] Accordingly, Eosin Y is practically enough stable in alcoholic solution in a short time of the irradiation. The singlet excited Eosin Y emits fluoresecnce in a quantum yield of 0.12[7] and undergoes intersystem crossing to the triplet state, which subsequently either deactivates into the ground state to emit heat or interacts with ground state Eosin Y to give a pair of their radical cation and anion followed by their recombination to recover the dye. Therefore, the excitation of Eosin Y by striped chopped laser beam is expected to give the transient fringes with electric susceptibility fluctuated from the unirradiated region due to either the formation of transient species or the evolution of heat by

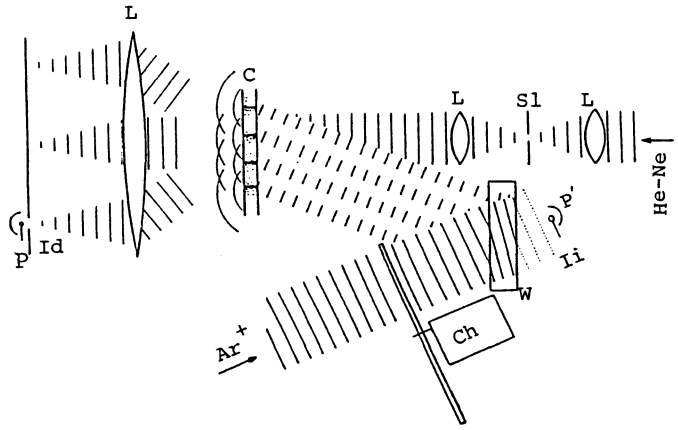

Fig. 1. Instrument of laser Fourier imaging of chemical reaction. Ar^+: argon ion laser, Ch: chopper, W: wedge, Ii: incident intensity, He-Ne: helium-neon laser, L: lens, Sl: slit, C: cell, Id: diffractive intensity, P and P': photodetectors.

the radiationless deactivation of the excited state and the recombination of the radical ions.

Figure 1 shows outline of the instrument employed. Eosin Y in ethanol solution (1.0×10^{-3} mol dm^{-3}) was excited in a thin cell, C, (1 cm x 4 cm and 1 mm in thickness). The incident light beam of argon ion laser (488 nm) was modulated with an appropriate frequency, ω, (varying between 10 and 10^2 s^{-1}) by a chopper, Ch. The light beam was multiply reflected by a narrow wedge, W, to give irradiated stripes, arranged with a wavenumber, k, (4×10^2 cm^{-1}) on the cell. The dye at the irradiated stripes was periodically excited to result in formation and decay of the fringe as schematically depicted in Fig. 3 C.

To detect the change at the stripes, light beam of helium-neon laser (632.8 nm), which was not absorbed by Eosin Y, was directed to the sample cell and diffracted on the stripes to give diffraction pattern on the photodetector, P, focussed through a lens, L; the resulting diffracted patterns were composed of many pairs of the fringes symmetrically arranged around the optical axis, as schematically shown in Fig. 3 D.

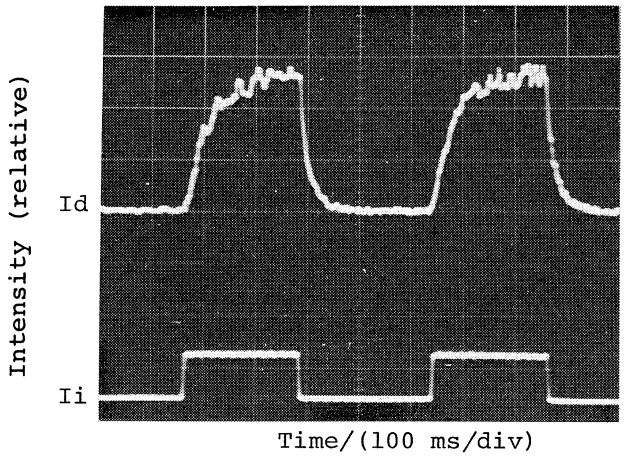

Fig. 2. Response of diffractive intensity to incident intensity on chopper striped laser excitation. On irradiation of incident light with intensity (Ii), diffractive intensity (Id) increases convexly and turns to a steady state. At off-irradiation, Id decreases concavely and finally diminishes completely.

The incident and diffracted lights were turned to electric signals by photoelectric detectors, P' and P, respectively, and their changes with time were observed on an oscilloscope, as shown in Fig. 2.

As Fig. 2 indicates, before the excitation there was no observable Id; however, when the irradiation began, Id started to increase, and gradually attained to a nearly constant value, and when the irradiation stopped, it began to decrease not instantaneously but gradually, and finally diminshed completely.

In the actual measurement, both the incident and the diffracted electric signals were put into a two-channel spectrum analyzer to turn both signals to the Fourier

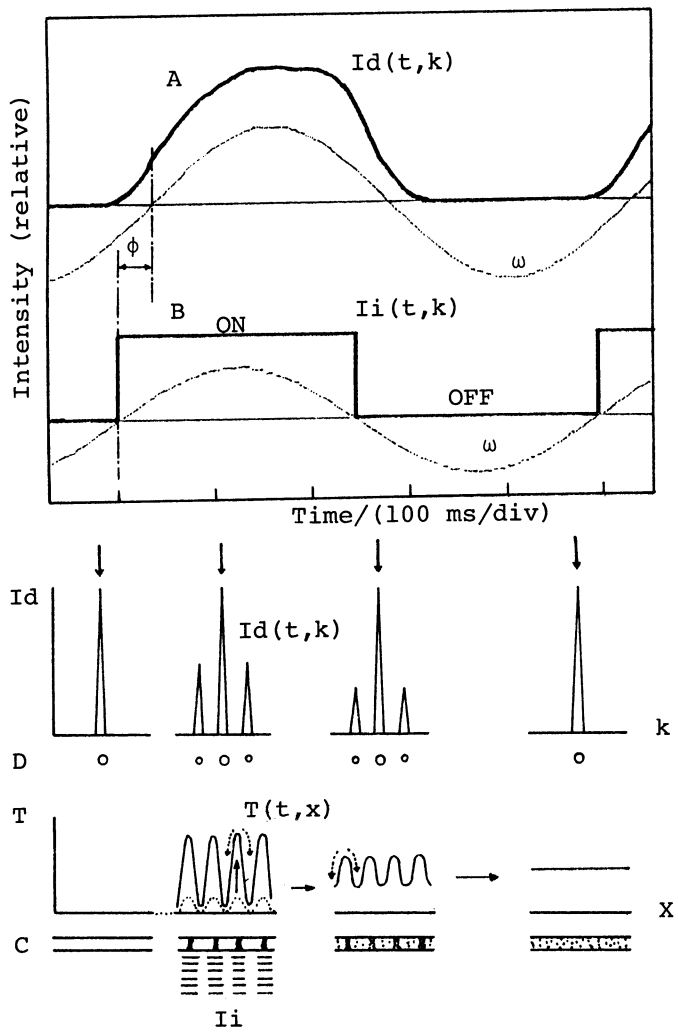

Fig. 3. Response of diffractive intensity to incident intensity on chopper striped laser excitation. On initiation of striped irradiation (Ii), fringes appear on the surface of the thin cell (C) as schematically depicted in C, which rapidly. disappear at off-irradiation. Formation of the fringe in C induces the changes of temperature distribution of the solution (T(t,x)), as shown in T, which gives diffraction pattern (D) as depicted, with the diffractive intesnity (Id(t,k)). These quantities change in corresponding to the change of the fringe with time. ϕ denotes phase shift between the incident and diffractive intensities.

components of a fundamental frequency defined by the chopper, as schematically illustrated with dotted lines in Figs. 3 A and B. The phase shift, ϕ, of the diffracted Fourier component from the incident Fourier component was measured with varying frequency of the chopper. By the same way, relative response intensity, the ratio of the light intensity of the diffractive Fourier component to the incident Fourier component was also measured.

To analyze the origin of the change at the stripes, we now consider a case in which the diffraction signal is proportional to the fluctuation of electric susceptibility due to the production and the diffusion of heat by the reaction. The excitation by the incident light, Ii, results in the evolution of heat, h(t,x), which subsequently leads to the change of temperature, T(t,x), in the solution, respectively, as illustrated in Fig. 3 T. The resulting temperature change will affect the intensity of the diffraction fringes, Id(t,x).

The change of temperature with the diffusion of heat evolved should obey the following equation,

$$dT(t,x)/dt=D_T\partial^2T(t,x)/\partial x^2+1/C\ h(t,x), \quad (1)$$

where D_T and C represent the thermal diffusivity and the heat capacity of the solution, respectively. The differential equation was mathmatically Fourier transformed to the algebraic relation with the chopping frequency, ω, and wavenumber of the stripes, k,

$$i\omega\hat{T}(\omega,k)=D_Tk^2\hat{T}(\omega,k)+1/C\ \hat{h}(\omega,k), \quad (2)$$

where $\hat{}$ is symbol of Fourier transform. The Fourier transform of the temperature distribution is

$$\hat{T}(\omega,k)=1/C(i\omega+D_Tk^2)\ \hat{h}(\omega,k). \quad (3)$$

The amplitude of diffracted light at the first fringe is proportional to

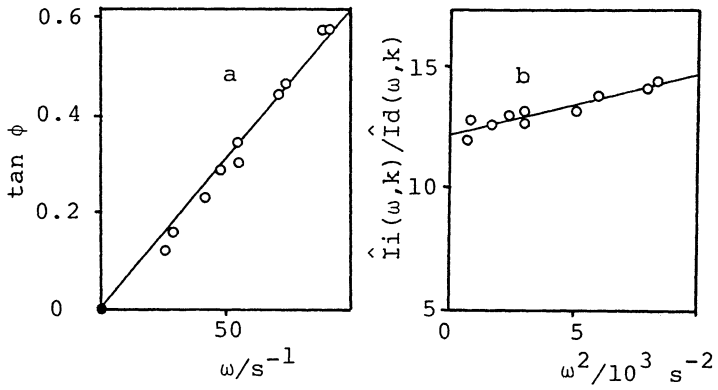

Fig. 4. Plots of the phase shift (a) and the reciprocal of the relative response intensity (b).

the fluctuation of electric susceptibility due to the change of temperature. According to the Fourier transformation technique, the tangent of phase shift of the diffractive signal from the incident signal should be linear with ω, as $\tan\phi = \omega/D_T k^2$. (4)

Since the heat evolved is proportional to Ii, the relative response intensity is proportional to the square of absolute value of the response function,

$$\hat{Id}(\omega,k)/\hat{Ii}(\omega,k) = R_o/C^2(\omega^2+D_T^2k^4), \quad (5)$$

where R_o is a constant. Accordingly, the reciprocal of the relative response intensity increases with ω^2 as follows:

$$\hat{Ii}(\omega,k)/\hat{Id}(\omega,k) = C^2(\omega^2 + D_T^2k^4)/R_o. \quad (6)$$

As Figs. 4a and 4b indicate , both the plots of tan ϕ against ω and $\hat{Ii}/\hat{Id}$ against ω^2 afford linear relationship, as predicted by equations 4 and 6. From the slope of Fig. 4a and from the slope of Fig. 4b divided by the intercept, the thermal diffusivities are obtained as $(1.0 \pm 0.1) \times 10^{-3}$ and $(1.4 \pm 0.4) \times 10^{-3}$ cm^2 s^{-1}, respectively, which are in good agreement with each other as well as the thermal diffusivity 9×10^{-4} cm^2 s^{-1} for ethanol estimated from reported heat capacity,[8] density,[9] and thermal conductivity.[10] Moreover, the excitation of other dyes like Rhodamine 6G and Ethyl red in ethanol solution resulted in the similar results to give the same thermal diffusivities as obtained from Eosin Y.

It is found that the phase shift determines more exactly the thermal diffusivity than does the response intensity. Therefore, the growth and decay of the resulting fringe are reasonably concluded to arise from the diffusion of heat.

It is noted that the new image processing of chemical gradient for the system analysis of chemical kinetics can be established by laser Fourier transformation technique.

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