Thermal Dynamics of Xanthene Dye in Polymer Matrix Excited by Double Pulse Laser Radiation

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Abstract. Double-pulse laser excitation of the eosin and silver nanoparticles embedded into polymer media is known to be a method of electronic-vibrational energy deactivation kinetic process information obtaining and polymer thermal dynamics investigation. We have studied the vibrational relaxation processes in dye molecules (eosin) and nanoparticles in polyvinyl alcohol after two time-shifted laser pulses with fast and delayed fluorescence kinetics study. In order to simulate thermal and photophysical processes caused by double photon excitation, we solved heat transfer and energy deactivation differential equations numerically. The simulation allowed us to obtain the value of heat conductivity coefficient of polymer matrix.

1. Introduction
Fluorophors and silver nanoparticles (NP) embedded into polymer media double-pulse laser excitation (DPLE) is known to be a method for molecule energy deactivation information obtaining and polymer thermal dynamics investigation [1–8]. Nowadays, DPLE in VIS/IR wavelength range can be considered as a tool for detailed investigation of fluorescence resonance energy transfer (FRET) in donor-acceptor molecular systems [9], electron-phonon interaction study [10–12] and fabrication of ablative NP [13], which can take part in plasmon energy transfer [14]. We aimed to consider vibrational relaxation processes in dye molecules (eosin) and NP embedded into polymer matrix (polyvinyl alcohol, PVA) after two time-shifted laser pulses with fast and delayed fluorescence (DF) kinetics.

2. Experiment
The experimental setup is illustrated in Figure 1. Eosin molecules in polyvinyl alcohol (PVA) DF and phosphorescence (Ph) after double laser pulse radiation (Vis and IR) were measured by photon counting unit (Hamamatsu C8855-01). A metallic plate with 5 mm diameter hole was covered by the PVA film. All measurements were carried out at a room temperature and a pressure of 10⁻⁴ torr.
Figure 1. Experimental setup: 1-2: fs-laser unit Teta-25/30 ($\tau = 60$ fs, $W = 0.12$ $\mu$J, $\lambda = 515$ nm); 3-6: YAG Nd$^{3+}$ laser unit LQ929 (Solar Laser Systems); 7: CO$_2$ laser unit (steady/pulse regimes, $\tau = 50$÷200 ms, $\lambda = 10$ $\mu$m); 8: Semiconductor laser unit ASG-1032 ($W = 50$ mW, $\lambda = 532$ nm); 9: cryostat Optistat VN-V; 10: monochromator ML44; 11: PMT/Photon counting unit C8855-01 (Hamamatsu C8855-01); 12: 2-channel pulse generator G-56; 13: PC.

3. Results and Discussion

Figure 2 illustrates the eosin (0.5 mM) fluorescence spectra at stationary (green) and 50 ms delayed IR pulse (red) excitation. Eosin DF and Ph in PVA film were studied at 555 and 680 wavelengths respectively after LQ929 YAG:Nd$^{3+}$ laser excitation ($\lambda = 532$ nm, $W = 15$÷20 J, $\tau = 11$ ns) and IR CO$_2$ laser pulse ($\lambda = 10.6$ $\mu$m, $P \approx 20$ W). The IR-pulse was time-shifted and irradiated the film within eosin DF decay time range.

It is known that fluorophors’ DF intensity depends on the interconversion transitions efficiency ($k_{ic} \sim 10^8$ s$^{-1}$) [15] and concentration of molecules in triplet state. The polymer matrix heating by the IR-pulse causes eosin triplet state electron-vibration levels population increase ($\Delta v_{st} = 3133$ cm$^{-1}$) [16].

Eosin DF intensity decay after IR pulse is shown in Figure 3. The DF kinetics lifetimes before and after the IR laser pulse 0.017 and 0.050 s respectively. It can be seen from the Figure 3 that there is a 20% local increase of DF intensity and lifetime directly after the CO$_2$ laser pulse.

Assuming that such enhance is caused by eosin singlet molecules population increase due to interconversion process, it is possible to estimate the temperature leap right after the IR laser pulse:
\[ \Delta T = T_0 \left[ \frac{1}{(1 - k_B T / \Delta E_{ST}) \ln \frac{I_1^{DF}}{I_2^{DF}} - 1} \right], \]  

(1)

where \( T_0 \) denotes an ambient temperature; \( k_B \) denotes the Bolzman constant; \( \Delta E_{ST} \) denotes the singlet-triplet energy splitting; \( I_1^{DF} \) and \( I_2^{DF} \) are the eosin DF intensities right before and after the IR pulse. The temperature leap was estimated to be 4 K.

**Figure 2.** Eosin (0.5 mM) fluorescence spectra at stationary (green) and 50 ms delayed IR pulse (red) excitation.

In the second series of the experiment, PVA films with eosin were excited by stationary semiconductor laser ASG-1032 radiation (\( \lambda = 532 \) nm, \( W = 50 \) mJ) and CO\(_2\) laser time-shifted (50 ÷ 200 ms) IR pulse (\( \lambda = 10,6 \) \( \mu \)m, \( P \approx 20 \) W), which allowed us to study the kinetic processes eosin singlet and triplet states population decay after IR heating.

DF kinetics was exponential with a lifetime of 4.7 s. Simulation of the eosin DF intensity decay in PVA allowed us to obtain the quantitative characteristics of the thermal energy transfer in the polymer matrix.

Heat equations with the corresponding initial and boundary conditions for the studied system were solved [17]:
\[
\frac{\partial T}{\partial t} = a^2 \frac{\partial^2 T}{\partial x^2}; \quad t > 0, \quad -R < x < R; \\
T(x,0) = \Theta(x);
\]
\[\left. -\lambda \frac{\partial T}{\partial x}\right|_{x=R} + \alpha [T_0 - T(+R,t)] = 0; \]
\[\left. -\lambda \frac{\partial T}{\partial x}\right|_{x=-R} + \alpha [T_0 - T(-R,t)] = 0,
\]

where \( R \) denotes the PVA film halfwidth; \( a \) and \( \lambda \) are the temperature conductivity and heat transfer coefficients, respectively; \( \alpha \) denotes the heat emission constant.

Figure 3. Eosin DF intensity decay after IR pulse.

Eq. (2) was solved for the temperature leap \( \Delta T \) by variables separation method: \( \Delta T = \psi(x) \exp(-\mu t^2/R^2) \) where \( \mu = 0.0316 \) [5]. The value of \( a \) was found to be \( 0.243 \cdot 10^{-6} \text{ m}^2/\text{s} \) which coincides with literature data for heat characteristics of PVA.

PVA film doped with silver NP heat transfer characteristics were investigated in the third series of our experiment. Silver NP ablation was performed by means of fs-laser unit Teta 25/30 (Avesta) (\( \tau = 60 \text{ fs}, W = 0.12 \mu J, \lambda = 515 \text{ nm} \)) in an aqueous medium. The silver target was placed in a cuvette with a liquid on the rotary platform. The laser beam was guided and focused on the surface of the target. Silver NP sizes were measured by photon correlation spectroscopy unit Photocor-C with 432 nm-laser.
NP average radius was 32 nm. Silver NP clusters with low silver concentrations can serve as heat point centers with a temperature much higher than the polymer matrix. The temperature field dynamics can be simulated by heat transfer equations with spherical Greene function. We solved the following heat transfer problem for above-mentioned system:

\[
\frac{\partial T}{\partial t} = \frac{a}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial \vartheta} \left( 1 - \vartheta^2 \right) \frac{\partial T}{\partial \vartheta} + \frac{1}{1 - \vartheta^2} \frac{\partial^2 T}{\partial \varphi^2} \right],
\]

\[
T(r, \vartheta, \varphi, 0) = f(r, \vartheta, \varphi);
\]

\[
\lambda \frac{\partial T}{\partial r} = \alpha_r \left[ T(R, \vartheta, \varphi, t) - T_0 \right];
\]

\[
\vartheta = \cos \theta; \ 0 \leq \varphi \leq 2\pi; \ -\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2};
\]

where \( T \) denotes the cluster’s temperature, \( R \) denotes the radius of the cluster. The standard solution of the eq. (3) can be expressed as

\[
T(r, t) = \frac{Q}{8\pi\alpha R c} \left[ \exp \left( -\frac{(r - R)^2}{4\alpha t} \right) - \exp \left( -\frac{(r + R)^2}{4\alpha t} \right) \right],
\]

where \( Q \) denotes the heat power after IR laser pulse; \( c \) and \( \rho \) are the heat capacity and density of the cluster. The estimated value of \( a \) for the system with silver NP as heat centers was \( 0.096 \times 10^{-6} \text{ m}^2/\text{s} \).

4. Conclusion

Thus, using double-pulse laser excitation (Vis and IR) of the fluorophor electron-vibrational states in polymer films, it is possible to obtain the information about thermal processes in homogeneous polymer films.

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