Vibrational energy relaxation of perylene in supercritical alcohols

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Abstract. The time resolved fluorescence spectra of perylene in sub- and supercritical methanol have been measured by using a streak camera in the lower-pressure region than 10 MPa and an optical Kerr gate spectroscopic method in the higher-pressure region than 10 MPa. The lineshape of the fluorescence spectrum has been found to be dependent on the time. By comparing the excess energy dependence of the fluorescence lineshape in vapour perylene without energy dissipation process, the spectral change was assigned to the vibrational energy relaxation process in the S1 state. The vibrational energy relaxation time at each solvent density in supercritical region was determined by the time-profile at the 0-0 band peak position in the fluorescence spectrum. The vibrational energy relaxation rate scaled by the square root of the temperature has been compared with the hydrogen-bonding degree between solvent molecules estimated by the NMR measurement (Hoffmann M M and Conradi M S 1998 J. Phys. Chem. B 102 263).

1. Introduction
Vibrational energy relaxation (VER) process in solution is one of the most fundamental processes after the photo-excitation of a molecule, and various aspects of the energy dissipation processes have been studied both experimentally and theoretically[1]. In the study of the VER, supercritical fluids (SCFs) have played an important role in determining important factors which affect the VER processes, because we can control the collision frequency between solute and solvent molecules which is one of the most important factors on the VER rate. Until now, a lot of studies have been done on the VER process by using the SCFs[2]. However, most studies until now are limited to the supercritical fluids with critical temperatures near the room temperature such as carbon dioxide and xenon, and the studies on the supercritical fluids with hydrogen-bonding ability are quite limited. Supercritical fluids with hydrogen-bonding ability such as supercritical water (SCW) and supercritical alcohols are a new class of solvent fluids which enables us to develop new kinds of chemical reactions and have been attracting attentions of a lot of chemists academically and industrially[3]. It is quite an interesting issue how the change of the hydrogen-bonding affects the VER process. Very recently the vibrational energy dissipation process of pure water has been investigated by the time-resolved IR spectroscopy by Schwarzer et al[4]. They found that the VER rate of the OH stretching mode is correlated with the number of the hydrogen-bonding, suggesting that the energy transfer through the hydrogen-bonding is quite effective in water.

In this paper, we will report the study on the VER of the S1 perylene in supercritical methanol. The vibrational energy relaxation in the S1 state of perylene was previously studied by the
fluorescence up-conversion technique by Kasajima et al[5]. They have found that there is an earlier dynamics of the fluorescence signal after the photo-excitation in methyl-tetrahydrofuran with an excess vibrational energy of ca. 2800 cm$^{-1}$. The peak position of the Franck-Condon progression (see Figure 1) shows an earlier rise of about 1 ps second, and determined the VER rate as 0.54 ps$^{-1}$ from $v = 1$ to $v = 0$. Pigliucci et al., also did similar experiments on perylene and its derivatives in various solvents, and found the VER time of the S1 perylene in methanol as 2.6 ps[6]. In the present study, we studied the VER process of the S1 perylene in supercritical methanol (SCMe) by the similar analysis when an excess energy of ca. 15000 cm$^{-1}$ is given.

2. Experimental setup
We measured the time-resolved fluorescence after the photo-excitation by the third-harmonic pulse (267 nm) from a regenerative amplifier of a Ti:Sapphire laser (Spectra Physics, Spitfire-Pro Xp). We used two different methods to measure the time-resolved fluorescence: a streak camera for the lower-pressure[7], and an optical Kerr gate method for the higher pressure. Figure 2 shows a schematic illustration of the optical Kerr gate system which is a similar system developed by Maroncelli’s group[8]. Since the detail will be described elsewhere[9], we briefly explain the system. The fluorescence from the sample solution was collected by a parabolic mirror and focused into a Kerr media by a lens after passing through the first polarizer. We used benzene as a Kerr media, and the fluorescence after the second polarizer was detected by an ICCD camera with a 200 ps gate (LaVision, Picostar HR) equipped with a spectrometer. The fluorescence image at each delay time of the gate pulse was evaluated after the proper correction of group velocity dispersion of light and sensitivity of the camera. The time response of the Kerr gate system was ca. 0.8 ps and that of the streak camera was ca. 20 ps.

The high-pressure and high-temperature system was described elsewhere[10]. We performed the experiments for methanol solution of perylene at various pressures to 37 MPa with a constant temperature of 540 K, and at constant pressure of 37 MPa with different temperatures, 373 K, 473 K,

![Figure 1](image1.png)  
**Figure 1.** Steady state absorption and fluorescence spectra of perylene in methanol at RT.

![Figure 2](image2.png)  
**Figure 2.** Experimental setup for the Kerr gate fluorescence measurement.

![Figure 3](image3.png)  
**Figure 3.** Excitation wavelength dependence of the fluorescence bandshape of perylene in vapour at 523 K.

![Figure 4](image4.png)  
**Figure 4.** Time-resolved fluorescence of perylene in methanol at 15.0 MPa and 540 K.
and 540 K. We have also measured the excitation wavelength dependence of the fluorescence spectrum of perylene vapor (ca. 1 torr) enclosed in a quartz cell at 523 K by using a nano-second dye laser (Continuum, ND6000) and an ICCD camera (Princeton, Pi-MAX).

3. Results and Discussion

Figure 3 shows the excitation wavelength dependence of the fluorescence spectrum of perylene in vapor. With increasing the photon energy for the excitation, the Franck-Condon progression of the fluorescence spectrum is gradually smeared out, and the band center shifts to the lower frequency region. The intensity at the Franck-Condon peak at the lowest energy is almost linearly dependent on the excess energy from the 0-0 excitation (416 nm) if the fluorescence intensity is normalized. Therefore the intensity change of this band can be measure of the excess energy as is previously used. Figure 4 shows the time-resolved fluorescence spectra at 15 MPa and 540 K in methanol. In the earlier time region after the photo-excitation the fluorescence spectrum is structureless, and the Franck-Condon progression becomes apparent with time progress. This change of fluorescence bandshape is quite similar to those observed for the excitation wavelength dependence of the fluorescence spectrum. Therefore we can follow the energy dissipation process by analyzing the time profile of the fluorescence.

Figure 5 show the time profile of the fluorescence intensities detected at the 0-0 fluorescence peak position (circles). The fluorescence intensity shows a slower rise after the instantaneous rise. By comparing with the excess energy dependence of the fluorescence spectrum shape, the rise is considered to be due to the VER process. The solid line in the figure represents the convolution fitting with the system response function with the fluorescence rise as

\[ I(t) = \int I_\text{rf}(t-t')\left(a_1 - a_2 \exp(-k_{\text{VER}}t')\right)\exp\left(-t' / \tau_\text{fl}\right)dt' \]

where \(a_1\) and \(a_2\) are the coefficients, and \(\tau_\text{fl}\) is the fluorescence lifetime. \(I_\text{rf}(t)\) is the system response function determined by the fit to the rise profile of the integrated intensity of the fluorescence, where the functional form of the response function is assumed to be

\[ I_\text{rf}(t) = \text{sech}^2\left((t-t_0) / \tau_\rho\right) \]

The black lines in the figures show the fitting results, and the blue lines are the response functions used to fit the data. For both data taken by streak camera (left figure) and Kerr gate system (right figure), the function simulates the data well.

The obtained VER rate \(k_{\text{VER}}\) is plotted against solvent reduced density \(\rho_\text{r}\) by the critical density of the solvent in Figures 6 and 7. In the figure we have divided the rate by the absolute temperature. According to the isolated binary collision (IBC) model, which may be a standard reference of the analysis of the VER rate in gases and frequently used for the analysis of the results in SCFs, the vibrational energy relaxation rate is proportional to the collision frequency between the solute and solvent \(Z\) and to the energy dissipation efficiency per collision \(P(T)\). In a simple model where a collision is defined as event where two molecules approach each other within a certain distance \(\sigma\), the rate of the vibrational energy relaxation is given by[1]

![Figure 5](image-url)
where \( g(\rho, T, \sigma) \) is the value of the radial distribution function between solute and solvent at the distance of \( \sigma \). Therefore \( k_{\text{VER}}T^{1/2} \) will be a measure of the local-density of the solvent molecules around the solute, which is effective to the VER process.

As is shown in Fig. 6, after the initial increase of \( k_{\text{VER}}T^{1/2} \) in the lower density region, \( k_{\text{VER}}T^{1/2} \) becomes almost independent of the solvent density to 1.5 in \( \rho_r \), then it comes to increase again in the higher-density (lower-temperature) region. According to ref. 6, \( k_{\text{VER}}T^{1/2} \) at room temperature (\( \rho_r = 2.85 \)) is estimated to be 22 ns\(^{-1}\) K\(^{-1/2}\), and therefore further increase in the higher density region is expected. In Fig. 6, the absorption and fluorescence peak positions are also plotted as a function of \( \rho_r \).

The spectral shift may reflect the change of the electrostatic interaction such as polar-quadrupolar interaction between solvent and solute, and often referred as the indicator of the local density enhancement near the critical density of the solvent. In the lower density region below 1.8 in \( \rho_r \), their density dependence are similar to \( k_{\text{VER}}T^{1/2} \). Therefore, the change of the local density around perylene is reflected in the change of the VER rate. However, the deviation between the spectral shift and the VER rate becomes significant in the higher-density region.

Figure 7 shows the correlation with the hydrogen-bonding ability between solvent methanol molecules determined by the NMR spectroscopy by Hoffmann and Conrad[11]. The hydrogen-bonding number is more sharply dependent on the solvent density in the higher-density region, which seems to correlate with \( k_{\text{VER}}T^{1/2} \). As a result the hydrogen-bonding seems to have some effect on the VER process. In the case of azulene, it has been proved that the VER process is faster in hydrogen-bonding solvents than aprotic solvents[7]. Therefore it is probable that the \( \pi \) electrons of perylene make some kind of hydrogen-bonding, and the energy transfer through the hydrogen-bonding becomes more effective at the higher-density region.

**Acknowledgement**

This work is supported by the Grant-in-Aid for Scientific Research (Nos. 16350010 and 19350010) from JSPS.

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