Anti-Stokes Fluorescence of Rhodamine Dyes in Polymer Gels

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It has been known that organic dyes such as rhodamine 101 and B in an aqueous solution emit anti-Stokes fluorescence of which peak wavelength is shorter than that of the excitation light (He-Ne laser at 632.8nm). A model that could explain the origin of such frequency (energy)-upconverted luminescence is absorption of a photon which induces a transition from a high vibrational level of the ground state to the first excited state. Such dyes doped polymers have been investigated from fundamental and technological point of view for application to optical waveguides and optical cooling. The presentation reports the anti-Stokes fluorescence properties of these dyes in poly(N-isopropylacrylamide)(NIPA) gels. As well known, NIPA gels immersed in water undergo a volume phase transition by a change in temperature, which is peculiar to polymer gels.

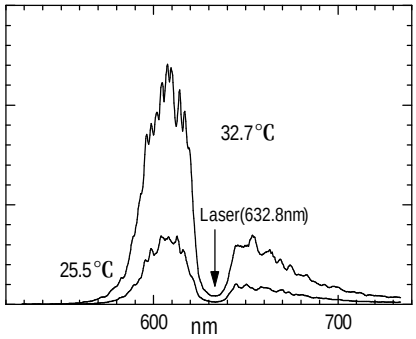

Fig.1 Anti-Stokes fluorescence spectra of rhodamine 101 in swollen and shrunken gels

Examples of anti-Stokes fluorescence spectra of rhodamine 101 in swollen and shrunken NIPA gels are shown in Fig.1. The excitation laser line at 632.8 nm is cut by a holographic notch filter. The spectra show that the peak of the fluorescence is about 730 cm^{-1} higher in energy than the exciting photon. The peak wavelength of the fluorescence does not differ with the swollen and shrunken gels, but the intensity for the shrunken gel is 3.5 times larger than that for the swollen gel.

Since the population of high vibrational level is given by the Boltzmann distribution, the intensity of the anti-Stokes fluorescence would be described by the following functional form,

$$I(T) = A\exp(-\Delta E/kT).$$

The intensity of the spectrum at 600 nm is plotted as a function of the inverse absolute temperature and compared with that for the aqueous solution of the dye of the same concentration in Fig.2. The figure shows that the intensity for the aqueous solution can be described by a strait line for the energy difference ΔE ~ 1400 cm^{-1}, and the intensity for the gel can fit two strait lines having different gradients. In lower temperature where the gel swells, the line has the same gradient as for the solution. In higher temperature where the gel shrinks, the intensity becomes higher as the temperature increases. This shows that the anti-stokes fluorescence is closely related to the shrinking of NIPA gels in water.

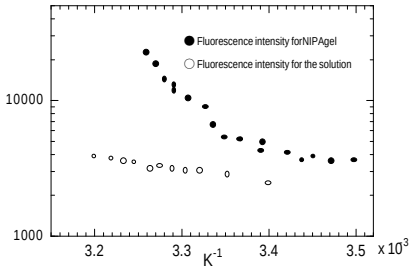

Fig.2 Anti-Stokes fluorescence intensity from rhodamine 101 in NIPA gels and the solutions vs. inverse absolute temperature

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Introduction

It has been known that organic dyes such as rhodamine 101 in fluid mixtures and solid mixtures emit anti-Stokes fluorescence of which peak wavelength is shorter than that of the excitation light (He-Ne laser at 632.8nm). A model that could explain the origin of such frequency (energy)-upconverted luminescence is absorption of a photon which induces a transition from a thermally activated high vibrational level of the ground state to the first excited state（1，2）. Such dyes doped polymers have been investigated from fundamental and technological point of view for application to optical waveguides and optical cooling. The present investigation reports the anti-Stokes fluorescence properties of these dyes in hydrogels, poly(N-isopropylacrylamide) (NIPA) gels. As well known, NIPA gels immersed in water undergo a volume phase transition by a change in temperature, which is peculiar to polymer gels. It is interesting to investigate how the phase transition affects the anti-stokes fluorescence properties.

Results and Discussion

Examples of anti-Stokes fluorescence spectra of the neutral NIPA gel in the aqueous solution of rhodamine 101 (10^{-4}mol) at 25.5℃ and 32.7℃ are shown in Fig.1. The gel is in the swollen state at both temperatures. The scattered excitation light at 632.8 nm is cut by a holographic notch filter. The spectra show that the peak of the fluorescence is about 730 cm^{-1} higher in energy than the exciting photon. The peak wavelength of the fluorescence does not change with temperature but the intensity of the spectrum greatly changes. The peak intensity at 32.7℃ is 3.5 times stronger than that at 25.5℃.

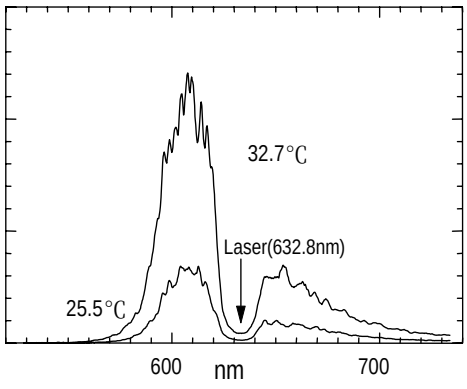

Fig.1 Anti-Stokes fluorescence spectra of rhodamine 101 in swollen gel

A peak height at 600 nm of the spectrum was measured as a function of temperature. The obtained data are plotted together with those of the aqueous solution of rhodamine 101 in Fig.2. It is seen that the fluorescence intensity of the gel is stronger than that of the solution and the intensity increases as the temperature increases. As approaching the volume phase transition temperature 33 ℃, the fluorescence intensity of the gel rapidly increases compared with

that of the solution.

Transmission efficiency of a He-Ne laser at 632.8 nm in the gel was measured and the obtained data are plotted, together with the swelling ratio, as a function of temperature in Fig. 3. It is seen that the swollen gel is perfectly transparent for the excitation He-Ne laser at 632.8 nm until the gel nearly approach the transition temperature. Comparing with Fig.2, one finds that the rapid increase in the intensity of the anti-Stokes fluorescence spectrum is closely related with the volume phase transition of the gel. A little shrinking process of the swollen gel nearing the transition temperature greatly affects on the spectrum and causes the increase in the intensity. Meanwhile, as mentioned above, in this temperature region where the gel is in the swollen state, the gel is transparent for the excited light. Transmission efficiency scarcely change in the temperature region.

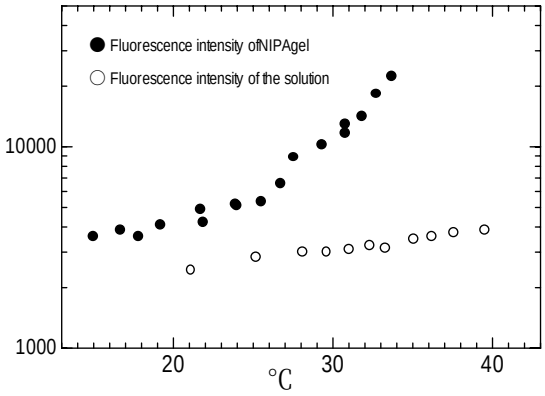

Fig.2 Anti-Stokes fluorescence intensity of rhodamine 101 in the NIPA gel and the solution as a function of temperature

The dependence of the fluorescence intensity at 600 nm on the excitation laser power was measured for the gel at 33 ℃ and shown in Fig.4. It is seen that the fluorescence intensity I increases in linear with the laser power P, $P \propto I^n$. n = 1. This means that one photon is involved in the anti-Stokes fluorescence of the gel.

Since the population of a high vibrational level is given by the Boltzmann distribution, the intensity of the anti-Stokes fluorescence would be described by the following functional form,

$$I(T) = A \exp(-\Delta E/kT) \qquad (1) .$$

The intensities of the spectrum at 600 nm shown in Fig.2 are plotted as a function of the inverse absolute temperature in Fig.5. The figure shows that the intensity of the aqueous solution can be described by a straight line for the energy

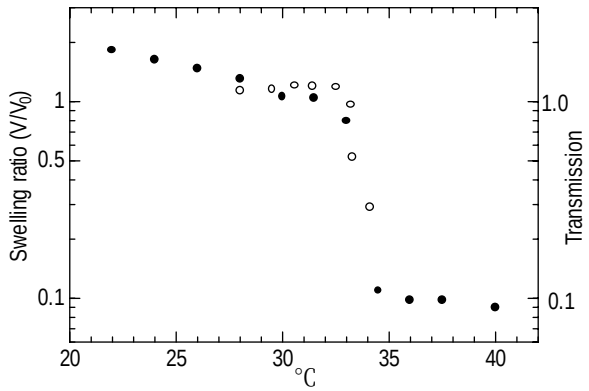

Fig.3 Swelling ratio of the neutral NIPA gel in the aqueous solution of rhodamine 101(●),and transmission of He-Ne laser light at 632.8 nm(○).

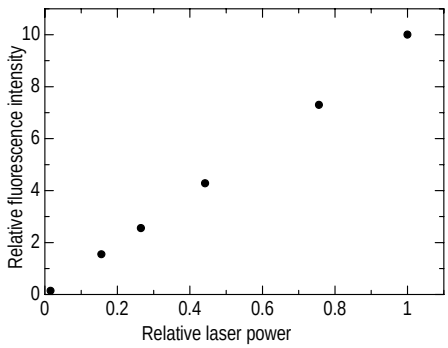

Fig.4 Dependence of anti-Stokes fluorescence intensity at 600 nm on the exciting He-Ne laser power.The highet power of the laser is 3 mW. The temperature of the gel is 33℃.

difference, ΔE = 1400 cm^{-1} , and the intensity of the gel can fit two straight lines having different gradients. In lower temperatures where the gel perfectly swells, the line has the nearly same gradient, that is, the same ΔE as the solution. In higher temperatures where the gel gradually gets to shrink approaching the transition temperature, the intensity rapidly increases and gives a higher value of ΔE than that of the solution. Normally, one can not expect such a change of ΔE. It has been reported that the fluorescence quantum yield for the acidic form of rhodamine 101 is 1.0 and does not change for the measured temperature region. And also, its fluorescence properties

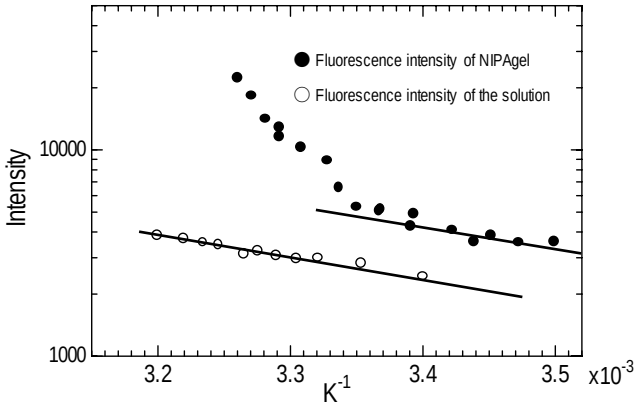

Fig.5 Anti-Stokes fluorescence intensities at 600nm of the NIPA gel and the solution vs. inverse absolute temperature

are sensitive to pH. So, one can suppose that the increase in the anti-Stokes fluorescence intensity with approaching the volume phase transition temperature is closely related with the formation of hydrophobic bonds between NIPA chains. Above results suggest a capability of application of anti-Stokes fluorescence of rhodamine 101 in the NIPA gel to an on-off switch.

References

1. D. Bloor, et al., *J. Chem. Faraday Trans.*, 89, 4013 (1993)
2. J. L. Clark, P. F. Miller, and G. Rumbles, *J. Phys. Chem. A*, 102, 4428 (1998)