Effects of Proton Motions on the Fluorescence from 2-Naphthol-Doped Ice Ih and the Proton Ordering Transition

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Fluorescence from 2-naphthol-doped ice Ih crystals was studied using a picosecond pulsed laser. Because of the incipient ESPT (excited state proton transfer) process of 2-naphthol in ice, the fluorescence lifetime is sensitive to the change in the proton configurations around the dopant. In addition to the sharp decrease above 120 K due to the increase in the mobility of proton defects, the lifetime shows a dip near 72 K, which is related to the Ih−XI proton ordering transition.

Introduction

Protons in ice Ih crystals are disordered even at 0 K, and they are mobile only with the help of defects which relax the ice rules.[1] In a pure ice Ih crystal at lower temperature, the disordered proton configurations are frozen, and it is only above 120 K (between 100 and 130 K) that the ionic and the orientational L-defects become mobile, which is too high for protons to be ordered. When a considerable amount (10^{-2} M) of KOH is doped in ice, however, it was found that a phase transition from Ih to the proton-ordered XI phase occurs at 72 K.[2,3,4] This transition shows a large latent heat,[4] indicating that the transition is of first-order. The strong first-order nature was also theoretically shown from an order−disorder model of proton system which satisfies the ice rules.[5]

In most structural phase transitions that are second-order or nearly second-order, a precursor of the transition is observed far from the phase transition temperature T_0, e.g., as a softening of a particular phonon mode. In contrast, in the case of a strongly first-order transition, macroscopic properties change discontinuously at T_0, and one can hardly see any precursor effect. Nevertheless, if one could measure a nonaveraged local property, it might be possible to see an effect of a first-order phase transition even at temperatures far from T_0. Since an excited electronic state itself is a metastable state and sensitive to fast time-varying perturbations, the fluorescence from the excited states can be a sensitive probe of the local fluctuations in crystals.[6] Electrons in an excited state relax to the ground state with a rate $k = k_r + k_{nr}$, where k_r is the radiative transition rate on the order of 10^8–10^9 s^{-1}, and k_{nr} is the rate of the nonradiative transition rate caused by the complex interactions with the thermal fluctuations of the atoms surrounding the fluorescing molecule. Therefore, the variation of the environment with temperature would manifest itself as a lifetime shortening. In this paper, we present results on an attempt to see if the fluorescence decay can be used to monitor the proton motion in ice, particularly the proton ordering transition at 72 K.

Experimental Section

In order to apply the fluorescence method to ice, we doped 2-naphthol molecules ($C_{10}H_8OH$, hereafter referred to as 2-NpOH) into ice crystals as a probe. A single crystal was grown from 2×10^{-3} M aqueous solution of 2-NpOH by a rapid growth modified-Bridgman method.[2] It is known that a
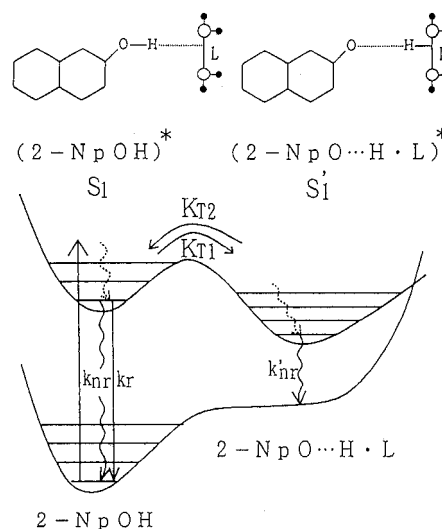
Figure 1. Proton transfer model of 2-NpOH in ice. (○ oxygen atoms, ● hydrogen atoms).

2-NpOH molecule undergoes a strong ESPT (excited state proton transfer) process in aqueous solution,[7] but when it is frozen, ESPT is totally suppressed.[8] However, as shown in Figure 1 one may expect that the excited state (2-NpOH)* (the S_1 state in Figure 1) in ice still has a tendency to transfer a proton to the "anion-like" transient state (S_1' state) and that the transfer rate between them will depend on the proton environment in the neighborhood of the probe molecule.

The fluorescence was excited by the 4 MHz pulse-trains from a synchronously mode-locked dye laser converted to UV ($\lambda = 295$ nm). The incident beam with an energy less than 1 nJ/pulse and a width of 10 ps was focused to about 100 μm in diameter. The fluorescence spectra and its lifetime at 350 nm ($\Delta\lambda = \pm 5$ nm) were measured simultaneously, using a multichannel detector and a time-correlated single-photon-counting system, respectively.

Fluorescence Spectrum from 2-NpOH-Doped Ice

Fluorescence spectra from aqueous solutions of 2-NpOH have two broad bands, one from a neutral NpOH peaked at 350 nm and the other from an anion NpOH$^-$ at 420 nm. In ice at low temperatures, only the neutral band with several vibrational structures remains. It is similar to the spectrum from a single 2-NpOH crystal grown by the vacuum sublimation method. The detailed structures in the spectrum of the doped ice at low

temperatures are not the same for all samples. They depend on NpOH concentration, the growth rate, and the thermal hysterisis. In most cases the fluorescence from the doped ice crystal consists of the strongest peak at 360 nm with bands at 344, 350 nm and shoulders at 366, 380 nm. On heating they gradually become broader and weaker. The sharp peaks that are occasionally observed correspond to those from an isolated molecule in ice. Among them, a peak at $\lambda = 370$ nm disappears rapidly with heating below 70 K.[9] Since the molecular size is larger than the oxygen cage in Ih ice and also the broad band spectrum at higher temperatures is similar to that observed in the molecular beam experiment for the clusters 2-NpOH(H$_2$O)$_n$ with large n,[8] it is most probable that 2-NpOH molecules are included in ice in the form of a clathrate structure and are wetted by water molecules rather than occupying a definite site.

Temperature Dependence of the Fluorescence Lifetime

The observed decay curves can be fitted well to a sum of the two exponential decays. The appearance of the two lifetimes (τ_f and τ_s) was analyzed by the model shown in Figure 1.[10] In this model, the excited electrons are transferred between the S$_1$ and S$_1'$ state with the rates K_{T1} and K_{T2}. Since the "anion-like" ground state is unstable in ice, the electrons in S$_1'$ will either go back to S$_1$ or decay nonradiatively to the neutral ground state. Solving the rate equations, it can be shown that the fluorescence from the S$_1$ state has two components, which are denoted by s (slow) and f (fast).

$$I(t) = k_r N_1(t) \tag{1}$$

$$= k_r A_s \exp(-t/\tau_s) + k_r A_f \exp(-t/\tau_f) \tag{2}$$

where

$$\tau_{s,f} = \frac{2}{(a_1 + b_1) \mp \sqrt{(a_1 - b_1)^2 + 4a_2 b_2}}$$

$$A_s = \{a_2 N_2(0) + (1/\tau_f - a_1)N_1(0)\}/(1/\tau_f - 1/\tau_s)$$

$$A_f = \{-a_2 N_2(0) + (a_1 - 1/\tau_s)N_1(0)\}/(1/\tau_f - 1/\tau_s)$$

and $a_1 = k_r + k_{nr} + K_{T1}$, $a_2 = K_{T2}$, $b_1 = k_r' + k_{nr}' + K_{T2}$, and $b_2 = K_{T1}$ (k and k' corresponds to S$_1$ and S$_1'$ states, respectively, and the number of the electrons in these states are denoted by N_1 and N_2). The transfer rates between S$_1$ and S$_1'$ are given by the sum of the Arrhenius-type thermal process and the tunneling rate, $K_{T1} = A_1 \exp(-\Delta E_1/k_B T) + C_1$, $K_{T2} = A_2 \exp(-\Delta E_2/k_B T) + C_2$. So, in this model the temperature dependence should be observed in both the two lifetimes and their intensities.

As shown in Figure 2a, the fluorescence lifetime τ_s from (2-NpOH)* is satisfactorily reproduced by the model, and it shows a significant decrease above 120 K. This indicates that when the protons and the defects in the neighborhood of a 2-NpOH molecule become mobile, the proton transfer in the 2-NpOH becomes easier and makes the lifetime of the S$_1$ state shorter.[10] The integrated fluorescence intensity also rapidly decreases above 120 K; that is, both of the intensities A_f and A_s decrease with temperature. We show the intensity ratio in Figure 2b rather than the intensity of each component since the former is much more reliable during an (long time) experiment on the temperature dependence. The parameters obtained from the lifetime (Figure 2a) are $k_r = 6.2 \times 10^8$ s^{-1}, $k_{nr} = 1.7 \times 10^5$ s^{-1} deg^{-1}, $A_1 = 1.3 \times 10^{13}$ s^{-1}, $A_2 = 1.3 \times 10^{16}$ s^{-1}, $\Delta E_1 = 0.14$ eV, $\Delta E_2 = 0.21$ eV, and $C_1 = 8.1 \times 10^8$ s^{-1}, $C_2 = 9.1 \times 10^8$ s^{-1}.[11] The temperature independent tunneling rates C_i ($i = 1$,
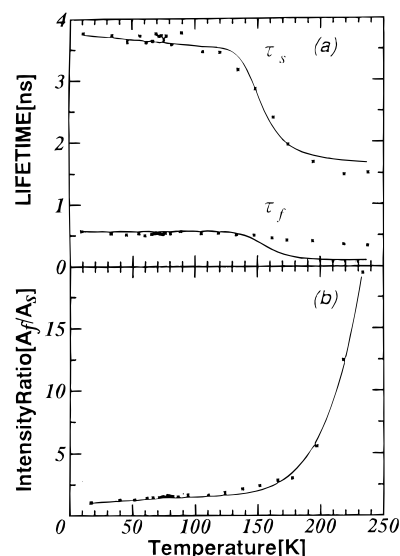

Figure 2. (a) Fluorescence lifetimes (τ_s, τ_f) in 2-NpOH-doped ice. (b) The intensity ratio of the two components in a, A_f/A_s. Solid lines are the values obtained from the fitting to the model given in the text.

2) were not included in ref 10. However, the small but finite intensity of the fast-lifetime component at low temperatures cannot be explained without the tunneling effect. The rates C_i have the same order of magnitude as that observed in benzoic acid,[12] and the values of the activation energies ΔE_i are close to that obtained from the conductivity data (0.19 eV),[13] but smaller than that from the IR data (0.35 eV).[14] Although the fitting to the τ_f for $T > 150$ K is rather poor, it should be noticed that the above parameters determined from the lifetime τ_s also explain the temperature dependence of the observed intensity ratio A_f/A_s of the two components as shown in Figure 2b.[15] Next we tried to see whether the proton ordering transition at 72 K is detectable by the fluorescence method or not.[16] For samples without any heat treatment, both of the lifetimes monotonously decrease on heating (Figure 2a). On the other hand, when a new sample was annealed at 60 K for 5 h[2] before starting a heating process from 10 K, while the change in τ_f is very small, the lifetime τ_s shows a dip at about 75 K (white circles in Figure 3a) and the intensity ratio of the two components A_f/A_s shows a maximum in the same temperature range (Figure 3b). Although the anomaly did not always happen after the annealing and the depth of the dip in the lifetime is not completely reproducible for different samples, it was confirmed that when anomaly is seen, it appears always around 70 K as a decrease of the lifetime and the increase of the intensity ratio. Thus, in spite of the absence of KOH in ice in the present work, the observed changes must be related to the proton ordering phase transition. The reason for the anomaly is considered as follows. In contrast to the dielectric or calorimetric measurements, the fluorescence method is sensitive to the local mobility of protons in the vicinity of probe molecules. Therefore, it does not require the ordering of protons in a macroscopic scale, and the local and short-lived ordering is enough to be detected by fluorescence. Once the local ordering is achieved by the annealing at about 60 K, the increasing instability of the ordered protons on heating toward the phase transition temperature (72 K) will stimulate the ESPT-like process of 2-NpOH and makes the lifetime short.

Discussion

It is interesting that the anomalies of the fluorescence are seen in an extended temperature range around $T_0 = 72$ K rather
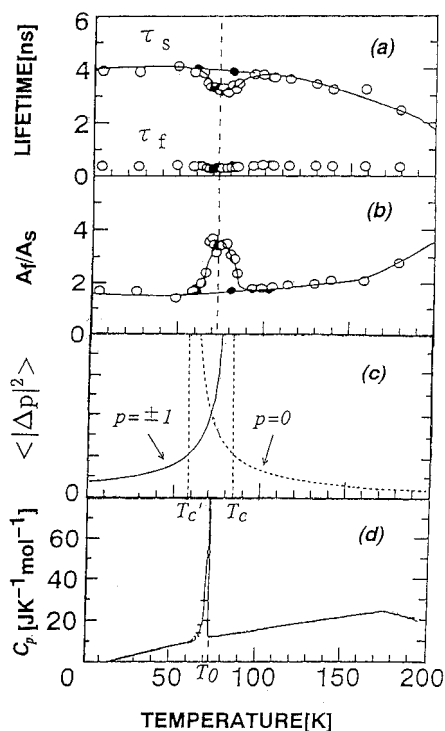
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Figure 3. (a) Fluorescence lifetimes (τ_s, τ_f) in 2-NpOH-doped ice near the Ih−XI transition temperature. The sample was annealed at 60 K for 5 h after the first cooling to 10 K. (b) Intensity ratio A_f/A_s corresponding to a. (● the data on cooling, ○ the data on heating). Solid lines are a guide for the eyes. (c) Fluctuation amplitude of the order parameter calculated from the free energy (ref 5). $p = \pm 1$ and 0 correspond to the ordered and the disordered phase, respectively. (d) Heat capacity of KOH-doped ice (ref 4).

than sharp at 72 K as in the calorimetric measurement (Figure 3d). In the following we shall discuss a possible reason.

Phenomenological theories on this phase transition were proposed by several authors.[5,17] The theory[5] shows that, although the transition should be of second-order from the symmetry requirement (from $P6_3mc$ to $Cmc2_1$), it becomes strongly first-order because of the ice rule restriction. So it would be reasonable that if the ice rule is locally relaxed, the proton ordering in that region occurs more easily than in a perfect crystal. In a first-order phase transition, the "superheating" and the "supercooling" generally occur and the fluctuation in the order parameter will increase toward the stability limit of each phase. We consider that this fluctuation makes the nonradiative decay rate k_{nr} large. Taking into account the entropy for various proton configurations that satisfy the ice rules, Ishibashi[5] has derived the free energy $F(p,T)$ as a function of the order parameter, $p = c_+ - b_+$, where c_+ and b_+ are the numbers of appropriately chosen two-proton configurations around an oxygen atom. In this model, the transition takes place at $T_0 = \gamma/[4Nk_B \ln(3/2)] = 72$ K, where γ is a parameter representing the intrinsic dipole−dipole type interaction which favors the ordering of protons and N is the total number of oxygen atoms. From the free energy one obtains that the stability limit of the disordered Ih phase is at $T_c' = \gamma/2Nk_B = 58.4$ K and that of the ordered XI phase is located at $T_c = \gamma/(2Nk_B \ln 2) = 84.2$ K. The mean amplitude of fluctuations $\langle |\Delta p|^2 \rangle$ can be estimated from the free energy $F(p,T)$ as $\langle |\Delta p|^2 \rangle \propto T(\partial^2 F/\partial p^2)^{-1}$. The calculated fluctuation amplitude is shown

in Figure 3c. Compared with the range of anomalies (Figure 3a,b), the two temperature ranges reasonably well agree. This suggests that when the ice rule restriction is loosened around the probe molecule, the local ordering takes place at a temperature lower than T_c. Then on heating, the proton fluctuations in the ordered structure will increase toward the stability limit $T_c = 84.2$ K and make the fluorescence lifetime shorter. On one hand, the number of probe molecules around which protons are ordered will decrease rapidly above T_0 since the ordered state ($p = \pm 1$) has higher energy than the disordered state ($p = 0$). Above T_c, no ordered region can exist. This would be the reason why the fluorescence anomalies are observed in the finite (65−85 K) temperature region in the present experiment. Similar precursor effects of strongly first-order transitions have been reported by the fluorescence method in a melting transition and the $\alpha-\beta$ transition of a molecular crystal.[6,18]

In conclusion, it was shown that the fluorescence can be used as a new method for the detection of proton motions in ice crystals. Near the Ih−XI transition, the fluorescence lifetime from the doped 2-NpOH molecules becomes shorter, reflecting the effect of the local fluctuations of the proton configuration, which increase toward the stability limit of the low-temperature phase.

References and Notes

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