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Precursor of a strong first-order phase transition: critical speeding-up of fluorescence lifetime in the α – β transition of resorcinol

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Abstract. A precursor of a strong first-order structural phase transition has been detected as the critical speeding-up of the lifetime of the fluorescence excited by a picosecond pulsed laser. In the α – β transition of a resorcinol ($C_6H_4(OH)_2$) crystal, a critical decrease of the lifetimes and an increase in the intensity of the impurity-induced fluorescence were found from about 30 K below T_c . This is in contrast with the fact that the temperature dependence of the Raman spectra and the dielectric constant shows no precursor effect. From a detailed polarization study, large-amplitude and short-lived vibrational fluctuations associated with the phase transition are suggested as a possible origin of the precursor. Despite the apparent contradiction of the fluctuation-dissipation theorem, the results indicate that divergence of the fluctuation also takes place in the first-order phase transition. The method provides a new approach to the study of a first-order phase transition.

1. Introduction

In second-order phase transitions, the average of the order parameter $\langle \eta \rangle$ emerges continuously below the phase transition temperature T_c , and the corresponding susceptibility χ and the fluctuation $\langle |\Delta Q|^2 \rangle$ diverge as $T \rightarrow T_c$. From a dynamical point of view, these divergences can be observed as a ‘softening’ of the collective motion of the order parameter. In displacive-type structural phase transitions of crystals, the ‘softening’ is observed as a decrease of a certain lattice vibrational mode frequency towards T_c (Hayes and Loudon 1979, Bruce and Cowley 1981), and in order–disorder-type transitions, a critical slowing-down of the dielectric response takes place as the ‘softening’ of relaxation rate of the order parameter. Therefore, the ‘softening’ can be regarded as a precursor of the phase transition.

On the contrary, in first-order phase transitions, the order parameter $\langle \eta \rangle$ abruptly jumps to a finite value at T_c . The transition occurs at a temperature where the free energy of one phase accidentally becomes lower than that of the other, and therefore there is no critical divergence of the fluctuations. In such cases it is impossible to detect a precursor of a transition by conventional soft-mode spectroscopic techniques, such as inelastic light or neutron scattering and dielectric dispersion measurements (Scott 1974). However, even when the averaged fluctuation amplitude is small, it may be possible that in a short time period and in a spatially localized region, the atomic displacement from its equilibrium position becomes much larger than the average. The number of occurrences of the large

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fluctuations increases with temperature, and eventually grows into a nucleus of the new phase as $T \rightarrow T_c$. Therefore, such short-lived local fluctuations can be taken as a precursor of a strongly first-order transition if they are detected at temperatures far from T_c .

Recently, it was shown that in the α - β transition of a resorcinol crystal, the precursor can be detected with a picosecond pulsed laser (Shigenari *et al* 1991). The lifetime of the fluorescence decreases sharply towards T_c , indicating critical speeding-up from about 30 K below the transition. In the present paper, we describe the related experimental results and the details of the method used for the detection of the precursor. The sample preparation, dielectric measurement as well as the Raman and fluorescence spectrum are given in the next section. The results of the analysis on fluorescence lifetime and a discussion of the possible mechanism of the 'critical speeding-up' are given in section 3.

2. Experiment and results

2.1. Sample preparation and the dielectric measurement

Resorcinol, *m*-dihydroxy benzene ($C_6H_5(OH)_2$), is a widely used organic chemical with two isomers, hydroquinone and pyrocatechine. It is a molecular crystal with four molecules in a unit cell as shown in figure 1. The stable structure at room temperature is called the α phase (Robertson 1936). It undergoes the α - β transition at about 80°C (Robertson and Ubbelohde 1938). The transition temperature T_c varies widely and cannot be precisely determined because of its first-order nature and large hysteresis. T_c was found to be dependent on the rate of heating and sometimes also on samples†. In our fluorescence lifetime measurements, the transition temperature was determined from both Raman spectra and direct observations, and we took it to be 358.7K, although the measured T_c was slightly different for different samples.

The space group of both phases is the orthorhombic (C_{2v}^9 , $Pna2_1$) (Bacon and Lisher 1980). Although the symmetry is the same, the atomic positions and the orientations of the molecules in a unit cell are drastically changed by the transition, resulting in an elongation of the unit cell along the *b* axis and a contraction along the *a* axis. The two hydroxy radicals are symmetrically attached to the benzene nucleus in the α phase but asymmetrically in the β phase. Accordingly, the network of hydrogen bonds in the two phases is completely different. The spiral network along the *c* axis in the α phase is changed to chains along the *a* axis. The difference is so large that a single α crystal becomes a milky-white β polycrystal when it is heated above T_c . Once an α sample undergoes the transition to β , it remains in the β phase at least a few days after it is cooled to room temperature. The supercooled β sample slowly goes back to the stable α phase with random orientations.

Crystals in the α phase were grown from an aqueous solution by a slow cooling method. Crystals of about $25 \times 10 \times 13$ mm in size were grown in 40 days and were cut and polished along the crystal habit parallel to the *a* and *c* axes. In the course of growing, the solution gradually became dark red in colour and the grown crystals also were of a thin brown colour. Crystals from a newly prepared solution are transparent and those from an old solution have a dark brown colour. This colouring is probably due to some complexes and/or impurities produced by a reaction in the solution. They might be benzene complexes, such as fluorescein or xanthene, which have a fluorescence band in the visible

† The value of T_c seems to scatter, depending on the sample. Ebisuzaki and co-workers (1987) reported $T_c = 369 \pm 4$ K, while $T_c = 347$ K is given by Bacon and Lisher (1980). In the present fluorescence experiment T_c was 358.7 K, but in a Raman measurement for a different sample, it was 354.4 K.

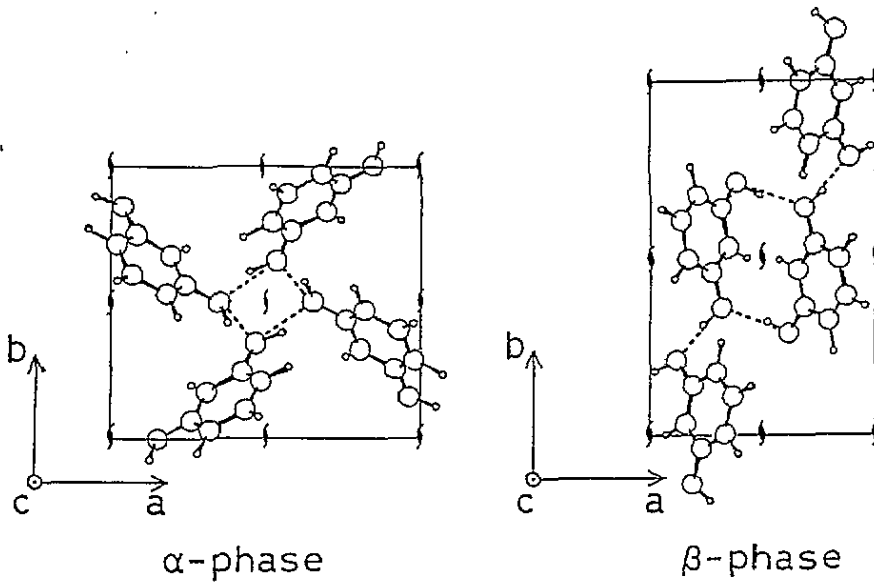


Figure 1. Unit cell of a resorcinol crystal (Robertson *et al* 1938). Large circles represent carbon and oxygen atoms. Small circles represent hydrogen atoms. The unit cell size, orientations of molecules as well as the hydrogen bond network (shown by the dotted lines) drastically change at the α - β transition temperature.

region, since it is known that by heating resorcinol with phthalic anhydride it changes into the dye 'fluorescein'. The amount of impurity is scarce, so that no conventional chemical analytic methods could assign the impurities. We took advantage of this impurity-induced fluorescence to investigate the precursor effect of the phase transition. Several samples with different darknesses were used for fluorescence lifetime measurements, but the results are not dependent on samples.

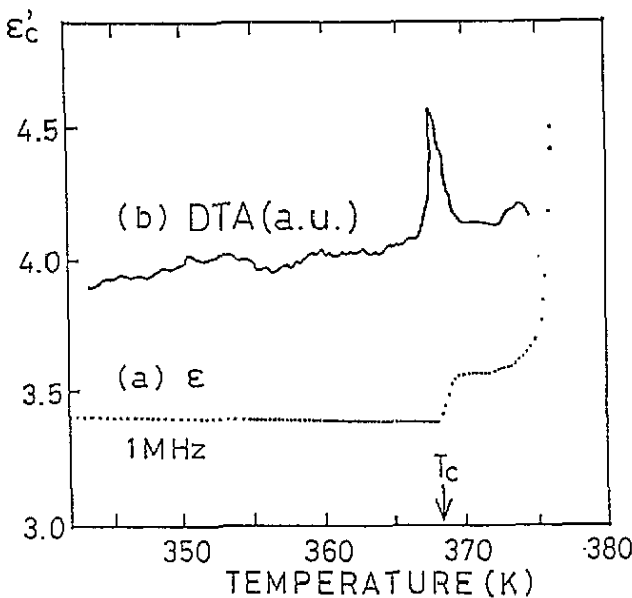


Figure 2. (a) Temperature dependence of the dielectric constant ϵ_c at 1 MHz, and (b) DTA signal. The sharp increase of ϵ_c at $T \approx 375$ K in the β phase is due to the decomposition of the sample.

Dielectric measurements and DTA (differential thermal analysis) were performed to check the overall temperature behaviour of samples (figure 2). The dielectric constant at 1 MHz along the *c* axis, $\epsilon_c = 3.4$, does not vary up to T_c , but starts increasing above T_c . The sharp increase at higher temperatures is probably due to the decomposition and evaporation of the sample. The DTA also showed a narrow peak at T_c . Both data confirm the first-order nature of the transition.

2.2. Raman and fluorescence spectrum

First, we measured the conventional fluorescence and Raman spectrum using a 514.5 nm Ar laser at room temperature (figure 3). In a newly prepared aqueous solution (figure 3(b)), several sharp Raman lines above 300 cm^{-1} were observed as well as the broad bands originating from the hydrogen bonds at about 3070 cm^{-1} . When the solution was left at room temperature for a few weeks, there appeared two fluorescence bands peaked at 545 nm and 610 nm and most of the Raman lines were masked by the fluorescence (figure 3(a)). The spectrum of a weakly fluorescing crystal sample (figure 3(d)) shows sharp Raman peaks below 300 cm^{-1} in addition to the higher-frequency modes observed in the pure liquid. In a strongly luminescing crystal sample, those Raman peaks are weakly seen on top of the fluorescence bands (figure 3(c)). Although the shape and intensity of the two fluorescence bands depend on the polarization configurations and the sample orientation, the overall profiles of the spectrum are the same in all cases. The integrated intensity of the fluorescence gradually decreases with heating; at about 70°C it is a fifth of that at room temperature.

Table 1. Symmetry of states and the selection rules for the dipole transition and Raman scattering in C_{2v} symmetry.

Irreps	Selection rule		Number of vibrational modes		
	Absorp. emission	Raman	Acoust.	Librat.	External
A_1	c	aa, bb, cc	1	2	3
A_2		ab		3	3
B_1	a	ca	1	2	3
B_2	b	bc	1	2	3

The high-frequency modes above 300 cm^{-1} observed both in solution and in crystal are the internal modes of a resorcinol molecule and are unaffected by the transition. Those below 250 cm^{-1} are the external lattice vibrational modes. Symmetries and the number of the external modes are shown in table 1. Since a soft mode, if it exists, must be totally symmetric and Raman active in the low-temperature phase (Worlock 1971, Shigenari 1973), we measured the temperature dependence of the spectrum in the (a,a)-polarization configuration (figure 4) (see Ebisuzaki and co-workers 1987). Details of the Raman spectrum will be reported elsewhere. The spectra mostly agree with those given by Penot and Mathieu (1955) and Tripathi (1981).

The A_1 mode frequencies below 200 cm^{-1} are plotted in figure 5. All the observed modes, including the relatively strong librational modes U, V and W, at about 100 cm^{-1} show no temperature dependence up to T_c , i.e. no softening was recognized. At T_c , however, they change significantly, jumping to the lower-frequency side, indicating that those modes are sensitive to the structural change by the transition. In the β phase, the modes again become insensitive to temperature. These sudden changes are generally expected for a strong first-order phase transition.

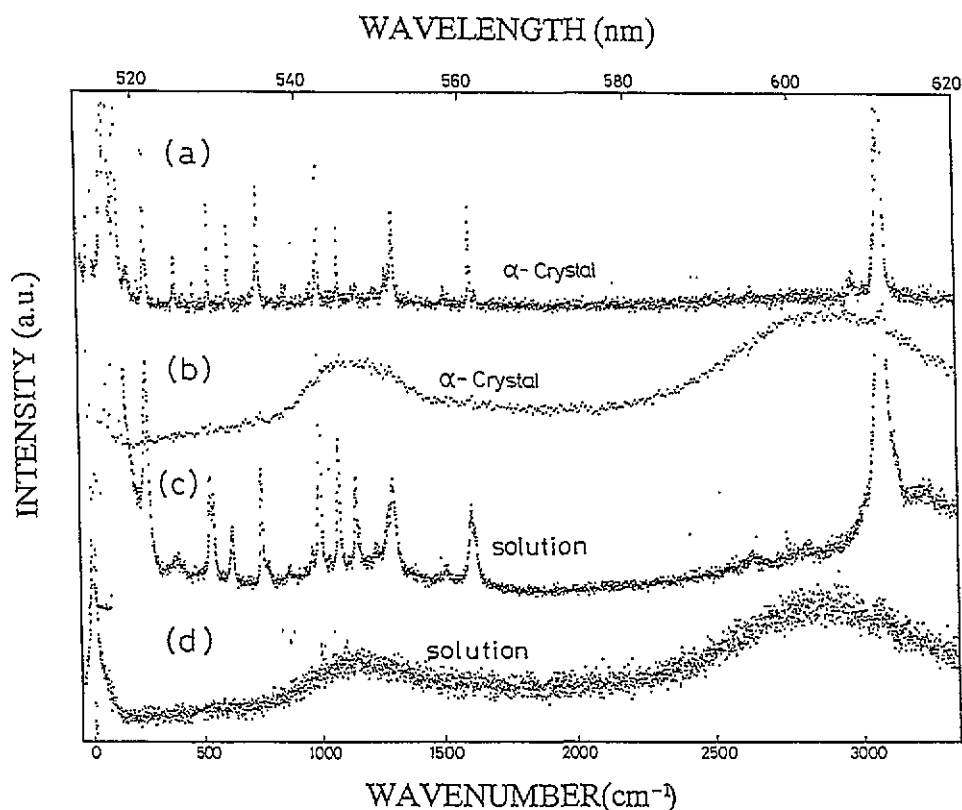


Figure 3. Raman and fluorescence spectrum at room temperature. (a) Spectrum of a pure crystal sample in c(a,c)b configuration. (b) Spectrum from a coloured sample with strong fluorescence bands. (c) Spectrum from a newly prepared aqueous solution of resorcinol (two hours after preparation). (d) Spectrum from an aqueous solution of resorcinol (three weeks after preparation).

2.3. Fluorescence lifetime measurement

2.3.1. Experiment. The lifetime of the fluorescence was measured using the time-correlated single-photon counting method (O'Connor and Phillips 1985). As the excitation light source, a mode-locked cw-YAG laser (Spectra-Physics 3800) and a cavity-dumped R6G dye laser system were employed. The output pulse has 8–10 ps width with a repetition rate of 4 MHz. The averaged output power of about 80 mW at 590 nm was focused into the sample set in an optical furnace. A single pulse energy was kept less than a few tenths of one nJ, so that one excitation pulse barely emitted more than one fluorescence photon. Fluorescence pulses near the band peak energy of 600 nm were analysed by a monochromator (Spex 1701) and detected by a MCP photomultiplier (HTV-1564U). In order to measure the time intervals between the excitation and the fluorescence photons, the outputs of the photomultiplier and an avalanche PIN photodiode (ANTEL ARS-5) which monitors the laser pulses were fed into a TAC (time-to-amplitude converter, Ortec 457) as a start and a stop pulse, respectively. Each time interval datum was sent to a pulse height analyser and stored into a computer. The signal was accumulated until the number of counts at the head of the decay curve reached 10^4 . It takes typically 15 min for a decay curve. The choice of the wavelength was not crucial because the bandwidth of the fluorescence is rather broad (about 20 nm).

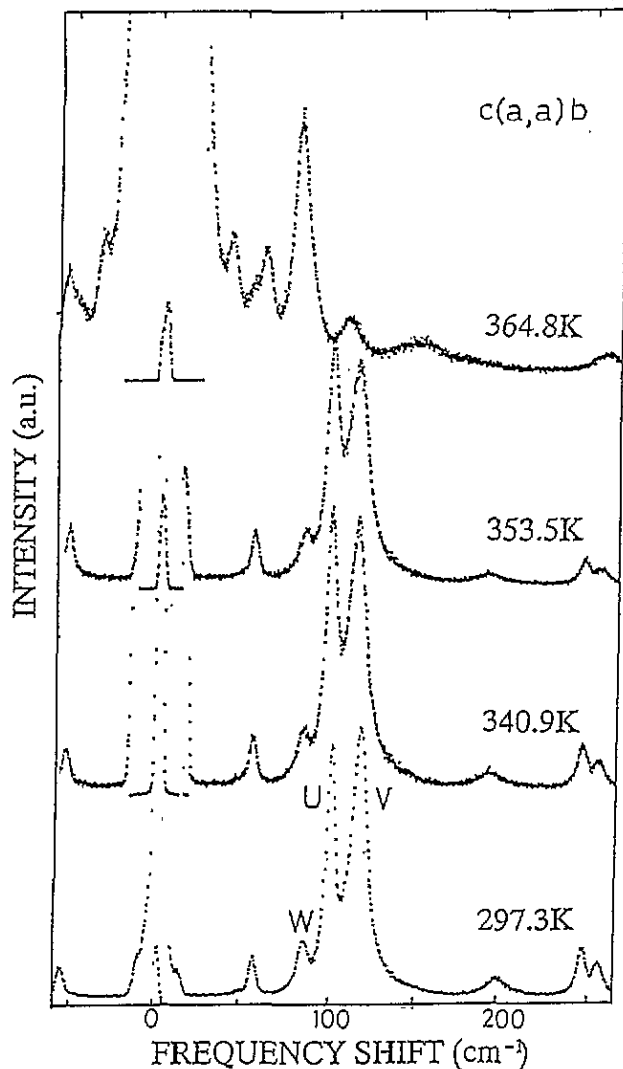


Figure 4. Raman spectrum of A_1 modes below 300 cm^{-1} measured in $c(a,a)b$ configuration. The modes denoted by U, V and W correspond to librational modes of a single molecule. Modes are named after Penot and Mathiu (1955).

2.3.2. Fluorescence decay at room temperature. Fluorescence decay curves at room temperature are given in figure 6 for various polarization configurations. Note that the vertical scale is logarithmic. The second small peak observed at 12.5 ns is the leak of the 80 MHz excitation laser pulses from the cavity dumper of the dye laser. We notice that the decay curves can be grouped into two types. If the polarization of either the incident laser or fluorescence is along the a axis, the fluorescence decay curve at room temperature can be well described by a single and relatively slow decay rate (about 2.3 ns), while if one or both of the polarizations are parallel to the b or c axis, the fluorescence is weak and the decay is mostly governed by much faster processes (table 2). This clear difference means that at least two different decay routes are involved, which will be discussed in the next section.

Since in most cases the decay curves could not be represented by a single time constant, we analysed the curves by fitting to a sum of two exponentially decaying functions:

$$f(t) = C_s \exp(-t/\tau_s) + C_f \exp(-t/\tau_f). \quad (1)$$

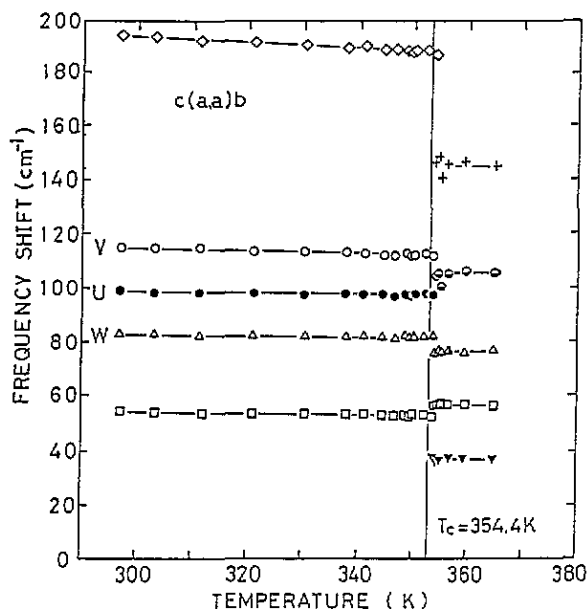


Figure 5. Temperature dependence of external lattice modes observed in the Raman spectrum in $c(a,a)b$ configuration.

In the data analysis, we first convoluted the above function with the instrumental response function measured from the elastic scattering of the excitation pulses. The halfwidth of the response function was 130ps, which is limited by the response of the photomultiplier and the electronics circuits. The data could be well fitted in the time range 0–8 ns by (1). Obtained decay constants are listed for various configurations of polarizations and crystal orientations in table 3. We note that the decay time is primarily determined, not by the crystal orientation, but by the polarization of light.

2.3.3. Temperature dependence of the fluorescence decay. The temperature dependence was measured using an optical furnace with the temperature controlled to within $\pm 0.2\text{K}$. To avoid surface deterioration, paraffin oil was thinly spread on the surface. The decay curves are given in figures 7 and 8 for the configurations $c(a,a)b$ and $c(b,c)a$, respectively. The uppermost curve of figure 7 is for the crystal in the β phase. In the β phase, the sample became a milky-white polycrystal and therefore no polarization dependence was observed. The most remarkable feature is that, as the temperature approaches T_c , an additional fast component appears at the head of the decay curves in the $c(a,a)b$ configuration, and gradually increases its intensity (see figures 9 and 10). We note that the two lifetimes in the α phase considerably decrease as the temperature becomes closer to T_c , and both of them seem to tend to zero towards a certain temperature above T_c .

The temperature dependence of the lifetime and the intensity in the $c(a,a)b$ configuration is given in figure 9. Note that the change in the fast component, as given in figure 10, is more significant than the slow component. The τ_f at T_c (0.2 ns) decreases to a value of less than a quarter of that at room temperature, and the relative intensity of the fast component (C_f/C_s in (1)), shows a critical increase towards T_c .

In the β phase above T_c , the fluorescence decay curve is again represented by a single lifetime which is approximately equal to the average of the two lifetimes in the α phase. When the sample is cooled to room temperature, it remains in the supercooled β phase for at least one week. The open circles and squares in figure 9, show the lifetime measured in the heating process of the supercooled β -phase sample. In contrast to the initial heating in

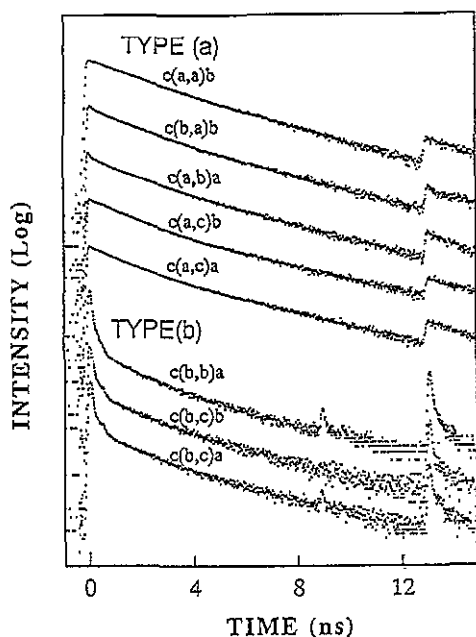


Figure 6. Fluorescence decay for several polarization geometries at room temperature. Note that the fast decay component is absent in type-a fluorescence, but it is dominant in the type-b geometry. Peaks at about 9 ns and 12.5 ns are artificial noise.

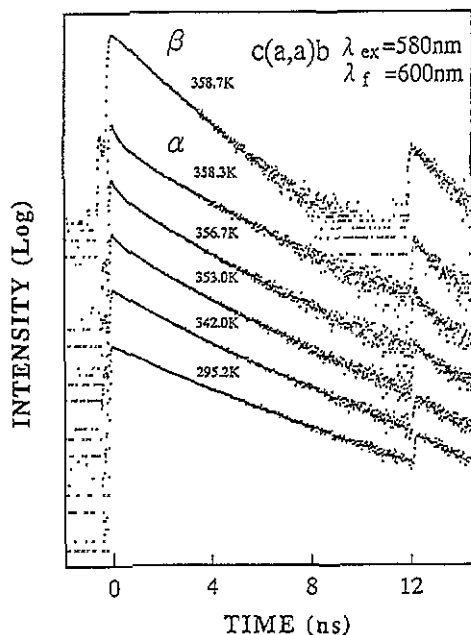


Figure 7. Temperature dependence of the fluorescence decay curve in $c(a,a)b$ configuration. Type-a decay has only a slow component at room temperature, and a fast component appears as $T \rightarrow T_c$. The uppermost data is in the β phase. A fast decay component appears at the head of the decay curve. The second peak at about 12 ns is due to the leak of the cavity dumper of the dye laser.

Table 2. Fluorescence lifetimes at room temperature for 24 possible polarization configurations and crystal orientations. In type-a fluorescence, the fast component τ_{fast} is very weak at room temperature, so it is shown in parenthesis. Inclusion of τ_{fast} gives a slightly better fit to data.

Polarization and orientation configuration	Type-a				Type-b	
	$c(a,a)b$ $b(a,a)c$	$c(b,a)b$ $c(a,b)a$ $a(b,a)c$	$c(a,c)b$ $c(a,c)a$ $a(c,a)c$	$a(c,a)b$ $b(a,b)a$ $b(a,b)c$	$a(c,c)b$ $b(c,c)a$	$c(b,c)b$ $c(b,c)a$ $a(c,b)c$ $a(b,c)b$ $b(c,b)a$ $b(c,b)c$
τ_{slow} (ns)	2.27 ± 0.10	2.39 ± 0.10	2.56 ± 0.10	2.30 ± 0.10	1.71 ± 0.10	1.95 ± 0.10
τ_{fast} (ns)	(0.80)	(0.60)	(0.82)	(0.65)	0.07 ± 0.05	0.058 ± 0.05

the α phase, the lifetime decreases monotonically with temperature and does not show any critical behaviour around T_c . This clearly indicates that the temperature behaviour observed in the α phase is directly related to the α - β structural phase transition.

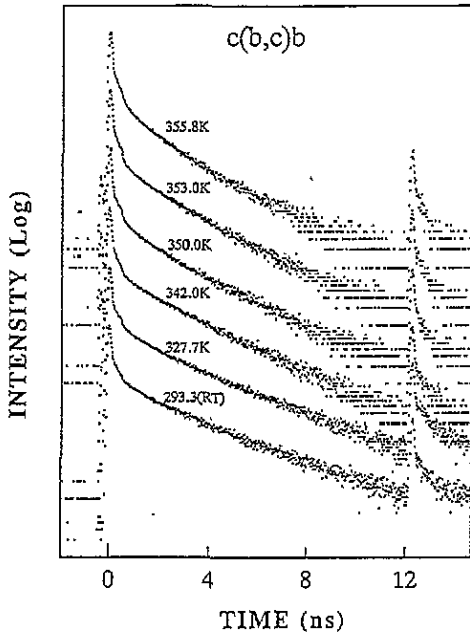


Figure 8. Temperature dependence of the fluorescence decay curve in $c(b,c)b$ configuration. Note that in type-b configurations, fast decay already exists at room temperature.

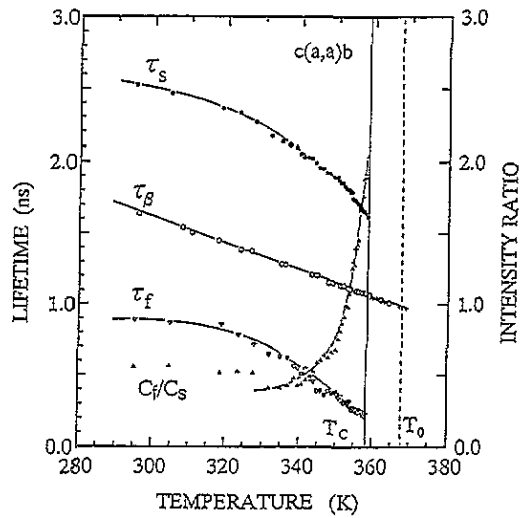


Figure 9. Temperature dependences of the fluorescence lifetime in $c(a,a)b$ configuration. The α -phase lifetimes τ_s (full circles) and τ_f (open triangles) decrease with temperature. The β -phase lifetimes τ_β are given by crosses for $T > T_c$ and by open circles for the supercooled β -phase. The full triangles are the intensity ratio (C_f/C_s) in equation (1). The full curves are the curves fitted to $(T_0 - T)^{-1}$ dependence (equation (5)) with $T_0 = T_c + 8.3$ K.

3. Discussion

3.1. The fluorescence lifetime and a new decay route

In this section we discuss why the fluorescence lifetime could be the precursor of a transition from far below T_c . In a three-level system shown in the left-hand side of figure 11(a), the fluorescence intensity $I(t)$ from the level $|e\rangle$ to $|g\rangle$ is given by

$$I(t) = kn_e(t)$$

$$n_e(t) = \frac{\gamma n_0 I_0}{\gamma - (\eta + k)} \{ \exp[-(\eta + k)t] - \exp(-\gamma t) \} \quad (2)$$

where k and η are the radiative and non-radiative transition rates from the excited state $|e\rangle$, respectively, and γ is the relaxation rate among the excited states. The number of electrons in the excited and the ground state are denoted by $n_e(t)$ and $n_0(t)$, the latter being proportional to the impurity concentration; I_0 is the exciting laser intensity at time $t = 0$. Since the relaxation rate γ is usually much larger than η and k , especially when the energy difference between the exciting and fluorescing photon is small as in the present case, the fluorescence intensity is simply proportional to the number of the electrons in the excited state $|e\rangle$:

$$I(t) = kn_0 I_0 \exp[-(\eta + k)t]$$

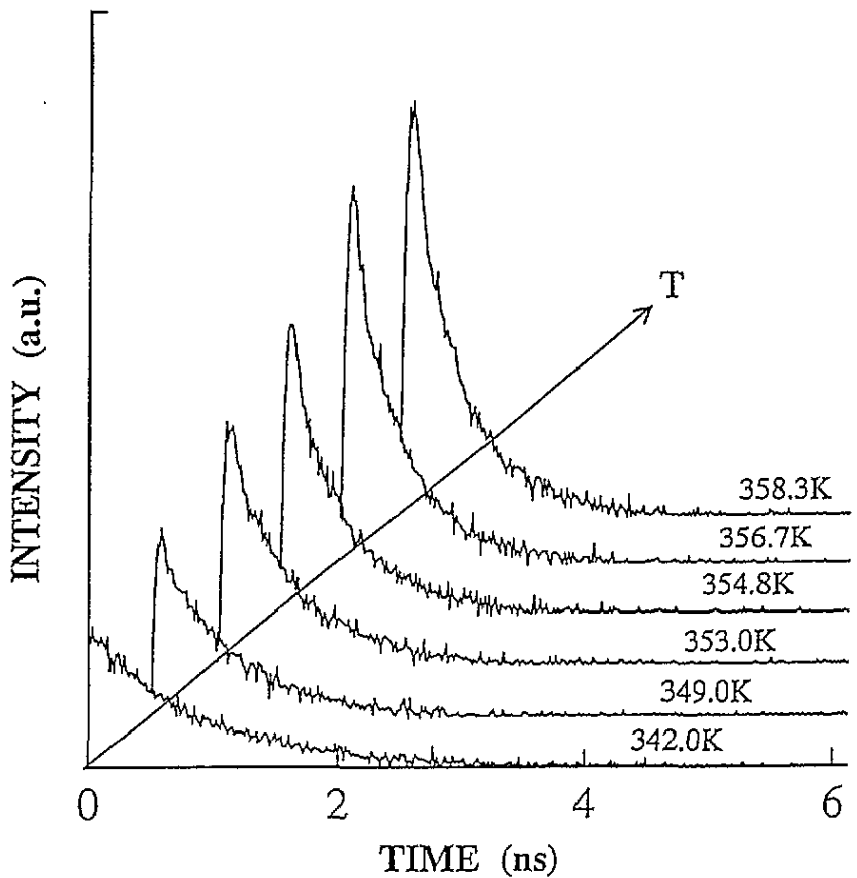


Figure 10. Temperature dependence of the fast component in c(a,a)b configuration. The curves were obtained by subtracting the slow component and the background from the raw data.

and the observed lifetime is given by $\tau = (\eta + k)^{-1}$.

The effects of temperature on fluorescence may be separated into two parts; one is the non-critical background due to thermal expansion and so on, and the other is a critical part reflecting the phase transition. We estimate the background $(1/\tau)_{\text{bgd}}$ from the temperature dependence in the supercooled β phase (figure 9) as $\tau_{\text{bgd}} = 1.2$ ns at T_c and $d\tau_{\text{bgd}}/dT = -9.3$ ps K $^{-1}$.

If the effect of the phase transition was simply to change the rate η and/or k in the above equation, the decay curves would still be a single exponential form. The appearance of the new fast component as $T \rightarrow T_c$ indicates that a new decay route is opened, and that the electrons in the excited states become more rapidly decreasing via a new route $|e'\rangle$ which is sensitive to the phase transition. Then, as shown in figure 11(a), the fluorescence intensity is represented by

$$I(t) = n_0 I_0 \{ k \exp[-(\eta + k)t] + k' \exp[-(\eta' + k')t] \} \quad (3)$$

which is equivalent to (1) with $C_s = n_0 I_0 k_s$ and $(1/\tau_s) = \eta + k$ for the slow component, and $C_f = n_0 I_0 k'$ and $(1/\tau_f) = \eta' + k'$ for the fast component, respectively.

We now discuss what kind of perturbation could open up the new decay route. As mentioned in section 2 (table 2), the decay curves at room temperature can be grouped

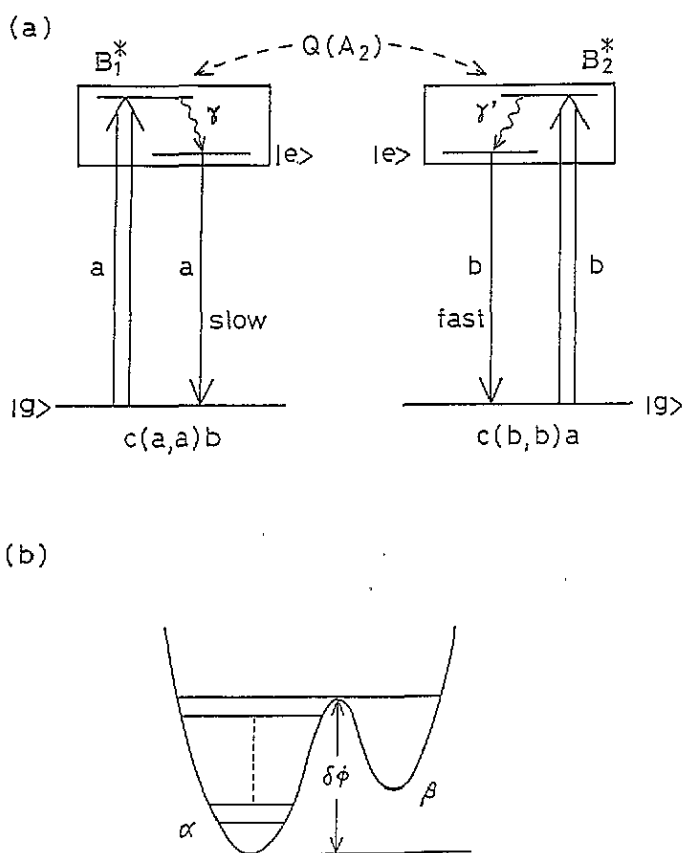


Figure 11. (a) A model of fluorescence decay routes; a slow decay via B_1^* and a fast decay via B_2^* . The two states are mixed by a A_2 vibration fluctuation. The case of $c(a,a)b$ and $c(b,b)a$ configurations correspond to cases a and b, respectively. The a or b beside the arrows represents the polarization of the light. (b) A model of the potential. A schematic potential for a resorcinol vibration. The left and right well correspond to the local α and β structures, respectively. When a large amplitude vibration with an energy close to the potential barrier $\delta\phi$ is excited, it may create a momentary β -phase structure and disturb the crystal field seen by the excited electronic states.

into two different types. Type-a fluorescence (upper half of figure 6), has only a slow ($\tau_s \sim 2.3$ ns) decay component, while type-b fluorescence (the lower half of figure 6), has an additional relatively strong fast decay component. We note that the temperature dependence of type-b fluorescence (figure 12) is also different from type-a fluorescence.

Although the slow component (τ_s^b) of type-b fluorescence decreases in a similar way to the τ_s of type-a fluorescence, the intensity and lifetime of the fast component ($\tau_f^b < 0.1$ ns), characteristic of type-b fluorescence, do *not* change from room temperature to T_c (see also figure 8). From the selection rules for dipole transitions in C_{2v} symmetry (table 1), the difference could be interpreted as follows (figure 11(a)): at room temperature, the fluorescence from a B_1^* state excited by a-polarized light, decays with a slow time constant $\tau_s = 2.3$ ns, while a B_2^* state excited by b-polarized light decays with a much faster rate at any temperature. As $T \rightarrow T_c$, one may think that the new fast decay route in type-a fluorescence was brought by a perturbation that causes a mixing between the excited states, B_1^* and B_2^* .

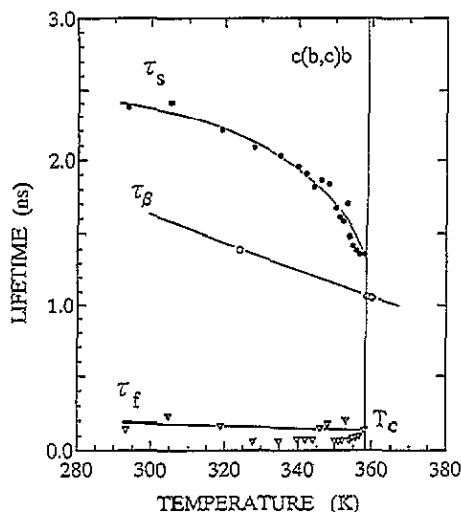


Figure 12. Temperature dependence of the fluorescence lifetime in c(b,c)a configuration (type-b).

More specifically, since $B_1 \otimes B_2 = A_2$, the perturbation H' can be represented as

$$\langle B_2^* | H' | B_1^* \rangle = \langle B_2^* | [dV/dQ(A_2)]_0 | B_1^* \rangle \Delta Q(A_2) \quad (4)$$

where V is the adiabatic crystal field potential seen by the excited state electrons. In other words, it is the fluctuation of a A_2 -symmetry vibration $\Delta Q(A_2)$ that causes the mixing[†]. The B_1^* excited electrons may then decay via two routes: (figure 11(a)). Since the decay time via the B_2^* state is already fast at room temperature and remains fast up to T_c (figure 12), the opening of the B_2^* route gives rise to the fast component in type-a data. The critical speeding-up of the lifetime and the increase in the intensity is, therefore, ascribed to the increase of the fluctuation $\langle |\Delta Q_{A_2}| \rangle$. Resorcinol has actually several A_2 symmetry vibrational modes (table 1). As shown in figure 4, the modes U, V and W change with the phase transition. These modes have been assigned as the librational modes of a single resorcinol molecule around the three principal axes of inertia (Ebisuzaki and co-workers 1987). Therefore, we suspect that the fluctuation in the A_2 librational mode is most effective in the appearance of the critical speeding-up.

It should be mentioned that because of the randomness of the perturbation H' , the effect of H' will not be a coherent mixing; otherwise, mixing of B_2^* with B_1^* would give a modified, but still a single, decay constant.

3.2. Divergence of the fluctuation and the precursor

Based on the idea that the critical perturbation of the excited state $|e'\rangle$ is proportional to the fluctuation of atomic displacement ΔQ , we assume that the average of this effect diverges at a certain temperature as $\langle |\Delta Q|^2 \rangle \propto (T_0 - T)^{-1}$, which is correct in mean-field theory of second-order transitions. Then, from (1) and (4), it is expected that the fluorescence will have the following temperature dependence:

$$(1/\tau_f) = \eta' + \text{constant} \times (T_0 - T)^{-1}$$

$$C_f = \text{constant} \times (T_0 - T)^{-1}.$$

[†] Here we consider only the case when the fluorescence is excited to B_2^* state by b-polarized light. If the polarization is along the c axis, A_1^* is excited, and a similar argument as in the text would be valid for B_2 vibrational fluctuations $\Delta Q(B_2)$.

Actually, as shown by the full curves in figure 9, we found that the data could be well fitted to the following equation:

$$(1/\tau_f) = (1/\tau)_{cr} + (1/\tau)_{bgd} = c/(T_0 - T) + aT + b \quad (5)$$

with $a = 5.6 \times 10^6 \text{ s}^{-1} \text{ K}^{-1}$, $b = -1.1 \times 10^9 \text{ s}^{-1}$, $c = 3.0 \times 10^{10} \text{ K s}^{-1}$ and $T_0 = 367 \text{ K}$. The temperature dependence of the non-critical part η and η' was included in the background $(1/\tau)_{bgd}$, which was determined from the data for the supercooled β -phase. It should be noted that not only the lifetime but also the intensity ratio C_f/C_s in (1) can be well fitted to $(T - T_0)^{-1}$ using the same $T_0 (= 367 \text{ K})$ as obtained from $(1/\tau_f)$. These results support the assumption that the fluctuations tend to diverge towards a temperature T_0 , being about 8 K above T_c . T_0 is considered to be the temperature where the local α -structure loses its stability.

It is interesting that, despite the discontinuous nature of the phase transition, the divergence of the fluctuation of $\langle |\Delta Q|^2 \rangle$ takes place in the present strong first-order case. Linear response theory (Kubo 1957), says that the power spectrum of the mean square average of the order parameter fluctuation in a thermodynamical equilibrium state is proportional to the susceptibility $\chi(\omega)$ (fluctuation-dissipation theorem). The apparent discrepancy must be ascribed to the difference in the nature of the fluctuation. In this experiment what was measured was the fluorescence photons emitted during a short time interval and from localized impurity centres. Consequently, the fluctuations that have influence over the fluorescence are different from the thermodynamically averaged fluctuations.

From this point of view, the difference between the precursor and the nucleation or embryo model of the first-order phase transitions (Gunton and co-workers 1983, Yamada 1988) might be understood by the following model. In the stable α -phase structure, a resorcinol molecule is considered to be in a deep asymmetric double-well potential shown in figure 11(b), which schematically represents a local thermodynamic potential as a function of the normal coordinate of vibration Q , being most effective to destabilize the α -phase (the A_2 mode in this case). The shape and depths of the potential would not change significantly with temperature up to T_c . For $T \ll T_c$, a molecule stays in the deep α -phase well. If the temperature is sufficiently close to T_c so that the average vibrational energy becomes comparable to the barrier $\delta\phi$, fluctuations give rise to a relatively long-lived cluster (nucleus) of the β -phase. But long before the average energy exceeds $\delta\phi$, it would be very probable that the vibrational energy surpasses the barrier for a short time. Such an instantaneous fluctuation, which is not detectable by conventional spectroscopic methods, could have an influence on electronic states as a perturbation of the crystal field. Therefore, the fluctuation can manifest itself as the precursor in the lifetime of the fluorescence at temperatures even far from T_c . The effect of such fluctuations may also appear either in a specific heat measurement or as broadening of the Raman spectra. Experimentally, no broadening was observed in Raman spectra. We think the fluorescence is much more sensitive to the short-lived fluctuations than the inelastic light scattering or heat measurement.

It is difficult to know how often or how long such a thermodynamically unfavoured fluctuation could exist in a real system. However, there are several interesting experimental evidences in the field of infrared-laser induced unimolecular reactions that might be related to our problem. It was shown that by exciting a polyatomic molecule with a sub-nanosecond pulsed IR laser, a part of the molecule can be excited to a high vibrational hot state while leaving the other part relatively cold (Bloembergen and Yablonoitch 1978). The highly excited molecules produced by the multi-photon absorption were detected with good time resolution by, for example, the resonance fluorescence method. This indicates

that highly excited states of a selected mode produced via a channel different from the thermodynamically favoured one can survive long enough to be detected before they vanish by relaxation to the rest of the molecule. The timescale may be of the order of 10^{-9} – 10^{-12} s $^{-1}$. In this context, we believe that the thermal energy and the large anharmonicity of the crystal related to the phase transition are sufficient to boost molecules into the above-mentioned high vibrational states surpassing the potential barrier $\delta\phi$.

4. Conclusion

A precursor of the strong first-order structural phase transition was detected in the α – β phase transition of a resorcinol crystal. It appears as the critical speeding-up of the fluorescence lifetime. The origin of the precursor is considered to be the critical divergence of large-amplitude short-lived fluctuations of a librational mode that disturb the crystal field seen by the optically excited electrons. Since the fluctuation is a localized one instead of a long-wavelength phonon mode (soft mode), the detection of the precursor in this work is consistent with the absence of the soft mode in the Raman spectrum. The results indicate a divergence of this kind of fluctuation, despite the apparent contradiction with the fluctuation-dissipation theorem.

The present method may provide a new approach to studies of other kinds of first-order phase transitions, including melting transitions of solids, and may be applied to foreseeing a transition without making a direct contact with a sample.

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