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Cryogenic studies, site selectivity and discrete fluorescence in salicylic acid dimer

P.B. Bisht [1], H.B. Tripathi, D.D. Pant

Photophysics Laboratory, Kumaun University, Sleepy Hollow, Nainital, 263 001, India

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Abstract

Cryogenic effects (10–293 K) on the photophysics of salicylic acid (SA) dimer have been studied using steady state and time-resolved spectroscopic techniques. SA dimer shows two emissions at approximately 390 nm (dimer, D) and approximately 430 nm (tautomer, T), formed by cyclic double proton transfer plus fast excited state intramolecular proton transfer (ESIPT), at low temperatures; a vibrational structure also develops which is due to C=O and OH stretches. On red edge excitation (REE), only the dimer-type (UV) emission is observed, which shifts with excitation energy resembling emission due to site selectivity. Due to the asymmetry of the double potential energy curves of D and T, all dimers can be trapped in the D minimum. The UV emission of the dimer is accompanied by the Stokes' shifted tautomer emission on excitation at 1050 cm^{-1} higher than the (0,0) band of D, which is interpreted as the barrier height of the double potential energy curves of D and T. Time-resolved studies at various temperatures have helped to clarify the photophysics of crystalline SA.

Keywords: Cryogenic studies; Site selectivity; Fluorescence; Salicylic acid dimer

1. Introduction

In previous papers, we have reported that concentrated solutions of salicylic acid (SA) in hydrocarbon solvents at 293 K show overlapped UV (approximately 370 nm) and blue (approximately 450 nm) emissions of the dimer, whereas the monomeric molecule emits only at 450 nm [1,2]. As suggested by Weller and others [3–5], an excited state intramolecular proton transfer (ESIPT) from the vicinal hydroxyl group to the carbonyl group takes place in the SA molecule. In the dimer, UV emission was suggested [1] to be due to the dimeric form D, and a tautomeric form T which undergoes a fast ESIPT reaction gives rise to a blue emission. Crystalline SA which is in the dimeric form behaves as a concentrated solution. In agreement with the behaviour of other carboxylic acid dimers, Raman spectra show that the SA dimers can undergo a fast ground state double proton transfer, but at 80 K the asymmetry of the double potential curves of D and T traps all the molecules in the D minimum [6]. The energetic difference between the two potential minima is approximately 150 cm^{-1}. On excitation at the resonance absorption band of D, only the UV emission is observed. With increasing excitation energy, the blue emission appears and the UV and blue emissions occur with optimum intensity on excitation above the barrier. At this stage, even at 80 K, both emissions have the same lifetime. The excitation and absorption spectra of the monomeric form are slightly blue shifted (311 nm) compared with the dimeric form (315 nm). Both emissions in the dimeric form have the same lifetime and identical excitation spectra at 293 K. This is possible because of the fast proton transfer in the ground state, so that the two potential curves merge. On the other hand, two lifetimes appear at 80 K, with resonance excitation of D, which finally become monoexponential on excitation at energies above the barrier. It appears that the distinction between D and T vanishes due to tunnelling. On absorption by D to a vibronic excited state above the barrier, where the nuclear coordinates remain unchanged and a new barrierless potential surface of the proton is established by the fast redistribution of electronic charge, the blue emission is observed.

Certain earlier observations, such as the two lifetimes on resonance excitation of D, are unclear. Possibly various oligomers or distorted emitters contribute weak emission. In this paper, we report our studies on solid SA up to 10 K. Emission from different sites (oligomers, etc.) has been observed with red edge excitation (REE). The excited state tautomerization of the dimer on higher energy excitation has been discussed and it has been found that the ESIPT reaction takes place

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[1] Present address: Laboratory of Chemistry, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan.

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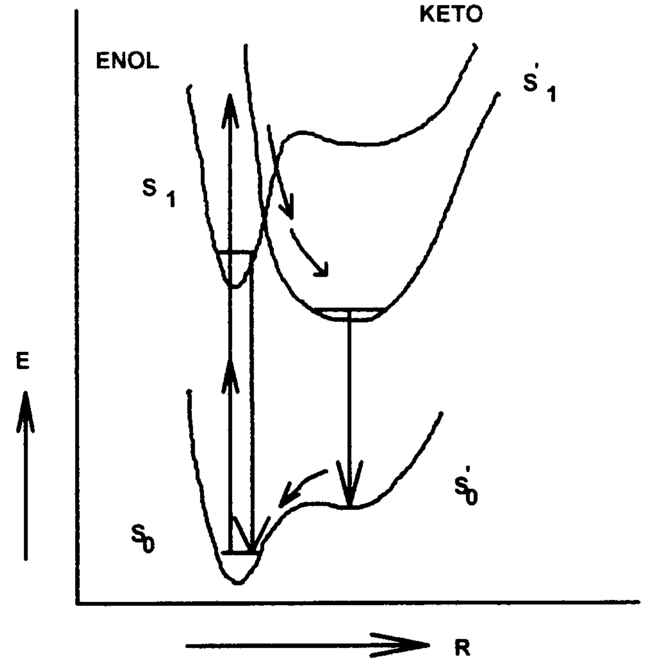


Fig. 1. Schematic diagram of the double potential minimum for the proton transfer reaction in the SA dimer. Enol and keto represent the D and T forms of the SA dimer respectively.

with a barrier of approximately 1050 cm^{-1}. The temperature seems to affect the barrier height. A discrete structure appears in the emission spectrum and the site emissions behave differently from the D emission.

2. Experimental details

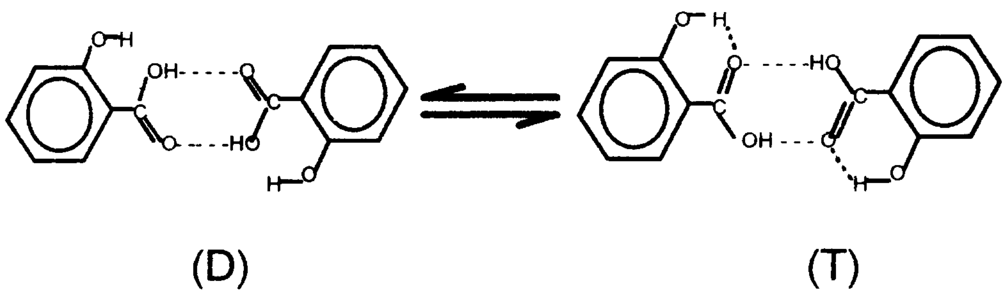
The steady state emission and excitation spectra were recorded using a spectrofluorophotometer (Jasco, FP777). The slit widths of the excitation and emission monochromators were kept at 1.5 nm to increase the resolution. The experimental details of the single-photon counting technique used in this study are given elsewhere [7]. Time-resolved fluorescence experiments were carried out with an Edinburgh Instruments model 199 fluorometer using the single-photon counting technique [8]. An XP2020Q fast photomultiplier was used in the detection electronics. The instrument response function has a full width at half-maximum (FWHM) of approximately 800 ps. The decay curves were collected at less than 2% of the repetition rate of the flash lamp, thereby minimizing the pile up effects in the decay. The fluorescence decays were deconvoluted by an iterative non-linear least-squares method. The validity of the results was checked using several parameters, e.g. χ^2, autocorrelation function, Durbin Watson parameter (DWP > 1.65 for monoexponential fit and DWP > 1.70 for biexponential fit) and residuals. The χ^2 values do not change appreciably on fixing τ_1. All the measurements at lower temperatures were made with an He-cooled Cryo tip (APD) at ± 1 °C. SA (Aldrich) was used after further crystallization from a water–alcohol mixture. All experiments were performed by keeping the SA powder inbetween two quartz plates. Front face excitation and appropriate filters were used to exclude the scattered light from the excitation source.

3. Results and discussion

In Fig. 1, we reproduce the potential energy diagram suggested earlier [1] to explain the photophysics of the SA dimer. As in all carboxylic acid dimers [9,10], a double proton transfer takes place converting D into tautomer T (Scheme 1). Since the rate of proton exchange is very fast (approximately 10^{10} s^{-1}) at room temperature, the two minima in the ground state will merge into a single minimum. However, at low temperatures, only D will be present in the S_0 minimum and, on excitation above the barrier, due to rapid proton transfer, the tautomer T will give rise to the ESIPT emission. At 10 K, as long as the absorption is at the red edge of S_0, the emission to the ground state will only give the UV band and, on excitation above the barrier height, the distinction between D and T will vanish due to tunnelling. The blue emission will also be observed which, surprisingly, has the same lifetime as the UV emission and involves a fast ESIPT.

3.1. Steady state fluorescence spectra and REE effect

Fig. 2 shows the emission spectra of solid SA at 10 K with REE, i.e. by excitation at energies lower than the (0,0) band of the D absorption (351–380 nm). (The (0,0) band was estimated only approximately by intersecting the wavelength of excitation and the emission spectrum of D.) The emission on excitation at 351 nm has a maximum at 390 nm, which shifts towards the red with increasing excitation wavelength.



Scheme 1.

The data in Table 1 show the variation of the emission band maximum with the excitation wavelength. The shift of the emission peak approximately correlates with the excitation energy and leads to the conclusion that, with a change in excitation energy, molecules with different sites are excited. The site emission is wavelength dependent. Such cryogenic effects have also been observed in tryptophan [11] and uranyl ion in borosilicate glass [12]. In the present case however, the sites may not only be distorted forms of the dimers but may also be different oligomers. The SA sample studied was microcrystalline and, probably, the excitation energy could not be trapped by the extraneous sites. The site effect is seen at low temperatures only. The sites do not give rise to any additional emission. This leads us to believe that these molecules may not have a suitable tautomeric configuration in which ESIPT can take place. The site effects are due to only a small energy difference and, as the temperature increases, they vanish. The decrease in intensity with excitation wavelength suggests that the percentage of such sites decreases as we move further towards the red.

Fig. 3 presents the excitation wavelength dependence on shorter wavelength excitation (SWE, higher energies than (0,0)). As expected, with higher energy excitation, the tautomeric blue emission is observed together with the dimeric UV emission. Both the emissions develop discrete structures. In Table 2, we give the assignments to some of the prominent structures such as C=O and OH stretches. It is interesting to note that the assignments agree well with the jet cooled studies of SA and methyl salicylate [13,14]. The intensity of the blue emission increases with the excitation energy and, finally, steady state is reached beyond which the blue emission does not increase in intensity. We believe that the excitation energy at which this takes place is indicative of the barrier height. The difference between the (0,0) band and this excitation energy is approximately 1250 ± 100 cm^{-1}. We will discuss the approximate nature of this value later. The temperature variation of the UV and blue emission (for 10 K onwards) is similar to that reported in Ref. [1]; the structures in the emission are not discernible above 160 K.

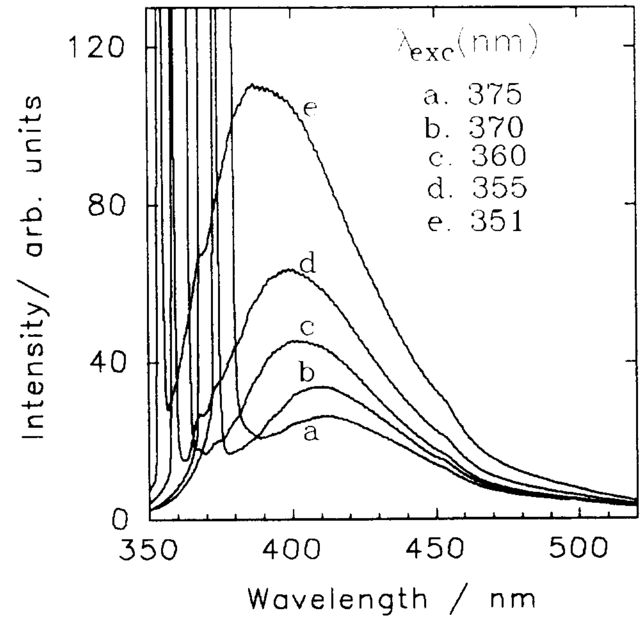


Fig. 2. Emission spectra of solid SA at 10 K with different excitation wavelengths longer than the (0,0) band as indicated in the figure. The truncated sharp peak in each spectrum is the scattered excitation light.

Table 1
Shift of the emission band of solid SA at 10 K with the excitation wavelength

λ_{exc} (nm)	λ_{em} (nm)	Shift (cm^{-1})
351	390	2849
355	397	2980
360	400	2777
370	410	2636
375	415	2570

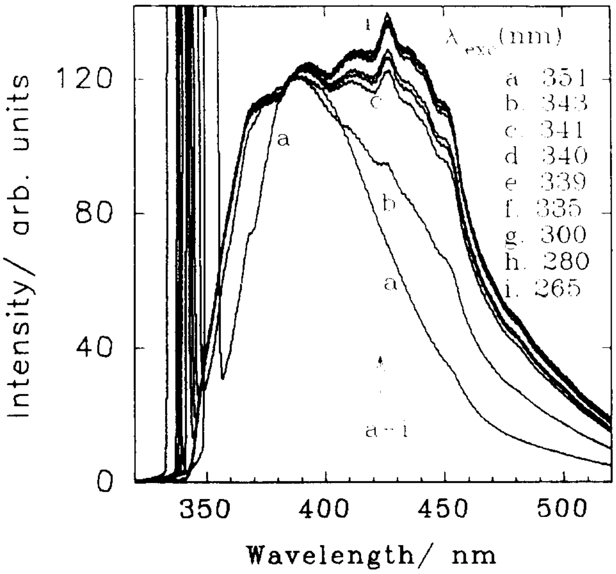


Fig. 3. Emission spectra of solid SA at 10 K with different excitation wavelengths shorter than the (0,0) band as indicated in the figure. The truncated sharp peak in each spectrum is the scattered excitation light.

Table 2
Observed vibrational bands on SWE in the emission spectrum of solid SA at 10 K and their probable assignments

Band position (nm)	Shift from 0,0 [a] of D (cm^{-1})	Assignment
375	1740	C=O [b]
393	3044	OH stretch [b]
412	4218	?
428	5125	C=O [c]
455	6512	OH stretch [c]

[a] 0,0 of D is at 28 490 cm^{-1}.
[b] Assignments for dimer.
[c] Assignments for tautomer by assuming (0,0) at approximately 400 nm.

3.2. Fluorescence excitation spectra and barrier for tautomerization

Fig. 4 shows the excitation spectra for the UV and blue emissions at 10 K. On monitoring the UV emission, the exci-

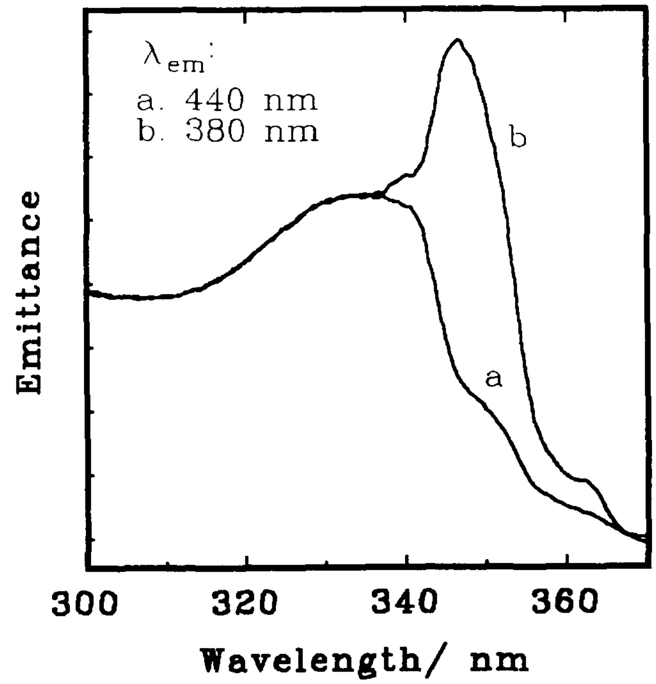


Fig. 4. Excitation spectra for blue (a) and UV (b) emission bands at 10 K.

tation spectrum shows a rather sharp peak at 343 nm. However, the blue band shows a broad excitation spectrum with a peak shifted towards higher frequency. Both excitation spectra become identical at higher energies, indicating the loss of the identity of the two potentials in the excited state at higher energies. The broad features of the excitation spectra reproduced here at 10 K are similar to those reported earlier for 80 K except for some differences in detail. Normally curves (a) and (b) exhibit a difference in wavelength at the red end. The shoulder in curve (b) is due to the absorption of the sites/oligomers ($\lambda_{max} \approx 363$ nm) and the shoulder in curve (a) is due to the presence of some UV emission at the monitoring wavelength. Since the site emission is more sensitive to temperature, the shoulder is not present in the excitation spectrum at 80 K. However, the excitation spectra are identical on the shorter wavelength side at 10 K, indicating the loss of identity of the two potentials in the excited state at higher energies. The barrier height, as calculated by the energy difference between the two excitation peaks, is 1050 cm^{-1}. A similar observation at 80 K of this system resulted in a barrier height of approximately 550 cm^{-1} [1]. We presume that the barrier height calculated here on the basis of the difference between the two excitation peaks, as suggested by Hetherington et al. [15], is approximate. The other method by which the barrier height can be calculated is more direct and involves the location at which the ratio of the blue and UV emission intensities approaches a constant value as a function of excitation energy (see Fig. 3). The barrier height calculated by this method is 1250 cm^{-1}. A better agreement between the two values is not expected because the location of the (0,0) band involves substantial error.

We also investigated whether a change in temperature brought about a decrease in the barrier height. The blue excitation spectrum does not change in shape appreciably and shifts to longer wavelengths with temperature. Fig. 5 shows the changes in the excitation spectrum of the UV emission with temperature. As can be seen, the excitation spectrum shifts towards the red and becomes broader up to approximately 200 K. Above 200 K, the two excitation spectra (for UV and blue) become identical. Normally, molecules having double potential minima are not liable to a change in barrier height with temperature. However, carboxylic acid dimers (including SA) undergo a fast double proton transfer with temperature even in the ground state. This proton exchange brings about the merger of the two potential minima [9,10]. Therefore the barrier height in the excited state can also be affected. When the rate of proton exchange is fast the barrier is no longer present.

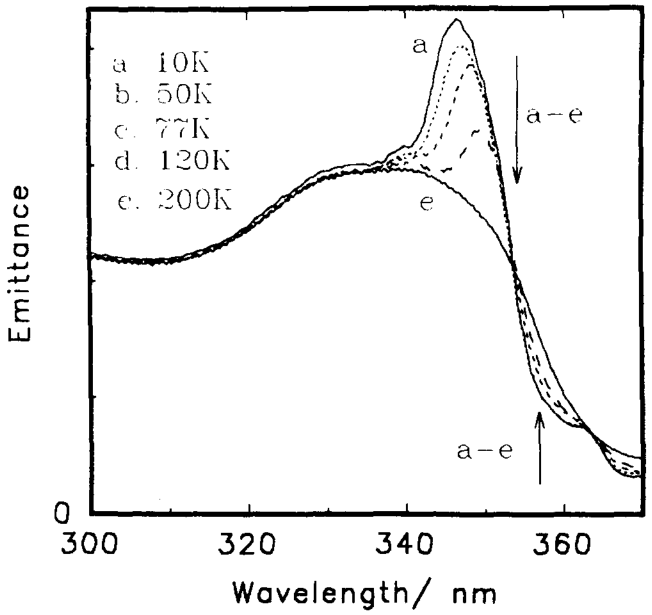


Fig. 5. Temperature variation of the excitation spectrum of the UV emission band.

3.3. Time-resolved emission

REE at 10 K involves UV emission together with emission due to various distortions of sites/oligomers. We investigated the lifetimes of these emissions by excitation at various wavelengths up to 368 nm (Table 3). The emission shows biexponential behaviour; the major component with a longer amplitude has a constant lifetime τ_1 of 3 ns, while τ_2 (varying) has a smaller amplitude but a longer lifetime of 7.9 ns. τ_2 varies from 7.95 ns to approximately 4.7 ns depending on the excitation energy. The relative amplitude also changes and is greater for τ_2 on longer wavelength excitation. Fig. 6 shows the fitted curves for the decay at different excitation wavelengths. On SWE, the site emission is so weak that the contribution due to τ_2 is negligible and almost a single exponential decay is observed. The earlier report of two lifetimes is due to contamination by extraneous site emission. As already reported [1], with increasing temperature (above

Table 3
Lifetimes and amplitudes [a] of solid SA at 10 K with various excitation energies as observed at 410 nm

λ_{exc} (nm)	τ_1 (ns)	Stand. dev. (ns)	τ_2 (ns)	Stand. dev. (ns)	α_1	α_2	χ^2
368	3.01	0.20	7.95	0.13	0.46	0.54	1.10
360	3.00	[b]	7.25	0.01	0.47	0.53	1.17
350	3.00	[b]	6.42	0.01	0.60	0.40	1.00
340	3.00	[b]	5.20	0.04	0.76	0.24	0.88
300	3.00	0.10	4.69	0.03	0.87	0.13	1.17

[a] Normalized to unity.
[b] With fixed τ_1.

160 K), the decay shows a single lifetime for both UV and blue emissions.

Fig. 7 shows the time-resolved emission spectra (TRES) (curves (a) and (b)) on SWE with time windows of 0–1 ns ("early" window) and 5–10 ns ("late" window). The intensities are normalized at 390 nm. Only the long wavelength emission decreases in the late window. This is because the emission at 390 nm is due to the SA dimer as well as oligomers which have a long lifetime. Therefore, on normalizing the intensities at 390 nm, the blue emission in curve (b) decreases with respect to that in curve (a). In curve (c), on REE, no blue emission is present; the late window shows only UV emission with a longer lifetime. The larger bandwidth (20 nm) used to record the TRES does not show any structure in the spectra.

The photophysics of the dual emission of SA dimers, its dependence on temperature and excitation wavelength and the features of the excitation spectra were rationalized previously by assuming a ground and excited state double proton transfer and simultaneous intramolecular fast proton transfer [1]. There is some similarity of this system with the dimers of 7-azaindole and azacarbazole [15,16], but the absence of tunnelling at low temperatures and the single exponential lifetime of the emission on SWE are unique to SA dimers.

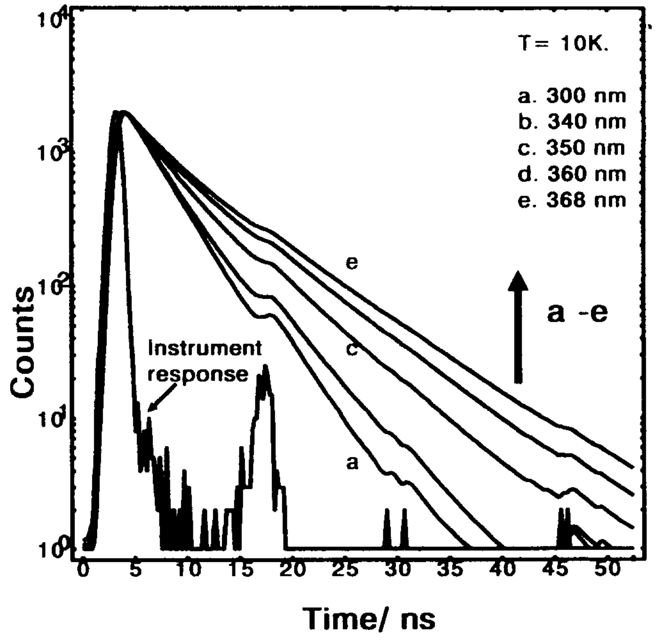


Fig. 6. Fitted decay curves for solid SA at 10 K, observed at 410 nm with the indicated excitation wavelengths.

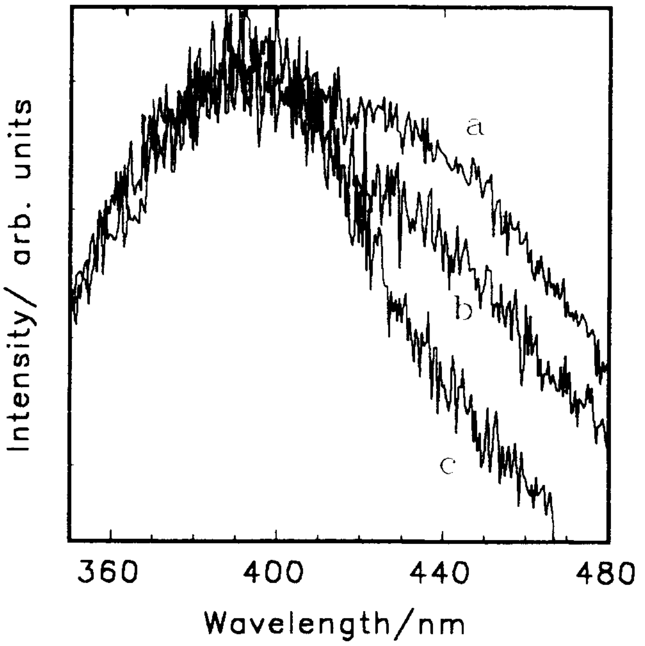


Fig. 7. Time-resolved emission spectra of solid SA at 10 K with time windows of 0–1 ns (300 nm excitation) (a), 5–10 ns (300 nm excitation) (b) and 5–10 ns (355 nm excitation) (c).

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