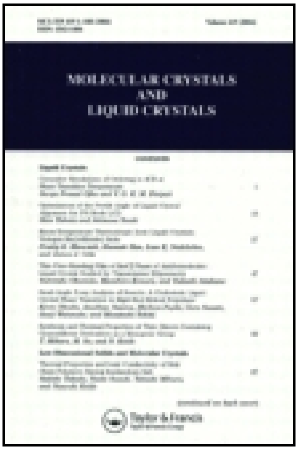

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The Excitation Wavelength Dependence of Adenine Cation Single Crystal Luminescence

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The Excitation Wavelength Dependence of Adenine Cation Single Crystal Luminescence

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The excitation wavelength dependence of luminescence measured in adenine cation crystals at 77 K is reported. The observed variations of all the luminescence parameters exhibit a marked correlation with a changing penetration depth of the excitation light. The alterations of luminescence intensity, vibronic structure of emission spectra, emission polarization and phosphorescence decay were attributed mainly to a variable contribution of the emission from local excited states which correspond to a different trap ensembles in the crystal bulk and near the surface, respectively.

INTRODUCTION

Adenine cation crystals may serve as a convenient molecular systems for modeling energy levels of polyadenylic acid and energy transfer between adenine molecules, at least in the case of triplet states.[1] The advantage of these model systems consists in the precisely known chromophore localization and the state of their protonation.

The aim of this paper is to investigate further the luminescence properties of adenine single crystals and, particularly, to investigate their dependence on the excitation wavelength.

EXPERIMENTAL

Crystals

Adenine cation crystals (adenine sulphate—Ade H_2SO_4, adenine hemisulphate monohydrate—Ade 1/2 H_2SO_4 H_2O, adenine hydrobromide hemihydrate—Ade HBr 1/2 H_2O and adenine hydrochloride hemihydrate—Ade HCl 1/2 H_2O) were grown from acidic solutions by lowering slowly the temperature.[2] Basic crystalographic data and crystal structures were obtained from X-ray diffraction studies.[3-7]

The luminescence was studied either on well-developed natural crystal faces or on cut and polished plates. No special precautions concerning the fluorescent impurities were taken. The flat samples of approximate size 3 × 3 × 0.5 mm were affixed by means of colloidal graphite on a copper sample chamber in an evacuated cryostat.

Luminescence measurements

The following parameters of luminescence in adenine single crystals at 77 K were examined: emission and excitation spectra of polarized fluorescence and phosphorescence, phosphorescence decay and thermoluminescence glow curves.

Emission spectra

The apparatus used for the measurement of the emission spectra was described elsewhere.[1] The polarization of crystal luminescence was analyzed by means of Polacoat 105 UV dichroic filter. The emission was observed perpendicular to the sample plane and its polarization was characterized in terms of the polarization ratio I_a/I_b; I_a and I_b indicate the intensity of luminescence polarized in directions parallel to the two defined crystalographic directions. A disadvantageous distortion of the measured polarization ratio due to the double refraction of the emission outgoing from the crystal surface could be eliminated only in the case of Ade H_2SO_4 orthorombic crystals cut in (100), (010), and (001) planes since the emission polarized parallel to the main crystalographic axes of these crystals is at the same time polarized parallel to the two of their indicatrix principal axes.

Excitation spectra

The luminescence was excited by the monochromatized light of a Narva (GDR) HBO 500 high pressure xenon discharge lamp. The spectral distribution of the excitation source was determined with the aid of a Zeiss Vth-1 thermopile. The luminescence intensity emitted within a defined narrow spectral interval was monitored. A quantity plotted in Figure 2 represents a relative number of photons emitted per unit number of incident photons of excitation light. In view of the fact that a spectral dependence of crystal reflectivity is only slight and an optical transmittance of the sample negligible (this condition is fulfilled for $E_{exc} \geq 4.2$ eV) these excitation spectra render satisfactorily the excitation dependence of the luminescence quantum efficiency at a given emission wavelength.

Phosphorescence decay

The phosphorescence decay after excitation shut off was registered with a Honeywell 540 fast-response Y-t plotter. The time-dependent photomultiplier current was measured with a Keithley 610C electrometer.

Thermoluminescence

The glow curves of thermoluminescence from the samples previously irradiated at 77 K by the monochromatic excitation light were measured. The dose of absorbed radiation was adjusted to the value sufficient enough to saturate the thermoluminescence light sum. The thermoluminescence intensity was measured using an EMI 6256S photomultiplier directly attached to a cryostat window. The rate of temperature rise was 30 K/min.

RESULTS

The remarkable changes of (i) emission spectra (ii) polarization of emission (iii) relative intensity of luminescence and (iv) phosphorescence decay due to the excitation at different wavelength appear to be common features of all the investigated samples.

Emission spectra

Under the excitation within the red shoulder of the first absorption band ($E_{exc} = 4.1$–4.2 eV) the luminescence of adenine single crystals is composed of structureless fluorescence of excimer nature and monomer-like phosphorescence with a well resolved vibronic structure. The description of these spectra was presented elsewhere.[1] Shift of excitation wavelength towards the region of strong absorption ($E_{exc} > 4.25$ eV) causes gradual blurring of the phosphorescence vibronic structure with a concomitant shift of the maximum of the phosphorescence spectrum. The phosphorescence that is excited within the region of strong absorption ($E_{exc} > 4.3$ eV) is quite structureless. As an example the emission spectra of Ade H_2SO_4 are presented, Figure 1.

The variations of fluorescence spectra are not so remarkable. Only

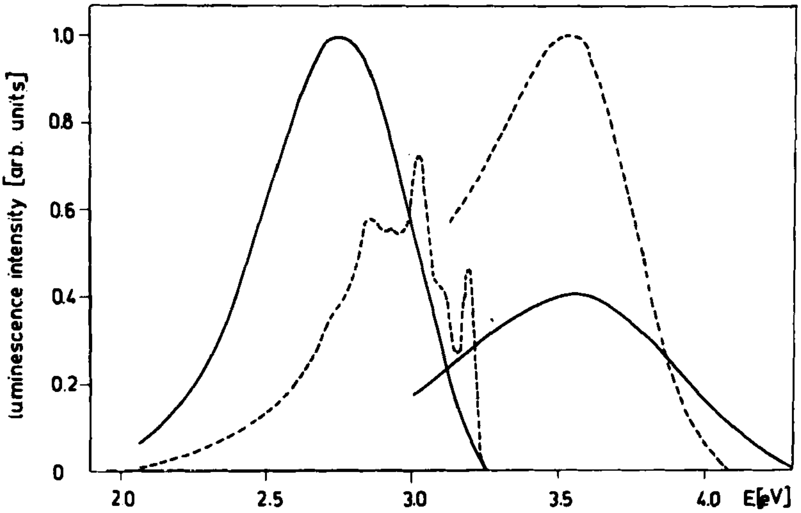

FIGURE 1 Luminescence of Ade H_2SO_4 crystal at 77 K; emission normal to (100) face. Full line—E_{exc} = 4.8 eV, dashed line—E_{exc} = 4.16 eV.

some blue shift of emission maxima and a relative intensification of emission at the blue tail of fluorescence bands were observed.

Polarization of emission

The luminescence of adenine single crystals is strongly polarized for E_{exc} = 4.1–4.2 eV. The degree of polarization alters with the exciting photon energy in a similar way as the phosphorescence vibronic structure does. The polarization ratios of both phosphorescence and fluorescence reach their maximal values for excitation near 4.2 eV and then continuously decrease with increasing photon energy, as it is demonstrated for Ade H_2SO_4 crystals, Figure 2c.

Relative intensity of emission

The luminescence excitation spectra were measured over the photon energy range 3.9–5.4 eV. The luminescence intensity was monitored within the narrow spectral band near the emission maximum (E_{em} = 2.9–3.0 eV for phosphorescence and 3.5–3.6 eV for fluorescence). The luminescence from all the samples of examined crystals exhibited a remarkable increase of the relative intensity of both phosphorescence and fluorescence when excited near the onset of the first absorption band (E_{exc} = 4.1–4.2 eV), Figure 2b. These changes in intensity of the luminescence coincide with a variation of the penetration depth of the

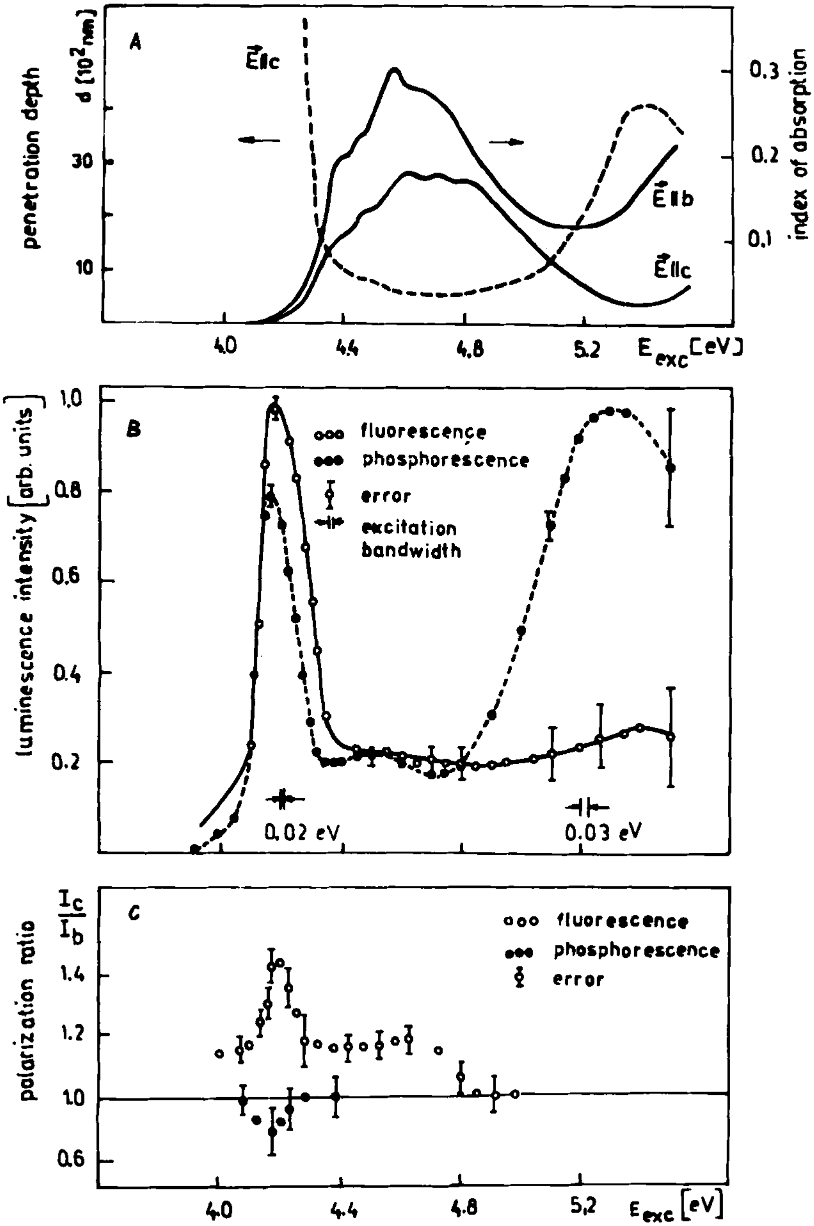

FIGURE 2 Luminescence of Ade H_2SO_4 crystal-comparison of the relative luminescence intensity and polarization ratio of emission with the penetration depth of excitation light; emission normal to (100) face, $T = 77$ K. (A) Spectral dependence of penetration depth d of excitation light polarized with electric vector parallel to c axis (within the surface layer of thickness d the 99% of incoming radiation is absorbed). The values of absorption index, determined by Kramers-Kronig analysis of crystal room temperature reflectivity spectra, are taken from Ref. 8. (B) Excitation spectra of fluorescence and phosphorescence; both the excitation light and emission are polarized with electric vectors parallel to c axis. (C) Excitation spectra of polarization ratio I_c/I_b of phosphorescence and fluorescence.

excitation light due to a spectral dependence of the extinction coefficient, Figures 2a, 2b.

Moreover an increase of phosphorescence to fluorescence intensity ratio *P/F* was observed for $E_{exc} > 4.8$ eV, Figure 2b. This effect can also be directly manifested by a comparison of the relevant emission spectra, Figure 1.

Phosphorescence decay

The decay of structural phosphorescence obeys a single exponential law

$$I(t) = I_0 \exp(-t/\tau_{ph}). \tag{1}$$

Phosphorescence lifetimes τ_{ph} measured for different vibronic bands were found to be the same within the limits of experimental error.[1] The lifetimes of the exponentially decaying phosphorescence are markedly shortened after the excitation above 4.2 eV, Table I. Moreover the phosphorescence decay becomes nonexponential for $E_{exc} >$ 4.3 eV, Figure 3.

Thermoluminescence measurements

The thermoluminescence of Ade H_2SO_4 and Ade 1/2 H_2SO_4 H_2O crystals was studied as an effect inherent to the existence of structural defects.[9] The thermoluminescence glow curves were measured under the condition of trap saturation after the irradiation of the sample by the monochromatic light at 77 K (E_{exc} was chosen to be either 4.16 eV or 4.9 eV). By means of this excitation wavelength choice, the preferential excitation of either bulk or surface parts of crystals could be accomplished.

It was found that the thermoluminescence curves exhibit four distinct maxima within the temperature range 77–300 K. The glow maxima appeared at temperatures 129 K, 155 K, 225 K and ≃300 K respectively. Using the Hoogenstraatens method, Jelínek has determined the corresponding thermoactivation energies of particular glow peaks.[10] The latter are 0.1 eV, 0.24 eV, 0.33 eV and ≃0.47 eV.

A significant difference exists between the thermoluminescence glow curves of the samples excited in the bulk and near the surface respectively. The irradiation of the sample by the strongly absorbed light (E_{exc} = 4.9 eV) results in the accentuation of the high temperature glow peaks. This effect was particularly conspicuous in the case of Ade 1/2 H_2SO_4 H_2O crystals, Figure 4.

TABLE I

Phosphorescence lifetimes of adenine single crystals at 77 K

	Ade H_2SO_4	Ade 1/2 H_2SO_4 H_2O
E_{exc}[eV]	τ_{ph}[s]	τ_{ph}[s]
4.10	2.42 ± 0.1	2.77 ± 0.1
4.15	2.30	2.54
4.20	2.30	2.43
4.30	1.84	1.98
4.35	nonexponential[a]	nonexponential[a]
4.4–4.8	$\bar{t} = 1.3$ s	$\bar{t} = 1.6$ s
5.1–5.4	$\bar{t} = 1.1$ s	$\bar{t} = 1.5$ s

[a] The lifetime of emission is defined as a mean value $\bar{t} = \int_0^\infty t\, I(t)\, dt / \int_0^\infty I(t)\, dt$.

DISCUSSION

The observations summarized above prove the strong dependence of the main parameters of low temperature luminescence in adenine cation single crystals on the excitation wavelength. The observed decrease of intensity and polarization of emission, as well as the simultaneous changes of phosphorescence lifetime and phosphorescence vibronic structure, apparently correlate with the sharply decreasing

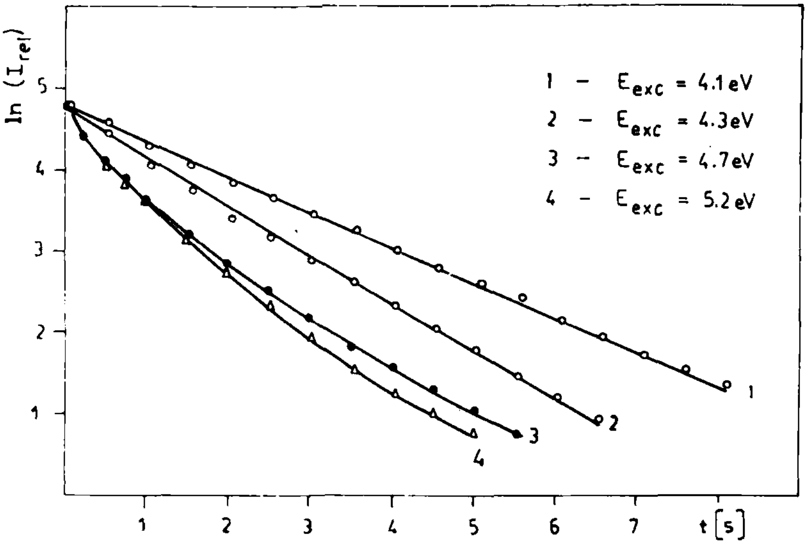

FIGURE 3 Semilogarithmic plot of Ade H_2SO_4 phosphorescence decay.

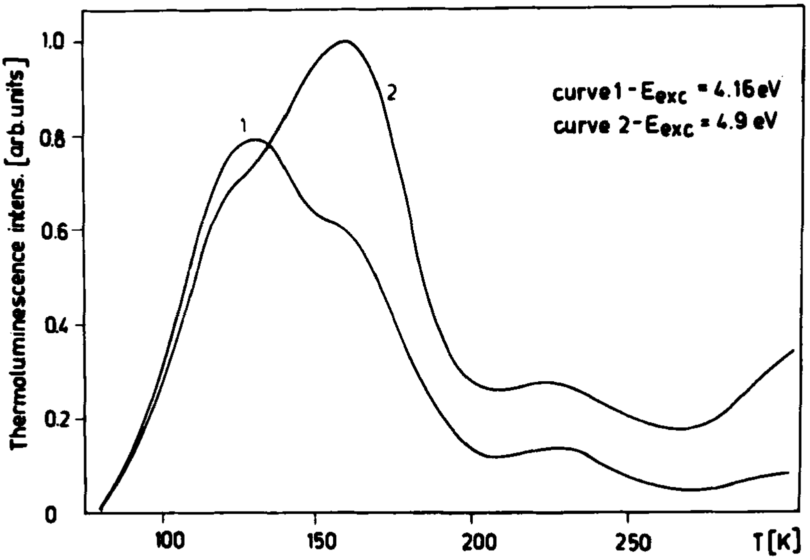

FIGURE 4 Thermoluminescence glow curves of Ade 1/2 H_2SO_4 H_2O crystals, excited at 77 K. Curve 1—E_{exc} = 4.16 eV, curve 2—E_{exc} = 4.9 eV.

penetration depth of excitation light. Within the spectral range 4.2–4.3 eV the penetration depth ranges from the values comparable with the crystal thickness to the values less than 1 μm, Figure 2a.

The observed effects can be plausibly interpreted in terms of dominating role of selective excitation of either bulk or crystal surface. From this viewpoint the changes of all the emission parameters over the excitation range 4.2–4.3 eV must be attributed to the existence of different sets of structural imperfections within the selectively excited zones of the crystal since the structural defects are generally responsible for the creation of local excited states.[11]

The evidence for the existence of different manifolds of imperfections within the bulk and near the crystal surface was provided by means of thermoluminescence method. Jelinek and Tale have concluded earlier that the UV-stimulated thermoluminescence of adenine in solid state is conditioned by the existence of electron traps which are formed due to the existence of structural defects.[9] Then the difference between the thermoluminescence glow curves obtained on the condition of trap saturation after 4.16 and 4.9 eV excitation, respectively, indicates the existence of different trap ensembles within the bulk and near the crystal surface. Particularly in the case of 4.9 eV excitation, more pronounced peaks corresponding to higher activation energies are to be taken as the evidence of an enhanced contribution of deep traps to the thermoluminescence from the surface zones. This suggests a comparatively high degree of structural disorder near the crystal surface with respect to the bulk of the crystal.

All the observed excitation dependences of luminescence in adenine crystals are consistent with the proposed model of selective excitation of different trap ensembles. Particularly (i) the blurring of the phosphorescence vibronic structure; (ii) the non-exponential phosphorescene decay, which in general can be taken as a sum of various exponentially decaying components, and (iii) the decrease of polarization ratio should be interpreted as a consequence of prevailing emission from wide distribution of local excited states which belong to irregularly oriented molecules embedded within the capacious defects near the crystal surface. The strongly polarized exponentially decaying phosphorescence with the well resolved vibronic structure, emitted after the 4.16 eV excitation, should be on return attributed to the comparably uniform set of triplet states associated with the bulk of the crystal. Furthermore, (iv) the decrease of luminescence intensity for $E_{exc} > 4.2$ eV is to be explained in terms of the well known fact that the rates of nonradiative transitions are substantially dependent on an microenvironment surrounding the excited molecule.[12] Thus far we may admit that the quantum yields of the luminescence associated with the local states near the surface are substantially lower than the quantum yields of the bulk luminescence. In case of phosphorescence this inference is further supported by the existing difference in decay rates. For $E_{exc} = 4.2$ eV τ_{ph} is significantly higher than for $E_{exc} = 4.3$ eV, Table I.

It should be emphasized here that the results presented in this paper only for the case of Ade H_2SO_4 crystals reflect satisfactorily enough the typical behavior of the rest of adenine cation crystals. Moreover, the fluorescence excitation spectra similar to that one presented in Figure 2b were also observed by Yamashita and Shibuya in the case of thick anthracene crystals.[13] This remarkable fact suggests that the effect of changing excitation light penetration depth may be expected to appear in various thick molecular crystals.

As regards the adenine cation crystals the only effect which cannot be simply explained in terms of selective excitation of different crystal zones is the remarkable enhancement of P/F ratio for $E_{exc} > 4.8$ eV, Figures 1 and 2b. Seeing that the associated changes of the excitation light penetration depth are small, Figure 2a, we must take into account a possibility of intramolecular nature of P/F enhancement. Our conclusion is supported by the earlier observations that the luminescence quantum yields of adenine in solutions depend markedly on the excitation wavelength.[14-16] The likely origin of *P/F* increase is an enhancement of intersystem crossing rate after either the excitation of vibronic sublevels of higher $\pi\pi^*$ singlet states of adenine or the direct excitation of its hidden $n\pi^*$ singlet states.[16]

CONCLUSION

The properties of adenine cation crystals luminescence have been found to be strongly dependent on the excitation wavelength. The observed dependences could be reasonably understood in terms of the interplay between the two substantionally different effects: (i) the manifestation of the selective excitation of different crystal regions due to spectral dependence of crystal absorption and (ii) the manifestation of a successive excitation of different molecular excited states.

The latter effect is responsible mainly for the *P/F* ratio enhancement for $E_{exc} > 4.8$ eV. So far the real mechanism of intersystem crossing rate increase has not been unambiguously identified. Anyhow the excitation dependence of luminescence in adenine single crystals at 77 K is dominated by the effect of selective excitation which is closely connected with the high value of adenine molar extinction coefficient.

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References

1. J. Slavík, O. Jelínek and J. Plášek, *Photochem. Photobiol.*, **29**, 497 (1979).
2. J. Zachová, *Czech. J. Phys.*, **B23**, 1038 (1973).
3. H. Moravcová, *Z. Kristallogr.*, **141**, 156 (1975).
4. V. Langer and K. Huml, *Acta Cryst.*, **B34**, 1881 (1978).
5. V. Langer and K. Huml, *Acta Cryst.*, **B34**, 1157 (1978).
6. V. Langer, K. Huml and L. Lessinger, *Acta Cryst.*, **B34**, 2229 (1978).
7. T. J. Kistenmacher and T. Shigematsu, *Acta Cryst.*, **B30**, 166 (1974).
8. J. Štěpánek, *PhD Thesis*, Fac. Math. Phys. of the Charles Univ., Prague, 1981.
9. O. Jelínek and I. Tale, *Journ. Lumin.*, **10**, 371 (1975).
10. O. Jelínek, *private communication*.
11. H. C. Wolf, *Advances in Solid State Physics/Festkorperprobleme*, **4**, 57 (1965).
12. N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra* (Dekker Inc., New York, 1970).

13. S. Yamashita and M. Shibuya, *J. Phys. Soc. Japan*, **48**, 1789 (1980).
14. J. W. Eastman and E. J. Rosa, *Photochem. Photobiol.*, **7**, 189 (1968).
15. M. Daniels, *Physico-Chemical Properties of Nucleic Acids*, Vol. I, Ed. J. Duchesne (Acad. Press, London, 1973), p. 113.
16. R. J. Wilson, J. P. Morgan and P. R. Callis, *Chem. Phys. Lett.*, **36**, 618 (1975).