The Effect of High Density Excitation on the Phosphorescence Spectra and Decay Times of Several Crystalline Uranyl(VI) Salts

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The effect of high density excitation on the phosphorescence spectra and their decay curves of crystalline uranyl(VI)nitrate hexahydrate, uranyl(VI)acetate dihydrate, and zinc uranyl(VI)acetate heptahydrate was studied using a nitrogen laser as the exciting light source. The relative emission intensity of the spectra in the shorter wavelengths decreased and the vibrational structure became broader at higher density excitations; these changes were attributed to the saturation in excitation and to the temperature increase in the irradiated volume of the sample crystal caused by the heat released in the radiationless decay process. A decrease in the decay time was also observed at high density excitations; this shortening was attributed to bimolecular quenching of triplet excitons in the crystal. The rate constant for this process in crystalline uranyl nitrate hexahydrate was measured at several temperatures between 77 and 295K; it was 2.6×10^{-13} cm^3 s^{-1} at 295K for example. From this rate constant the hopping rate for a triplet exciton in crystalline uranyl nitrate hexahydrate was obtained: 4.3×10^8 cm^3 s^{-1} at 295K. The activation energy for the exciton migration was found to be 320 cm^{-1}.

Uranyl salts with the simplest monomolecular type of luminescence have been extensively investigated for more than a century.[1,2] Tolstoi *et al.* observed decreases in both the phosphorescence lifetime and the quantum yield at high density excitations.[3,4] They measured the relative quantum yield and the average lifetime at various excitation densities. They determined the bimolecular quenching rate constants in a uranyl(VI)-nitrate hexahydrate crystal by matching the theoretical curves to the experimental points. The bimolecular quenching rate constant obtained by them is erroneous because of the following two reasons: (i) The decay curve is not exponential when both monomolecular and bimolecular decay processes are present, as is shown in the later part of this paper, whereas they assumed it to be exponential, and (ii) the decrease in the phosphorescence yield was assumed to be caused only by biexcitonic quenching; the saturation effect in the excitation and other effects were disregarded.

In the present paper the effect of high density excitation on the phosphorescence decay curves was studied for crystalline uranyl(VI)nitrate hexahydrate ($UO_2(NO_3)_2\cdot6H_2O$), uranyl(VI)acetate dihydrate ($UO_2(CH_3COO)_2 : 2H_2O$), and zinc uranyl(VI)acetate heptahydrate ($Zn(UO_2)_2(CH_3COO)_6\cdot7H_2O$) (hereafter abbreviated as UN, UA, and ZUA, respectively) and the rate constants for bimolecular quenching and hopping of excitons in a UN crystal were obtained as a function of temperature between 77 and 295 K by analyzing the phosphorescence decay curves.[5,6] The critical concentration for bimolecular quenching and the activation energy for the exciton hopping were also obtained.

The effect of high density excitation on the phosphorescence spectra was also studied for the three uranyl salts. The cause of the spectral change at high density excitation is interpreted in terms of the saturation in excitation and the temperature increase in the irradiated volume of the sample crystal which is caused by the heat released in the radiationless decay process.[6]

Experimental

A nitrogen laser described in a previous paper[7] was used as the excitation light source for observing the phosphorescence decay curves and their time-resolved spectra. The laser beam intensity was attenuated by quartz plates with evaporated aluminium. The intensity of the phosphorescence from the crystalline samples was also reduced by appropriate neutral density filters of copper mesh. A Spex 1704 monochromator, an EMI 6256S photomultiplier, and a Hitachi V1000 oscilloscope were used to record the phosphorescence decay curves. The time constant of the detecting system was about 10 μs. A PAR model 160 boxcar integrator was used in order to obtain time resolved phosphorescence spectra and to improve the signal to noise ratio. The aperture time, time base, and time constant of the boxcar integrator were 10 μs, 0.1 ms, and 0.1 ms, respectively. The phosphorescence was detected at right angles to the excitation light beam.

The triplet-triplet ($T_n\leftarrow T_1$) absorption spectrum of UN in acetonitrile solution was measured by a newly developed method which was described in a previous paper.[8]

Reagent grade UN and UA (Wako Pure Chemical Industries) and GR grade ZUA (Kanto Chemical Co., Inc.) were used without further purification. For study of the high density excitation effect, crystalline powder was used. The spectral dependence of the phosphorescence lifetimes was checked for these three crystals at 295, 201, and 77 K. The phosphorescence lifetimes were constant all over the spectral region for the three crystals, UN, UA, and ZUA, at these three temperatures. This shows that the effect of the impurity emission on the phosphorescence spectra of these three crystals of the uranyl salts is negligibly small.[9,10]

The phosphorescence excitation spectrum of the UN crystal was measured on a HITACHI MPF spectrophotofluorometer at Ochanomizu University.

Results and Discussion

Spectral Changes. Phosphorescence spectra of UN, UA, and ZUA within the first 10 μs after the laser excitation were measured at 295 K at high and low excitation densities; the results are shown in Fig. 1(a).

Vibrational bands in the phosphorescence spectra of the three kinds of crystals, UN, UA, and ZUA, are hereafter referred to as bands h, a, b, c, d, and e, as

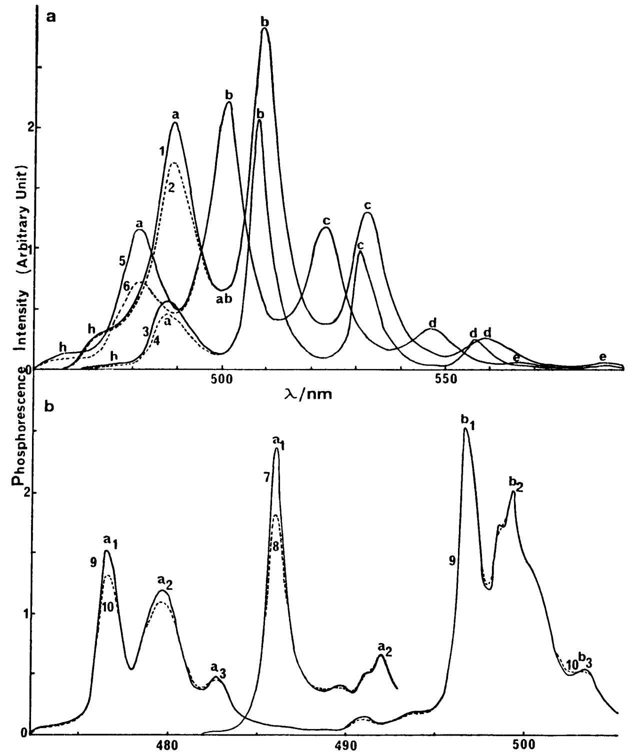

Fig. 1, (a) Time resolved phosphorescence spectra of crystalline UN (curves 1 and 2), UA (curves 3 and 4), and ZUA (curves 5 and 6) just after low (solid curves) and high (broken curves) density excitations at 295 K. Exciting light intensity at high density excitation is about 100 kW per 0.08 cm^2 (=1.25 MW/cm^2).

(b) Time resolved phosphorescence spectra of UA (curves 7 and 8) and ZUA (curves 9 and 10) crystals just after low (solid curves) and high (broken curves) density excitations at 77 K. Only band a and bands a and b are shown in the spectra for UA and ZUA, respectively, since the change is observed only in the regions of those bands.

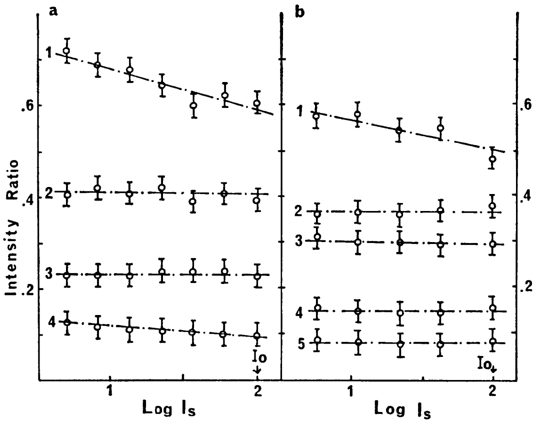

Fig. 2. Phosphorescence intensities of crystalline UN(2a) and UA(2b) at intensity maxima h, a, c, d, and of minima ab and bc relative to that at the maximum b in the time resolved spectrum just after excitation, as functions of logarithmic exciting light intensity (I_s). I_0 is the highest intensity in the present experiment, 100 kW per 0.08 cm^2. Plotted lines 1, 2, 3, and 4 in Fig. (2a) indicate I_a/I_b, I_c/I_b, I_{ab}/I_b, and I_h/I_b respectively, and those 1, 2, 3, 4, and 5 in Fig. (2b) indicate I_a/I_b, I_c/I_b, I_{ab}/I_b, I_{bc}/I_b, and I_d/I_b, respectively.

indicated in Fig. 1. Band h is a hot band. The intensity minima between the two maxima are referred to as ab, bc, cd, and de, *etc.* (Fig. 1). I_a and I_{ab} represent the emission intensities at the wavelength of band a and at the intensity minimum ab in the spectrum, respectively.

The common change in the phosphorescence spectra of UN, UA, and ZUA crystals with high density excitation at room temperature is the decrease in the intensity relative to that at the peak position of the phosphorescence spectra at shorter wavelengths. The relative intensities of bands h and a are weaker at high density excitation than at low density excitation. This can be shown more clearly from Figs. 2a and 2b, where the ratios of phosphorescence intensities at several wavelengths are shown for various excitation intensities, I_s. We can see that I_h/I_b and I_a/I_b decrease as I_s increases, while I_c/I_b, I_{ab}/I_b, and I_{bc}/I_b remain constant.

The effect of high density excitation on the phosphorescence spectra of UA and ZUA at 77 K is shown in Fig. 1(b). A change in the phosphorescence spectra of UA is observed in the spectral region between 483 and 493 nm, as shown in Fig. 1(b). Vibrational bands in the phosphorescence spectra of UA and ZUA are hereafter referred to as a_1, a_2, and a_3··· and b_1, b_2, and b_3···, as indicated in Fig. 1(b).

The relative intensities of band a in the spectrum of UN,[11] of band a_1 in the spectrum of UA, and of band a_1, a_2, and a_3 of ZUA decrease at high density excitations, as shown in Figs. 1 and 2. The amount of the decrease is in the order of $a_1 > a_2 > a_3$ for the spectrum of ZUA at 77 K.

In the spectra shown in Fig. 1(b) another spectral change can be found for UA and ZUA crystals. This is a vibrational band broadening. The vibrational bands become slightly obscure at the high density excitation in the 489—492 nm region of the UA spectrum, and in the 476—483, 490—493, and 498—500 nm regions of the ZUA spectrum. This broadening is also observed in the 506—509 nm region of the UN spectrum at 77 K.[12] The spectral change caused by high density excitation is observed also at 201 K. The change observed at this temperature is quite similar to that at 295 K.

The changes commonly observed to appear in the spectra of UN, UA, and ZUA crystals at high density excitations are therefore summarized as follows.

(1) The relative intensity of the spectra in the shorter wavelengths decreases at high density excitations.

(2) The vibrational band at 77 K becomes obscure at high density excitation. These spectral changes are reversible. Neither color change nor decomposition of the crystals was observed after exposure to about 10^4 shots. Furthermore, low density excitations before and after the high density excitation at the same spot on the sample crystal gave the same spectral distribution of fluorescence intensity, within 1%. Therefore, the main cause of the spectral change at high density excitation is not an irreversible chemical reaction.[13]

There are four possible interpretations for the observed reversible spectral change (1):[14] (a) At the high density excitation the temperature in the irradiated volume of the crystal is increased not only by the heat given off in the ordinary linear radiationless decay processes of the molecules whose number increased at the high density excitations but also by the heat released in the nonlinear bimolecular quenching process referred to in a later part of the present paper. This temperature increase causes an increase in the absorbance of the hot band. Therefore, the relative intensity of the spectra at the shorter wavelengths is decreased because of their large overlap with the hot band of the absorption spectra. (b) The ratio of the phosphorescence emitted from the surface of the crystal to that from the inner part decreases at high density excitations because of the saturation effect.[7] Since the phosphorescence was detected at right angles to the excitation light beam, the phosphorescence suffers from the reabsorption because the phosphorescence and $T_1 \leftarrow S_0$ absorption spectra overlap with each other to some extent. The phosphorescence emitted from the inner part is more seriously affected by the reabsorption than that emitted from the surface of the crystal. Therefore the reabsorption effect becomes more prominent at high density excitations. (c) Induced emission appears at high density excitations. (d) The emission spectrum is affected by reabsorptions due to transitions from the lowest excited triplet state (T_1) to higher triplet states (T_n).

Possibility (c) can be excluded since no spectral narrowing, but only broadening, could be found. In order to check possibility (d) we measured the $T_n \leftarrow T_1$ absorption spectrum of a saturated solution of uranyl nitrate in acetonitrile. The result is shown in Fig. 3. The $T_n \leftarrow T_1$ spectrum of UN has maxima at 570 nm.[15] Figure 3 shows $A_a < A_{ab} < A_b < A_c < A_d$, where A_a and A_{ab} are the absorbances of T_1 at the wavelength of band a and of intensity minimum b. Therefore, if possibility (d) is the main cause of spectral change (1), then I_h/I_b and I_a/I_b should increase in the spectrum of UN measured at 295 K with the increase in excitation intensity. However, as is shown in Fig. 2a, the actual spectral change of (1) is in the opposite direction. This implies that possibility (d) is not the main cause of spectral change (1) at high density excitations for UN crystals.

If possibilities (a) and (b) are the main causes of spectral change (1), I_h/I_b and I_a/I_b should increase with high density excitation for all three crystals, since bands a and h suffer from reabsorption less seriously than the other bands. This was what was actually observed for UN, UA, and ZUA crystals; therefore, it is concluded that (a) and (b) are the dominant causes of spectral change (1).

Two tentative explanations for spectral change (2) are as follows: (a) The vibrational structure becomes obscure at high density excitations because of the temperature increase caused by the heat given off by radiationless decay at high density excitations. (b) The new emission which appears is caused by the exciton-exciton interaction.

Possibility (b) is ruled out by the fact that the change in the phosphorescence decay time which accompanies the high density excitation can be completely interpreted in terms of the bimolecular collisional quenching of the triplet exciton, there is no evidence that there appears any new emission originating from some interacted state of two excitons with a possibly different decay time from that of the normal phosphorescence at low density excitation.

In order to check possibility (a), the phosphorescence spectra of a ZUA crystal at low density excitations at several temperatures higher than 77 K by steps of ten degrees were measured (Fig. 4); these were compared with that at the high density excitation at 77 K. From the comparison of Figs. 2 and 4, the ratio $I_{a_2}/I_{a_1a_2}$ at the high density excitation at 77 K is between those at 95 and 103 K with low density excitations. This shows that the temperature increase, ΔT, in the irradiated volume of crystalline ZUA at the high density excitation can be estimated at between 18 and 26 K.

The ratio $I_{a_1}/I_{a_1a_2}$ is much more seriously decreased

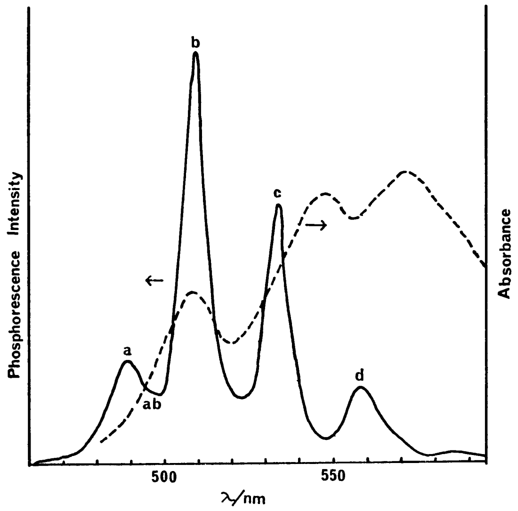

Fig. 3. Time resolved phosphorescence spectrum of UN crystal at 295 K just after low density excitation (curve 1) and the $T_n \leftarrow T_1$ absorption spectrum of a saturated solution of UN in CH_3CN (curve 2).

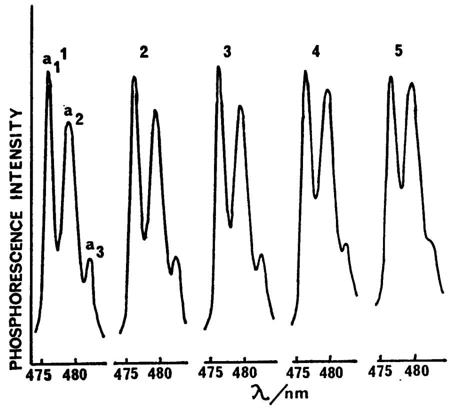

Fig. 4. Time resolved phosphorescence spectra of crystalline ZUA just after low density excitation at different temperature between 77 and 108 K. Figs. 1, 2, 3, 4, and 5 indicate the spectra at 77, 93, 95, 103, and 108 K, respectively.

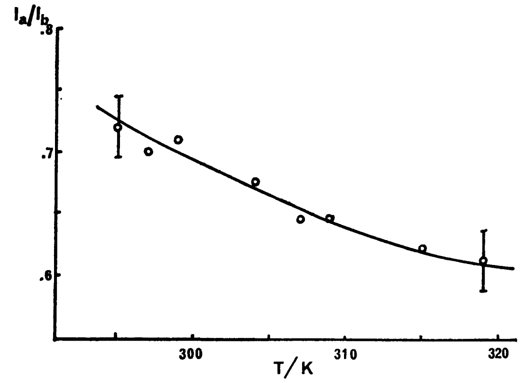

Fig. 5. Temperature dependence of the intensity ratio I_a/I_b between 295 and 319 K in the time-resolved spectrum just after low density excitation of UN.

than $I_{a_2}/I_{a_1a_2}$. This is because the band a_1 is decreased not only by the increase of the reabsorption effect caused by the temperature increase but also by the excitation saturation of the sample crystal already mentioned as possibility (b) for the cause of spectral change (1).

The temperature increase in the irradiated volume in crystalline UN can be also estimated to be ≈25 °C by a comparison with Figs. 3a and 5, which show the intensity ratio I_a/I_b as functions of temperature at low density excitation and of excitation density at 295 K, respectively.

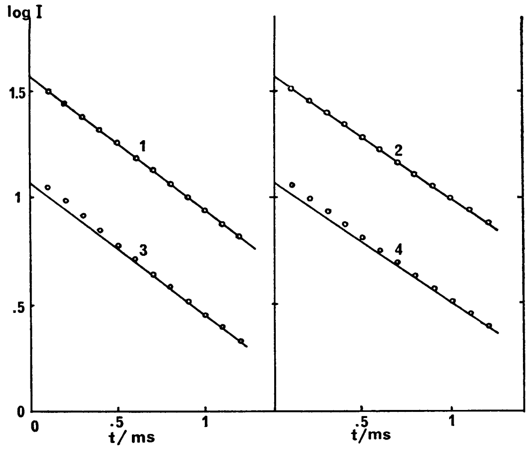

Fig. 6. Semilogarithmic plots of phosphorescence intensities *versus* time after excitation at low (1 and 2) and high (3 and 4) density excitations at 295 (1 and 3) and at 77 K (2 and 4).

Change in Decay Curve. In Fig. 6, the logarithm of the phosphorescence intensity (I) of the UN crystal is plotted against time for high and low density excitations at 295 and 77 K. The phosphorescence lifetimes, τ's, at the low density excitation are 697 μs at 295 K and 764 μs at 77 K. The decay times obtained from the initial slope of the phosphorescence decay curve are 620 μs at 295 K and 690 μs at 77 K at the high density excitation. Therefore, the decreases in the lifetimes τ are 77 μs at 295 K and 74 μs at 77 K. This is contrary to the expected effect of temperature upon τ. From Fig. 7, it can be seen that $\Delta\tau/\Delta T$ is smaller at high temperatures, where $\Delta\tau$ and ΔT are the change in lifetime and temperature. The decreases in the phosphorescence lifetimes, $\Delta\tau$, caused by the temperature increase, $\Delta T \cong 25$ °C, estimated above by the spectral change, were calculated to be much less than 10 μs at 295 K and 25 μs at 77 K. These decreases are too small to be the cause of the decrease in the lifetime. Induced emssion has also been ruled out. Therefore, the only possible cause of the lifetime shortening is biexcitonic quenching of triplet excitons in the crystal. When the bimolecular quenching process becomes significant, the time dependence of the exciton density $n(t)$ is given by the following equation:

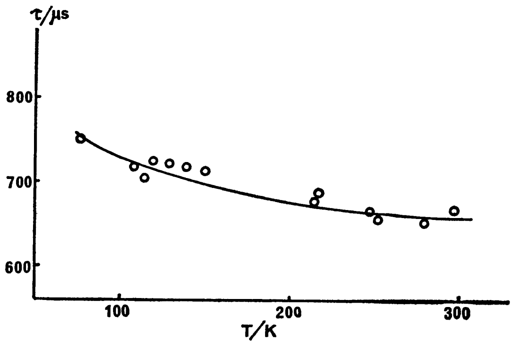

Fig. 7. Temperature dependence of phosphorescence lifetime of crystalline UN.

$$1/n(t) = (1/n_0 + \gamma/\alpha)\exp(\alpha t) - \gamma/\alpha, \tag{1}$$

where n_0 is the initial excitation density and α and γ are the rate constants for the monomolecular and bimolecular decay processes, respectively. As is expected, $1/n(t)$ was found to be linearly proportional to $\exp(\alpha t)$ at several temperatures between 295 and 77 K. From the slopes of the lines, γ was obtained at various temperatures, the results are given in Fig. 8. This figure shows that the plot of log γ *versus* $1/T$ is approximately linear and, therefore, γ can be written in the form

$$\gamma = \gamma_0 \exp(-\Delta E/kT). \tag{2}$$

From the slope of the line in Fig. 8, ΔE was found to be 320 cm^{-1}. The following relation between γ and the exciton hopping rate, λ, has been derived in a previous paper:[6]

$$\gamma = \frac{\lambda\mu}{\lambda+\mu}\,\frac{z_n V_0}{z_u}(2-A), \tag{3}$$

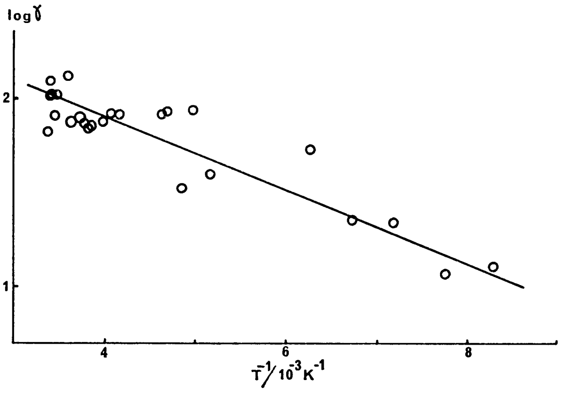

Fig. 8. Temperature dependence of γ of an exciton in crystalline UN. γ is in an arbitrary unit.

where μ, z_n, z_u, V_0, and A have the same meaning as in the previous paper.[6)] As is expected for a triplet exciton, if the exciton hopping rate, λ, is much slower than the monomolecular quenching rate constant, μ, of the two neighboring excitons, Eq. 3 may be simplified to

$$\gamma = \lambda \frac{z_n V_0}{z_u}(2-A). \tag{4}$$

By combining Eqs. 2 and 4, we obtain

$$\lambda = \lambda_0 \exp\left(\frac{-\Delta E}{kT}\right), \tag{5a}$$

$$\lambda_0 \equiv \gamma_0 \frac{z_u}{z_n V_0} \frac{1}{2-A}. \tag{5b}$$

We found the activation energy for bimolecular quenching and hence for exciton migration to be 320 $\mathrm{cm^{-1}}$.

The Absolute Values of γ and λ. In order to estimate the absolute values of γ and λ, it is necessary to know the concentration of the triplet excitons. The triplet exciton concentration in the irradiated volume the exciton is estimated from the following equation, since the intersystem crossing yield is nearly equal to unity in uranyl salts because of the heavy atom effect:[1,2)]

$$n_0 = L I_0 \frac{0.6321 \varepsilon_{3371} c}{\Delta S}, \tag{6}$$

where L is a loss factor of the laser pulse intensity caused by reflections off the surfaces of the lens, the sample tube, and the crystalline sample; ΔS is the area of the focused spot; I_0 is the number of photons per pulse; ε_{3371} is the molar extinction coefficient of the sample at the excitation wavelength; and c is the molar concentration of UN in the crystalline state. I_0 and ΔS were measured experimentally to be 1.0×10^{14} photons per pulse and 0.08 $\mathrm{cm^2}$, respectively. From the crystal structure,[16)] c was found to be 5.37 M.

When the laser intensity is greater than 3×10^{14} photons/pulse, the phosphorescence intensity is not proportional to the laser intensity. This saturation effect may be caused by two photon excitations (both simultaneous and stepwise), by reabsorption of the phosphorescence associated with the $\mathrm{T}_n \leftarrow \mathrm{T}_1$ transitions, and by ground state depletion.

The absorption spectrum of UN in $\mathrm{CH_3CN}$ solution and the uncorrected phosphorescence excitation spectrum of a UN crystal were measured at room temperature (295 K), the result is shown in Fig. 9. The vibrational structures of the spectra resemble each other, and the crystal shift is very small; thus, ε_{3371} of UN in the crystalline state is not much different from that in solution. Therefore, ε_{3371} for crystalline UN is assumed to be 9.2 $\mathrm{M^{-1}\,cm^{-1}}$, the same as the molar extinction coefficient of UN in $\mathrm{CH_3CN}$ solution.

By substituting these experimental data in Eq. 6, n_0 was found to be $2.2\times10^{18}\ \mathrm{cm^{-3}\,s^{-1}}$.[17)] Since it is difficult to determine A experimentally,[6)] it is assumed to be zero. This assumption only changes the calculated exciton hopping rate by a factor of two and the error caused by this assumption is smaller than possible experimental errors which accompany the determination of n_0 and, therefore, γ and λ as well.

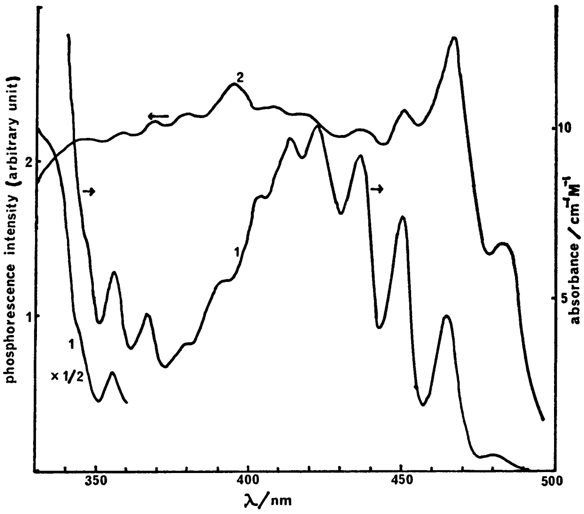

Fig. 9. Absorption spectrum of UN in $\mathrm{CH_3CN}$ solution (curve 1) and phosphorescence excitation spectrum of crystalline UN (curve 2) at 295 K.

With this assumption, we obtained $4.3\times10^{8}\ \mathrm{s^{-1}}$ for λ at 295 K. This value is reasonable for the migration rate of a triplet exciton. From the values of λ and τ at 295 K, we deduce that the exciton travels over about 3×10^{5} sites in crystalline uranyl nitrate during its lifetime.

TABLE 1. CHARACTERISTIC DATA FOR TRIPLET EXCITONS IN CRYSTALLINE URANYL NITRATE HEXAHYDRATE AT 295 K

τ	697 μs
α	$1.43\times10^{3}\ \mathrm{s^{-1}}$
γ	$2.6\times10^{-13}\ \mathrm{cm^3\,s^{-1}}$
λ	$4.3\times10^{8}\ \mathrm{s^{-1}}$
n_c	$5.5\times10^{15}\ \mathrm{cm^{-3}}$
R_c	352 Å
D	$5.5\times10^{-6}\ \mathrm{cm^2\,s^{-1}}$
l	8800 Å
d	7.8×10^{5} Å

In the same manner as was used in the preceding work,[6)] we determined the critical concentration, n_c, the diffusion coefficient, D, the mean diffusion length, l, and the critical radius, R_c, for bimolecular quenching at room temperature (295 K). The results are shown in Table 1. The relations between these parameters are as follows:

$$n_c\gamma = \alpha, \quad \frac{4\pi}{3}(R_c)^3 n_c = 1, \quad D = 2a^2\lambda, \quad l = (2D\tau)^{1/2}, \tag{7}$$

where $a = V_0^{1/3}$ is the mean distance between neighboring sites and V_0 is the volume of a unit cell. This table shows that the mean diffusion length, l, is much smaller than the absorption depth of the exciting light, d, in crystalline uranyl nitrate, which was found to be $d = 7.8\times10^{5}$ Å by use of the relation $d = (2.303\varepsilon_{3371}c)^{-1}$. Therefore, almost none of the triplet excitons initially generated by the nitrogen laser pulse escape from the irradiated region during their lifetime. This justifies the neglect of the diffusion term,

$$\sum_{i,j} D_{ij} \frac{\partial^2 n(t,x)}{\partial x_{ij}^2},$$

in the equation determining the behavior of $n(t,x)$, *viz.*,

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \alpha n + \gamma n^2 + \sum_{i,j} D_{ij} \frac{\partial^2 n}{\partial x_{ij}^2}. \qquad (8)$$

The neglect of the last term on the right hand side of Eq. 8 leads to Eq. 1. The diffusion coefficient of the triplet exciton at room temperature was obtained for anthracene (2×10^{-4} cm^2 s^{-1}),[18] pyrene (($8\pm4)\times10^{-4}$ cm^2 s^{-1}),[19] and *p*-dibromobenzene (($2\pm1)\times10^{-4}$ cm^2 s^{-1}).[20] The diffusion coefficient at room temperature obtained for the UN crystal in the present paper is about 100 times smaller than those in the three aromatic molecular crystals. The difference may be explained in the following way. The magnitude of the diffusion coefficient of the triplet exciton in the crystal is closely related to the exchange interaction between two neighboring molecules. The average distance between two neighboring molecules in the UN crystal is 10.6 Å which is much longer than those of anthracene (6.2 Å), pyrene (6.4 Å), and *p*-dibromobenzene (5.5 Å). Therefore the exchange interaction between two neighboring molecules and therefore the exciton hopping rate in the UN crystal are much smaller than those in anthracene, and *p*-dibromobenzene crystals.

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10) T. Kobayashi, S. Iwasima, S. Nagakura, and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, **18**, 117 (1972).

11) The spectra of UN at high and low density excitations at 77K are not shown, but they are quite similar to that at room temperature except that a slight sharpening of the bands are observed. The changes observed at 77K are quite similar to those at room temperature.

12) The reason why the vibrational band broadening is only observed in the spectra measured at 77K is as follows: The vibrational bands in the spectra measured at 295 and 201K are much broader than those measured at 77K, and the slight change which appears in the vibrational bands is more difficult to be detected for the broad spectra. So it is reasonble to consider that the undetectably slight vibrational band broadening is also occurring in the spectra mesured at higher temeratures.

13) More than 10^4 repetitions of high and low density excitations at the same spot of the crystal caused slight changes in the phosphorescence spectrum of the uranyl nitrate crystal. The following discussion uses only data obtained before the sample showed any irreversible change.

14) T. Kobayashi and S. Nagakura, *Mol. Cryst. Liq. Cryst.*, **25**, 153 (1974).

15) Since the phosphorescence spectra of UN in the crystalline state are quite similar to those in solution, the electronic state of the lowest triplet in the crystalline phase and that in solution are considered to be quite similar to each other. Therefore the absorption spectrum of T_1 shown in Fig. 9 is thought to be quite similar to that in the crystalline phase. From this it is assumed that the $T_n \leftarrow T_1$ absorption in the crystalline phase is the same as that in solution.

16) V. M. Vdovenko, E. V. Stroganov, A. P. Soklov, and V. N. Zandin, *Radiokhimiya*, **2**, 24 (1960).

17) This value is 12 times greater than 1.8×10^{-14} cm^3 s^{-1} the value determined by Tolstoi *et al.*[3]

Their value is erroneous for the following two reasons.

(1) The saturation effect was not taken into account and therfore, the number of excitons was overestimated and, hence, the value for γ was underestimated.

(2) The γ value of Tolstoi *et al.* results from their method of analysis of the experimental data. They determined γ from the initial slope of the phosphorescence decay curve. In practice, γ can not be determined with high enough accuracy by this method, because not enough data can be obtained with small errors in the short interval of time during which the initial slope is measured. In the present paper the exact solution of the equation was applied. To determine γ from the experimental data by using the exact solutions, one makes use of all the data points, not just the ones which are taken during the short time interval. Therefore the slopes can be determined from the experimental data with greater accuracy and, hence, γ can be calculated more accurately than by the method of Tolstoi *et al.*