

LETTERS TO THE EDITOR

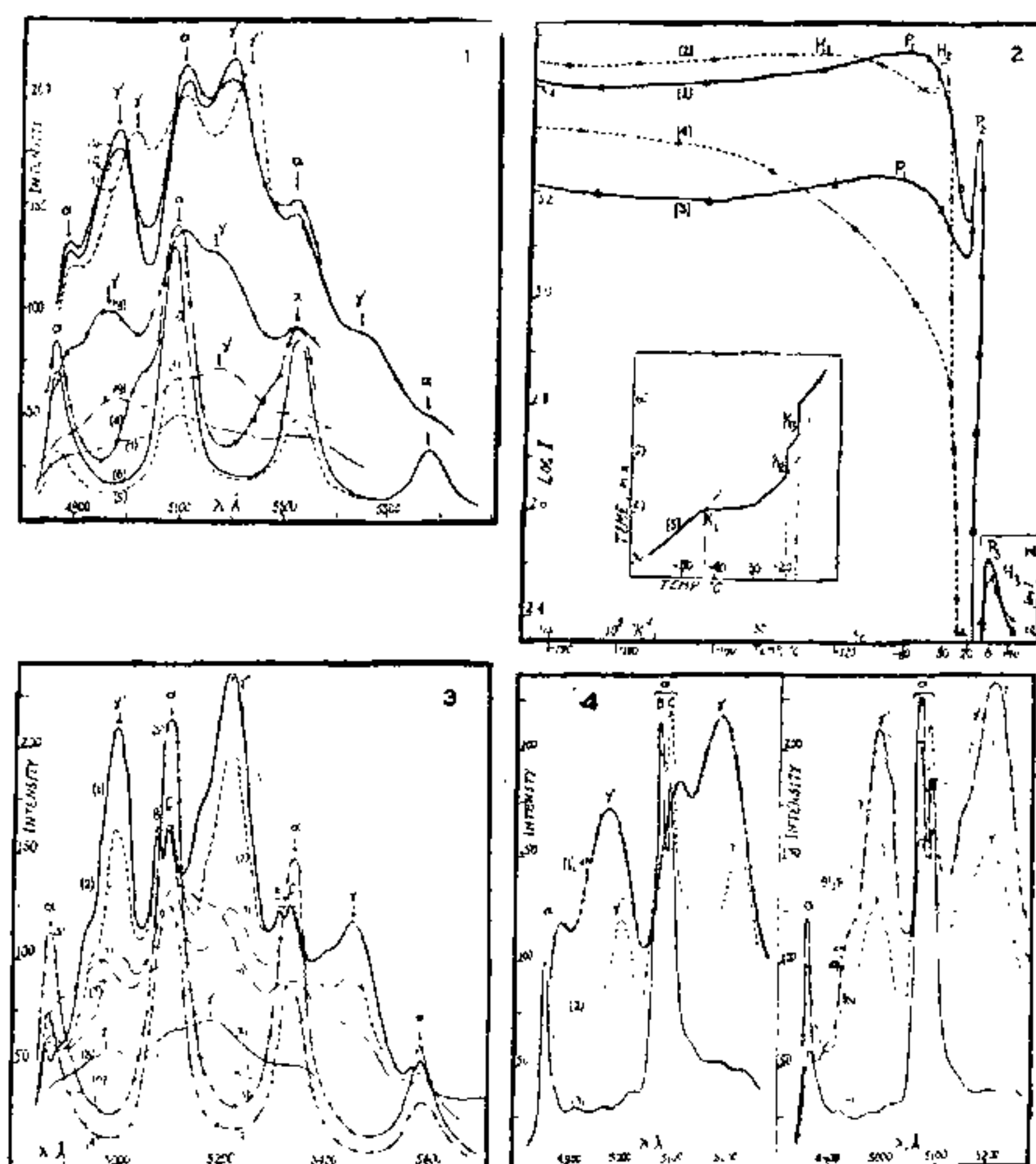
TEMPERATURE DEPENDENCE OF
FLUORESCENCE BANDS OF URANYL
NITRATE SOLUTIONS

RECENTLY Hayakawa and Hirata¹ have reported intensity variations in the fluorescence of uranyl nitrate solutions. They observe two peaks in the T-I curve at -85° and -25° C., of which the latter is ascribed to melting. We have been interested in quantitative measurements of intensities in these spectra for some time now and one of us had earlier observed several complex changes in the T-I curves,² the elucidation of which needed further detailed study. We are now in a position to report the specific conditions under which these intensity changes take place.

What is of profound significance is that for the solution of a given pH and concentration the spectrum not only depends upon temperature, but also upon the manner in which the solution is brought to that temperature. Spectral changes in the range $+25^{\circ}$ to -193° C. have been studied in six different ways: (a) Slow warming of a solution rapidly cooled to -193° C., (b) Slow warming of a solution previously slowly cooled to -193° C., (c) Slow cooling from $+25^{\circ}$ to -193° C., (d) Warming of a rapidly cooled solution to an intermediate temperature θ and recooling rapidly to -193° C., (e) Warming of a slowly cooled solution to an intermediate temperature θ and recooling rapidly to -193° C., and (f) Slow cooling up to an intermediate temperature θ and rapid cooling further up to -193° C.

Figure 1 represents the spectral changes in case (a). The spectrum at -193° C. contains α and γ bands and the intensity variations of these with temperature are shown in Fig. 2. The curve for α bands shows three peaks: P_1 (-75° C.), P_2 (-20° C.) and P_3 (-2° C., melting point). The curve for γ bands similarly shows three peaks: H_1 (-120° C.), H_2 (-60° C.) and H_3 (-2° C.). Just at H_2 the γ bands shift towards the red (Fig. 1, Curve 3), after which they disappear rapidly. They can hardly be traced in the range -35° to -5° C. and then they reappear in the original γ position. In the range H_3 to $+25^{\circ}$ C. their intensity falls less rapidly than that of α bands. Curve 5 in Fig. 2 (inset) shows the variation of temperature with

time for a conc. (4 M)[†] solution. It shows three discontinuities: K_1 (-43° C.), indicating an exothermic change; K_2 (-20° C.) indicating an endothermic change; and K_3 (-17° C.), corresponding to melting in this case. The correspondence between K_1 and the steep fall



FIGS. 1-4. Fig. 1. Fluorescence spectra of rapidly cooled 0.2 M aqueous solution of Uranyl Nitrate at different temperatures during warming: (1) -193° C., (2) -75° C., (3) -60° C., (4) -45° C., (5) -30° C., (6) -20° C., (7) -10° C., (8) 0° C., (9) $+25^{\circ}$ C. (I scale for 7, 8, 9, to read 1/50). Fig. 2. Temperature-Intensity curves (T-I curves) for different bands during warming from -193° C. Curves (1), (2) for α , γ bands respectively of rapidly cooled solution. Curves (3), (4) for α , γ bands respectively of slowly cooled solution. Curve (5) shows variation of temperature with time for a rapidly cooled 4 M solution. Fig. 3. Fluorescence spectra of slowly cooled 0.2 M aqueous solution of Uranyl Nitrate at different temperatures during warming: (1) -193° C., (2) -100° C., (3) -75° C., (4) -35° C., (5) -20° C., (6) -10° C., (7) 0° C., (8) $+25^{\circ}$ C. (I scale for 6, 7, 8 to read 1/60). Fig. 4. Fluorescence spectra at -193° C.: (1), (2), (3) and (4) for rapidly cooled solution warmed up to -100° , -45° , -20° and -10° C. respectively and re-cooled rapidly; (5) (6), (7) and (8) for slowly cooled solutions warmed up to -100° , -45° , -20° and -10° C. respectively and re-cooled rapidly; (9) and (10) for solutions cooled slowly up to -20° and -45° C. respectively and rapidly cooled thereafter.

* Temperatures in the lower range may be in error by 5° C.

† Changes are not so distinct in 0.2 M solution for which the spectra have been taken.

in γ intensity, as also between K_2 and peak P_2 in α intensity, is notable.

In case (b) a well-resolved spectrum is obtained at -193°C , containing α bands (split into two components, B and C) and γ' bands (shifted towards the red w.r. to γ). The spectral changes are given in Fig. 3 and T-I variations in Fig. 2. The T-I curve for γ' shows no noticeable hump. In case of α bands the intensity at -193°C is rather low and peak P_2 is very prominent. It may be observed that up to -80°C (about P_1) the C component of α gains over B. Case (c) differs from (b) in the conspicuous absence of peak P_2 .

The spectra observed at -193°C under processes (d), (e) and (f) are given in Fig. 4. The notable features are that by warming the frozen mass up to different intermediate temperatures θ (below melting) and then recooling (i) the spectrum of a rapidly cooled solution can be changed to that of a slowly cooled one and *vice versa*, (ii) the ratio of C to B components can be changed and (iii) the intensities of γ and γ' bands relative to α can be reduced to any extent. The critical values of θ are related with discontinuities K_1 and K_2 (Fig. 2, Curve 5). For example, a rapidly cooled solution warmed to θ between -43° to -20°C on recooling gives a resolved spectrum, the γ' bands diminishing in intensity with increasing θ .

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DAY-LIGHTING EQUATIONS FOR A STANDARD OVERCAST SKY

EQUATIONS for sky factors for a "Uniform sky" were derived by Yamauti¹ (1924) using a geometrical method. Those equations were used by Rivero² (1958) in the preparation of his tables for a rectangular window of known dimensions.

The International Commission on Illumination (C.I.E.) in its sessional meeting at Zurich³ (1955) defined and recommended for general

adoption a "Standard Overcast Sky" in which the surface intensity of illumination varied with the altitude in accordance with the equation $B_\theta = B_z (1 + 2 \sin \theta/3)$, where B_z and B_θ were the intensities at zenith and at an altitude θ respectively. Tables of sky components for this standard overcast sky were also drawn up by Rivero² (1958) based on his initial tables of sky factors for a uniform sky and using an indirect method of computation.

The author has now derived rigorous trigonometrical equations which can be employed directly. For a point P on the normal to the plane of the window passing through one of its lower corners and distant D from it, the equations

$$L/D = \tan \beta, \quad H/D = \tan \gamma,$$

$$\tan \beta' = \tan \beta \cos \gamma; \quad \tan \gamma' = \tan \gamma \cos \beta$$

define the angles β , β' , γ and γ' subtended at P by the lower and top horizontal sides and nearer and farther vertical sides respectively of the rectangular window of length L and height H. In terms of these angles the derived equations for the different sky components at the point P for a C.I.E. Standard Overcast Sky, for a vertical rectangular unglazed window opening are as follows:

$$F_h = \frac{3(\beta - \beta' \cos \gamma)}{14\pi} + \frac{2 \sin^{-1}(\sin \beta \sin \gamma)}{7\pi} - \frac{1}{7\pi} \sin 2\gamma \sin \beta'$$

$$F_{v,\perp} = \frac{3(\gamma - \gamma' \cos \beta)}{14\pi} + \frac{2}{7\pi} (1 - \cos \beta - \cos \gamma + \cos \beta \cos \gamma)$$

$$F_{v,\parallel} = \frac{3(\gamma' \sin \beta + \beta' \sin \gamma)}{14\pi} + \frac{2}{7\pi} (\sin \beta - \cos^2 \gamma \sin \beta')$$

where F_h , $F_{v,\perp}$ and $F_{v,\parallel}$ are the sky component ratios in the horizontal plane, vertical plane perpendicular to the window and vertical plane parallel to the window respectively, passing through P. The angles are expressed in radian measure.

It is also possible to use the same equations to determine the sky components at any other point not on the perpendicular from one corner of the window.

The first terms in the equations above, but with $1/2\pi$ replacing the factor $3/14\pi$ are the respective Yamauti's equations for a uniform sky. Those equations are also derivable by the general analytical method adopted by the author.