Polarised Photoluminescence of Adsorbed Molecules of Dyes

I HAVE investigated the degree of polarisation of fluorescence and phosphorescence from 'Cellophane' films coloured by Kautsky's method[1] ('Cellophane' phosphors). The molecules of the dye, adsorbed on the surface of the microcrystals of the film, cannot rotate ; therefore the luminescence cannot be depolarised by rotation.

The films used, 0·09 mm. in thickness, are optically anisotropic. It is known that the orientations of the axis of the microcrystals are regular to a certain extent. The observations were made with a Savart analyser and a set of compensating glass plates approximately in the direction of the exciting light, perpendicular to the surface of the 'Cellophane' phosphor. The latter could be rotated around this direction and the azimuth (α) could be read. The analyser gave the value of $P = (I_1 - I_2)/(I_1 + I_2)$, where I_1 and I_2 are the intensity of the components the vibrations of which are parallel and perpendicular respectively to the direction of the vibrations of the exciting light transmitted through the polariser. When natural light was used for excitation, the same position of analyser was used.
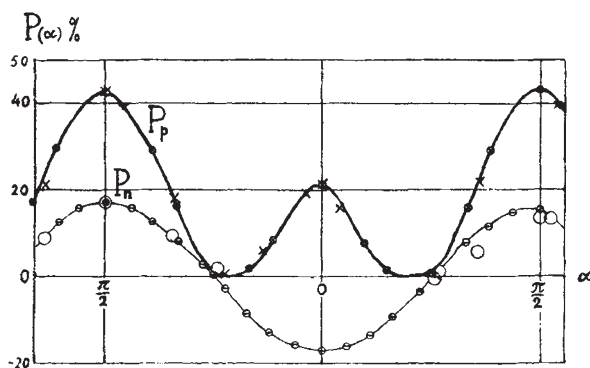

FIG. 1. P as a function of azimuth (α) for euchrysine-'Cellophane'-phosphor.
P_p, excitation with polarised light.
P_n, excitation with natural light.
x and o observed values, ⊗ and ⊖ calculated values from the formulæ

$$P_p = \frac{(\varepsilon_1{}^2 \cos^2 \alpha - \varepsilon_2{}^2 \sin^2 \alpha) \cos 2\alpha - \cos^2 2\alpha}{\varepsilon_1{}^2 \cos^2 \alpha + \varepsilon_2{}^2 \sin^2 \alpha + 1} \quad \text{and}$$

$$P_n = \frac{(\varepsilon_1{}^2 - \varepsilon_2{}^2) \cos 2\alpha}{\varepsilon_1{}^2 + \varepsilon_2{}^2 + 2}$$

Fig. 1 shows the $P(\alpha)$ curves for the fluorescence of a euchrysine-'Cellophane'-phosphor, for natural and polarised exciting light. In the latter case, it is clear that the degree of polarisation for $\alpha = \pi/2$ is higher than for $\alpha = 0$. For these two azimuths, the exciting light vibrates to one or to the other principal direction of vibration in the 'Cellophane' film. Also when excited with natural light, the fluorescence shows partial polarisation in a certain direction (Fig. 1, P_n).

Similar curves were obtained for phosphorescence but the values of $P(\alpha)$ were somewhat smaller.

Anisotropy was also examined by absorption ; the absorption coefficients show an anisotropy, however. The position of the absorption band does not depend upon the direction of light vibration.

Although different dyes have $P(\alpha)$ curves of the same character, the values of $P(\alpha)$ differ very much.

This indicates that the phenomena are not only due to the anisotropy of the field intensity of the exciting light (caused by the birefringence of the medium) but also to the polarisability tensor of the dye molecules and anisotropy of the distribution of the directions of their axes.

Details of this investigation will be shortly published elsewhere.

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[1] H. Kautsky and A. Hirsch, Chem. Ber., 65, 401 ; 1932.

Predissociation in the Upper Level of the Ångström Bands of Carbon Monoxide

IN taking a photometer curve of the $0 \to 1$ band $^1\Sigma \to {}^1\Pi$ ($\lambda = 4835$), we observed that in all three branches, P, Q and R, beginning with the same value $J = 38$ of the upper level, the lines abruptly decrease in intensity to less than half the original value. It seems to us reasonable to assume that this remarkable feature is caused by a predissociation of $^1\Sigma$ into the triplet dissociation term ^3P (oxygen) $+ {}^1D$ (carbon).

Triplet-singlet intercombinations in the emission spectrum of CO have already been observed by Cameron. In this case the selection rule forbidding singlet-triplet transitions does not hold, but at any rate the Cameron bands are much more difficult to get than most of the other CO-bands, even though no other transition to a lower state of the molecule does exist. In the same way a predissociation of a singlet by a triplet term may occur. As the transition to the dissociated molecule must be rather improbable, it seems that the life time of predissociation here becomes of the same order of magnitude as that which belongs to a transition with radiation. In this case the emission lines do not disappear, but only decrease in intensity as has been observed. A triplet-singlet intercombination with predissociation has also been observed by Herzberg[1] in the case of P_2. But for this much heavier element the probability of the triplet-singlet intercombination is already so large, that for P_2 the band lines totally disappear.

From the energy of the predissociation we were able to calculate the dissociation energy of the normal state. We found $D = 9·82$ volts, in good agreement with the value generally assumed (10 volts). For the other molecular terms we found as dissociation energies : $A\,{}^1\Pi$, 1·82 volts ; $B\,{}^1\Sigma$, 2·28 volts ; $a\,{}^3\Pi$, 3·84 volts ; $a'\,{}^3\Sigma$, 3·94 volts ; $d\,{}^3\Pi$, 3·10 volts.

The upper zero vibration level of the Herzberg bands lies about 3100 cm.$^{-1}$ *higher* than the dissociation term $^3P + {}^1D$. Thus these bands from their beginning already suffer from predissociation and it is easy to understand why they are much more difficult to get than the Ångström bands.

Further particulars will be given shortly in the new Dutch periodical *Physica*.

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            Dec. 16.

[1] G. Herzberg, Phys. Rev., 40, 313 ; 1932.