LETTERS TO THE EDITOR

ULTRA VIOLET BAND SPECTRUM OF HgBr

IN continuation of the work on HgCl bands,[1] the ultra-violet band systems of the homologous molecules, HgBr and HgI have been investigated under similar experimental conditions. The characteristic bands between λ2900 and λ2650, designated as the Class II system and suggested by Wieland[2] as belonging to the triatomic molecule $HgBr_2$, have been ascribed by the author to the diatomic molecule HgBr and a vibrational analysis has been obtained. The constants determined for the band heads of $Hg^{202}Br^{81}$ are

ω_e'	459·0 cm.$^{-1}$	ν_e (mol)	34537·8 cm.$^{-1}$
ω_e''	372·3 ,,	ν (atom)	4·92 volts
$x_e'\omega_e'$	3·6 ,,	D'	1·81 ,,
$x_e''\omega_e''$	3·8 ,,	D''	1·15 ,,

The assignment of the quantum numbers is confirmed by observations of the isotopic heads due to $Hg^{202}Br^{79}$, for which the agreement between the observed and calculated positions is very close. The electronic transition giving rise to the band system is probably $^2\Sigma - {}^2\Sigma$ with negligible spin doubling, the dissociation products being $Hg(^1S) + Br(^2P)$ and $Hg(^3P) + Br(^2P)$ for the two electronic states. A full account of the work will be published shortly.

M. G. SASTRY.

Andhra University,
Waltair,
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[1] *Curr. Sci.*, 1941, **10**, 669.
[2] *Helv. Acta Phy.*, 1929, **2**, 46, 77.

CRYSTAL STRUCTURE OF COUMARIN

COUMARIN crystallises in the orthorhombic system with the axial ratio 0·9833 : 1 : 0·3696.[1] The dimensions of the unit cell obtained from measurements of a number of rotation photographs about the three crystallographic axes, using Cu K_α radiation, are 15·44, 7·92 and 5·66 Å. $a : 2b : c$ is in agreement with the axial ratio quoted above. In the rotation photographs, spots of the type *hkl* are present in all orders while *okl* is halved if *k* is odd and *hko* is halved if *h* is odd. The possible space-groups are therefore V_h'' and C_{2v}^5, the former being a holohedral group and the latter a hemimorphic hemihedral one. Since coumarin exhibits hemimorphism about the *b* axis[1] it is to be concluded that C_{2v}^5 is the correct space-group.

Examination under a polarising microscope with convergent light reveals that the *c* axis is normal to the optic axial plane. The crystal is positive and the acute bisectrix is parallel to the *b* axis. This would mean that the vibration directions for the largest, mean and smallest refractive indices correspond to the *a*, *c* and *b* axes respectively.

The diamagnetic anisotropy of the crystal, determined for me by Dr. P. Nilakantan, is as follows:

$(\chi_a - \chi_c)_M = 31{\cdot}8 \times 10^{-6}$, $(\chi_a - \chi_b)_M = 109 \times 10^{-6}$ and $(\chi_c - \chi_b)_M = 79{\cdot}0 \times 10^{-6}$.

Hence the anisotropy in the *ac* plane is comparatively small and $\chi_b > \chi_c > \chi_a$.

From the optical and magnetic data it is to be concluded that the molecule is orientated in the unit cell with its plane parallel or nearly so to the *ac* plane. Also the long axis of the molecule is parallel or nearly so to the *a* axis. A complete analysis of the crystal structure is in progress.

S. RAMA SWAMY.

Department of Physics,
Central College, Bangalore,
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[1] A. Cathrein, *Zs. Krist.*, **11**, p. 402.

OPTICAL SENSITISATION AND PHOTOVOLTAIC EFFECT OF DYES

VARIOUS attempts have been made from time to time to connect optical sensitisation with other physico-chemical properties. Zchodro[1] found complete correlation between light absorption and photo-conductance of three sensitising dyes, cyanine, pinaverdol and pinachrome. Bancroft, Ackerman and Gallagher[2] have connected the sensitising power of a dye with its capacity as a halogen acceptor. Kornfeld[3] thinks there may be some correlation between fluorescence and optical sensitisation and suggests an investigation of this property in sensitised emulsions. Leermakers, Carroll and Staud[4] have shown that absorption and optical sensitisation run parallel. A close comparison of the absorption and sensitisation of a photographic plate by the two dyes, Eosin and Erythrosin, reveals the fact that the maximum of sensitisation does not coincide with the region of maximum absorption of the dye, but is displaced a few wave-lengths to the red. It has however been stated, on the basis of the generally known fact that the absorption of a dye is appreciably altered by the properties of the solvent, what is of account in determining its sensitising action is not its individual absorption, but of the complex it may form with the sensitive emulsion. (This complex is in the nature of an adsorption complex and in some instances a peculiar edge-on adsorption or a nematic state has been assumed with entirely different properties of absorption.)[5]

I have shown elsewhere with reference to Erythrosin[6] that the maximum of photo-voltaic effect in aqueous solutions of the dye (where obviously no complicated adsorption phenomena may come into play) occurs in a region shifted a few wave-lengths to the red from the absorption head and does coincide with the region of maximum sensitisation of the photographic plate. At the same time I ventured the suggestion that the same factors probably come into play in giving rise to the two effects. I have since been able to extend these observations on three more dyes[7]—Methylene blue, Methyl green and Malachite green—all of which possess a second band of absorption in the less refrangible part of the visible spectrum. In every case may be seen two maxima of photo-potential corresponding to the two absorption bands and the wave-length displacement or shift is also unmistakably present. The sensitising action of these dyes on the light sensitive compound, HS.Hg.CNS., has already been noted[8] and a comparison of the photo-potential with the amount of optical sensitisation along the spectrum shows a definite parallelism, which is indeed more than a mere coincidence and suggests identity of origin for the two effects. The accompanying table illustrates this point.

TABLE I

	Absorption	Sensitisation	Region of maximum photo-potential
	$\mu\mu$	$\mu\mu$	$\mu\mu$
Erythrosin ..	455—560	560—600	580
Chrysoidin ..	360—540	..	546
Methyl green ..	550—680	580—690	580—690
Malachite green	from 550	530—620	615
Methylene blue	540—615 & 665—695	530—600	580

N B.—In the case of the last three dyes the absorption in the blue-violet has not been given. Against sensitisation is noted only the region where it is very appreciable and amounts to a second maximum. In a general sort of way all the three dyes sensitise upto 700$\mu\mu$.