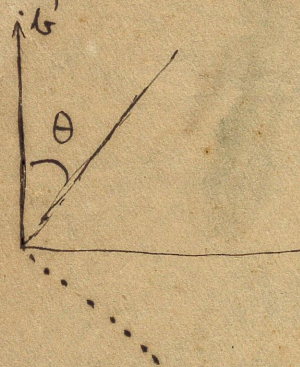


On the fluorescence of chrysenes
and other monoclinic organic crystals.

Consider a crystal flake parallel to (001) plane.



Let half the molecules in the unit cell be oriented in such a way that the normal to the plane of the molecule makes an angle of θ with the (001) plane, and its projection on (001) makes an angle θ with the 'b' axis.

Case I. Let the incident light vibrations which excite fluorescence, be along the 'b' axis.

Let For unit ~~length~~^{electric vector} electric field of the incident light wave ~~parallel to the~~ along the normal to the molecular plane, let the fluorescence excited, which also has the same vibration direction, be equal to K_{\parallel} . Let K_{\perp} be value ~~for~~ when the incident light vector is in the plane of the molecule.

→ amplitude Then it can be

into three components:

(1) of amplitude $E \sin \theta$ in the plane of the molecule.

This will give rise to ~~$E \cdot K_{\perp} \sin \theta$~~
 $E \sin \theta \cdot K_{\perp} \cdot \sin \theta$ amp. of fluor. vibr. along 'b'

$E \sin \theta \cdot K_{\perp} \cdot \cos \theta$ amp. fluor. along 'c'

(2) of amp. $E \cos \theta \sin \phi$, also in the plane of the molec. This ~~will~~ will give rise to

$E \cos \theta \cdot \sin \phi \cdot K_{\perp} \cdot \cos \theta \sin \phi$ amp. fl. along 'b'

$E \cos \theta \sin \phi \cdot K_{\perp} \cdot \sin \theta \sin \phi$ " " " "

(3) of amp. $E \cos \theta \cos \phi$ along the normal to the plane of the molec. This will give rise to

$E \cos \theta \cos \phi \cdot K_{\parallel} \cdot \cos \theta \cos \phi$ amp. fl. along 'b'

$E \cos \theta \cos \phi \cdot K_{\parallel} \cdot \sin \theta \cos \phi$ " " " "

Total intensity of fluorescence along 'b' axis

$$I_{bb} = E^2 \cdot \left[K_{\perp}^2 (\sin^4 \theta + \cos^4 \theta \sin^4 \phi) + K_{\parallel}^2 (\cos^4 \theta \cos^4 \phi + \sin^4 \theta \cos^4 \phi) \right]$$

Total intensity along 'a' axis

$$I_{ba} = E^2 \cdot \left[K_{\perp}^2 (\sin^2 \theta \cos^2 \theta + \sin^2 \theta \cos^2 \theta \sin^4 \phi) + K_{\parallel}^2 (\sin^4 \theta \cos^2 \theta \cos^2 \phi + \cos^4 \theta \sin^2 \theta \sin^2 \phi) \right]$$

Case ii 'Incident vibration of amplitude E is along the 'a' axis.

This can be resolved in the same manner as \neq before, and will give for the intensity of fluorescent light = vibrating along 'b' axis

$$= E^2 \left[K_{\perp}^2 (\sin^2 \theta \cos^2 \theta + \sin^2 \theta \cos^2 \theta \sin^4 \phi) + K_{\parallel}^2 (\sin^2 \theta \cos^2 \theta \cos^4 \phi) \right]$$

and ^{in the} intensity of flu vibrating along 'a' axis

$$= E^2 \left[K_{\perp}^2 (\cos^4 \theta + \sin^4 \theta \sin^4 \phi) + K_{\parallel}^2 (\sin^4 \theta \cos^4 \phi) \right]$$

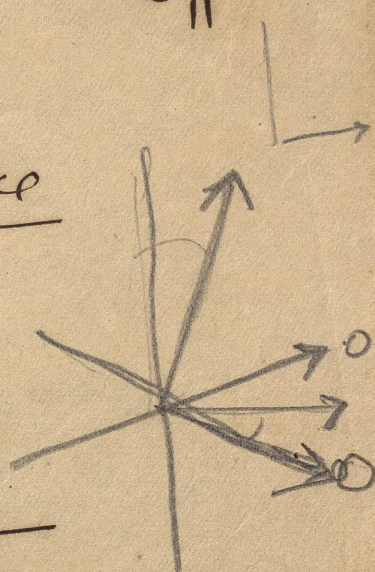
Now ~~in crystals and in other crystals~~
if we assume that $K_{\parallel} = 0$

$$\frac{I_{\perp b}}{I_{\parallel a}} = \frac{\sin^4 \theta + \cos^4 \theta \sin^4 \phi}{\sin^2 \theta \cos^2 \theta + \sin^2 \theta \cos^2 \theta \sin^4 \phi}$$

If now we assume that $K_{||} = 0$

$$\frac{I_{ba}}{I_{bb}} = \frac{\sin^2 \theta \cos^2 \theta + \sin^2 \theta \cos^2 \theta \sin^4 \phi}{\sin^4 \theta + \cos^4 \theta \sin^4 \phi}$$

$$\frac{I_{aa}}{I_{ab}} = \frac{\cos^4 \theta + \sin^4 \theta \sin^4 \phi}{\sin^2 \theta \cos^2 \theta + \sin^2 \theta \cos^2 \theta \sin^4 \phi}$$



Now in chryseine, ~~the~~ from X-ray data, the angle between the normal to the molecular plane and 'a' axis $[= \arccos \alpha_3$ in the notation adopted in R.S. paper in the Mrs L] = $\arccos .8549$.

i.e. $\sin \theta \cos \phi = .8549$

\angle betw the normal to molec. plane and 'b' axis $(= \arccos \beta_3) = \arccos .4819$

$$\cos \theta \cos \phi = .4819$$

$$\tan \theta = \theta = 60.6^\circ$$

$$\phi = 11.0^\circ$$

Using these values for θ and ϕ \rightarrow

$$I_{bb} = E_0^2 \left(\frac{.5759 \sin^4 \theta - \cos^4 \theta \sin^4 \phi}{.0001} \right) \times \left(.5760 K_{\perp}^2 + .0539 K_{\parallel}^2 \right)$$

$$I_{ba} = E_0^2 \left(\frac{.1829 K_{\perp}^2 - .0002 K_{\parallel}^2}{.1831} \right) \times \left(.1831 K_{\perp}^2 + .1697 K_{\parallel}^2 \right)$$

$$I_{ab} = E_0^2 \left(\frac{.1829 K_{\perp}^2 - .0002 K_{\parallel}^2}{.1831} \right) \times \left(.1831 K_{\perp}^2 + .1697 K_{\parallel}^2 \right)$$

$$I_{aa} = E_0^2 \left(\frac{.0581 K_{\perp}^2 - .0006 K_{\parallel}^2}{.0589} \right) \times \left(.0589 K_{\perp}^2 + .5346 K_{\parallel}^2 \right)$$

$$\frac{I_{ba}}{I_{bb}} = \frac{.1831 \times \left(\frac{K_{\perp}^2}{K_{\parallel}^2} \right) + .1697}{.5760 \frac{K_{\perp}^2}{K_{\parallel}^2} + .0539}$$

$$\frac{I_{aa}}{I_{ab}} = \frac{.0589 \frac{K_{\perp}^2}{K_{\parallel}^2} + .5346}{.1831 \frac{K_{\perp}^2}{K_{\parallel}^2} + .1697}$$

$r =$ ratio of the
amp. of fluorescence
when E is along
the molecular
plane to that
when E is \perp to
molecular plane
 $r =$ ratio of corresponding
intensities

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Now experimentally $\frac{I_{ba}}{I_{bb}} = .51$

from ii we obtain

$$.1831 r^2 = \frac{.1422}{.1107} = 1.28$$

From iii value

$$\frac{I_{aa}}{I_{ab}} = .51$$

$$r = 13.0$$

The two values are different. If $\frac{I_{ba}}{I_{bb}} = \frac{I_{aa}}{I_{ab}}$ then they can not be equal to 0.51.

If $\frac{I_{ba}}{I_{bb}} = \frac{I_{aa}}{I_{ab}}$ as experimentally observed, then ~~$r =$~~

$$\begin{aligned} (.1831 r^2 + .1697)^2 &= (.5760 r^2 + .0539) \left(\frac{.0589 r^2}{.1831 r^2} + .5346 \right) \\ .03353 r^4 + .06215 r^2 + .02880 &= .03392 r^4 + .3111 r^2 + .02880 \\ .00039 r^4 + .2489 r^2 &= 0 \end{aligned}$$

of θ the angle in i corner
between the two positions of equilibrium = $2 \times 29\frac{1}{2} = 32^\circ$

Anthracene

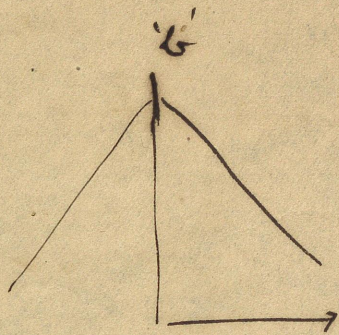
From x-ray measurements

$$\sin \theta \cdot \cos \varphi = \frac{.8549}{.7947}$$

$$\cos \theta \cdot \cos \varphi = \frac{.4819}{.4602}$$

$$\theta = \frac{60.6}{59.9}$$

$$\varphi = 23.3$$

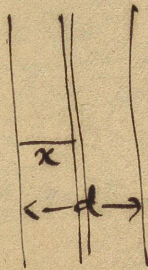


Let I_0 be the intensity of the incident radiation polarised with its electric vector along 'b'.

Let $I_0 \times A$ be the intensity of the fluorescent vibration along 'a' axis, and $I_0 \times B$ along 'b' axis.

Let k be the absorption coeff. for the incident monochromatic radiation which excites the fluorescence, and k_a, k_b for the fluorescent radiations polarised with their electric vectors along 'a' and 'b' axes resp.

Then



Let t be the thickness of the crystal.

Consider a layer of thickness

dx at a dist. x from the surface on which light is incident. Then the intensity of exciting light at $x = I_0 e^{-kx}$.

The intensity of the 'a' component from this layer = $A I_0 e^{-kx} \times e^{-k_a dx}$

The total A component as observed

$$\equiv \frac{I_0 A}{R} \cdot e^{-k_a t} \int_0^t e^{-(k-k_a)x} \cdot dx$$

$$= \frac{I_0 A e^{-k_a t}}{R - k_a} \left[1 - e^{-(k-k_a)t} \right]$$

$$= \frac{I_0 A}{R - k_a} \left[e^{-k_a t} - e^{-kt} \right]$$

These two terms are quite known.