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Research Note

Dichroic Ratio of a Group of Overlapping Bands in the Near Infrared Region

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Hitherto, dichroic ratios of vibrational bands have been investigated only for single, isolated bands. Such bands occur very rarely in the IR and this fact among others limits the validity of dichroim measurements in structural research. It is also possible to define the dichroic ratio for a group of overlapping bands as can be shown from an example of thiourea single crystals. The theoretical treatment of this phenomenon will be published later.

The spectrum of thiourea has been measured in polarized light in the 6000–7200 cm^{-1} region. The absorption bands in this range are due to the overtones and combination tones of the $—NH_2$ group. On the basis of group theory analysis it was found that six vibrations of A_1 symmetry type and four of B_1 can contribute in the integrated intensity of the spectrum in question. Therefore in the oriented gas model approximation,[1] the intensity of a group of bands measured in one direction of polarized light can be regarded as a sum of dipole moment projections of A_1 and B_1 vibrations on a chosen direction:

$$I_i = 6a_1 \cos^2(\mathbf{A}_1, \mathbf{i}) + 4b_1 \cos^2(\mathbf{B}_1, \mathbf{i}) \tag{1}$$

where

I_i = integrated intensity of group of bands measured for electric vector $\mathbf{E}_i$, of the electromagnetic wave polarized along the direction i in the crystal,

i = direction of one of the crystallographic axes: a, b, c, of orthorombic system in which crystalizes thiourea,

$(\mathbf{A}_1, \mathbf{i})$ = angle between the transition moment $\mathbf{A}_1$ and vector $\mathbf{E}_i$,

a_1, b_1 = coefficients of intensity of normal vibrations of A_1 and B_1 respectively:

$$a_1 \sim \left(\frac{\partial \mu}{\partial q}\right)^2_{A_1}, \qquad b_1 \sim \left(\frac{\partial \mu}{\partial q}\right)^2_{B_1}$$

By assuming that for vibrations of different symmetry types of the same oscillator $a_1 = b_1$, we obtain:

$$I_i \sim [6\cos^2(\mathbf{A}_1, \mathbf{i}) + 4\cos^2(\mathbf{B}_1, \mathbf{i})]a_1 \tag{2}$$

the dichroic ratio of the band group in thiourea single crystals in the 6000–7200 cm^{-1} region will be:

$$R_{i/j} = \frac{I_i \cdot n_j}{I_j \cdot n_i} = \frac{[6\cos^2(\mathbf{A}_1, \mathbf{i}) + 4\cos^2(\mathbf{B}_1, \mathbf{i})]n_j}{[6\cos^2(\mathbf{A}_1, \mathbf{j}) + 4\cos^2(\mathbf{B}_1, \mathbf{j})]n_i} \tag{3}$$

where n_i, n_j are the refractive indices along the i, j directions in the crystal.[1]

The direction cosines of the transition moments of A_1 and B_1 vibrations have been calculated on the basis of the structural data.[2] The direction of the transition moment for the symmetrical —NH_2 vibration was assumed to be parallel to the sum of both —NH vectors, whereas that for antisymmetrical vibration of symmetry B_1 was assumed to be parallel to their difference. The values of the direction cosines and the dichroic ratios for two differently oriented platelets of thiourea are given in table I.

TABLE I

	A_1	B_1	$R^{calc.}_{b/c}$	$R^{exp.}_{b/c}$	$R^{calc.}_{c/a}$	$R^{exp.}_{c/a}$
a	0.2418	0.3893				
b	0.8691	−0.5428	1.70	1.77 ± 0.02	3.18	2.78 ± 0.06
c	−0.4313	−0.7441				

Experimental dichroic ratios have been determined by integrating the area under the absorption curve by means of weighting of the diagrams. The measurements have been performed for four plates (100) and for two plates (010).

In order to study another example, the same method was applied to *p*-nitroaniline single crystals. Linear dichroism of these crystals has been previously determined for single bands of overtones and combination tones of the —NH_2 group in the 6400–7200 cm^{-1} range.[3] The integrated intensities of particular bands have been calculated by numerical integration of the area under the absorption curve by means of the Cauchy-Gauss product function. A good agreement between experimental and predicted dichroic

ratio values has been obtained only in the case of the best isolated bands of the antisymmetric $-NH_2$ overtone stretching.

In the 6400–7200 cm^{-1} region, in *p*-nitroaniline crystals, three vibrations of A_1 symmetry type and two of B_1 symmetry type can occur and the corresponding bands partially overlap. The dichroic ratio of the overall profile with respect to the two perpendicular directions lying on the cleavage plane (101), as given by formula:

$$R_{a'/b} = \frac{I_{a'} \cdot n_b}{I_b \cdot n_{a'}} = \frac{[3\cos^2(\mathbf{A}_1, \mathbf{a}') + 2\cos^2(\mathbf{B}_1, \mathbf{a}')]n_b}{[3\cos^2(\mathbf{A}_1, \mathbf{b}) + 2\cos^2(\mathbf{B}_1, \mathbf{b})]n_{a'}} \tag{4}$$

In table II are given the values of direction cosines of the transition moments of A_1 and B_1 vibrations, and of experimental and calculated dichroic ratios of the band group average for five samples.

TABLE II

	A_1	B_1	$R^{calc.}_{a'/b}$	$R^{exp.}_{a'/b}$
a'	−0.5516	0.4760	1.51	1.52 ± 0.08
b	0.5560	0.8490		

It seems that the above described method should facilitate dichroic ratio measurements but it is necessary to verify its use for other oscillators. We will continue such a study.

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