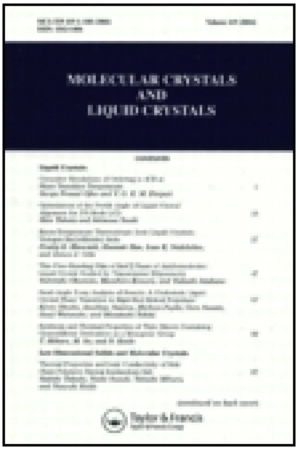

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The Application of Oriented Gas and Effective Charge Models to the Infrared Dichroic Ratio of β-Naphthol Crystals†

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Spectra of β-naphthol single crystals in the 5700–6800 cm^{-1} range in polarized light have been measured. Dichroic ratios of $2\nu_{CH}$ and $2\nu_{OH..}$ bands have been calculated and compared with experimental values. The results confirm the assumption concerning the linearity of a hydrogen bond in β-naphthol. It has also been found that it is possible to sum contributions of transition moments of different oscillators in the total intensity of a group of overlapping bands. This fact may be understood in terms of an effective charge model concept.

INTRODUCTION

The application of an oriented gas model to isolated infrared bands in molecular crystals has already been demonstrated in several examples.[1,2] It was also shown that it is possible to sum the contributions of different symmetry type vibrations of the same oscillator in the integrated intensity of the group of overlapping bands.[3] Weak interactions of hydrogen bonding type occuring in *p*-nitroaniline and thiourea single crystals[1c,3] do not disturb such a geometric model in the calculation of dichroic ratio.

We were interested in studying the applicability of oriented gas model approximation in the case of a stronger hydrogen bridge which occurs in

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† Preliminary results were presented at the VII Bulgarian Conference on Spectroscopy with International Participation, Sunny Beach, 1976.

the low-temperature phase of β-naphthol. Another aim of this work was to see if it would be possible to sum contributions of different oscillators in the total intensity of the group of overlapping bands as expressed in terms of accurate dichroic ratio values.

EXPERIMENTAL

Commercial β-naphthol (BDH) was purified by the zone refinement method and single crystals were grown from toluene solution by slow evaporation at room temperature. Platelets suitable for near infrared measurements (ca 5 × 5 × 0.5 mm^3) were obtained in the shape of a rombhus with a short diagonal parallel to the crystallographic axes *b* and a long axis parallel to the *a* axis.[4] The plane of plates was (001) as determined by means of X-ray rotation photographs.

Spectra in the 5700–6800 cm^{-1} region were measured with the spectrophotometric assembly described earlier[5] in which a new Carl Zeiss monochromator, SPM-2, type was used.

The spectrum of β-naphthol single crystals in the near infrared region of polarized light is shown in Figure 1.

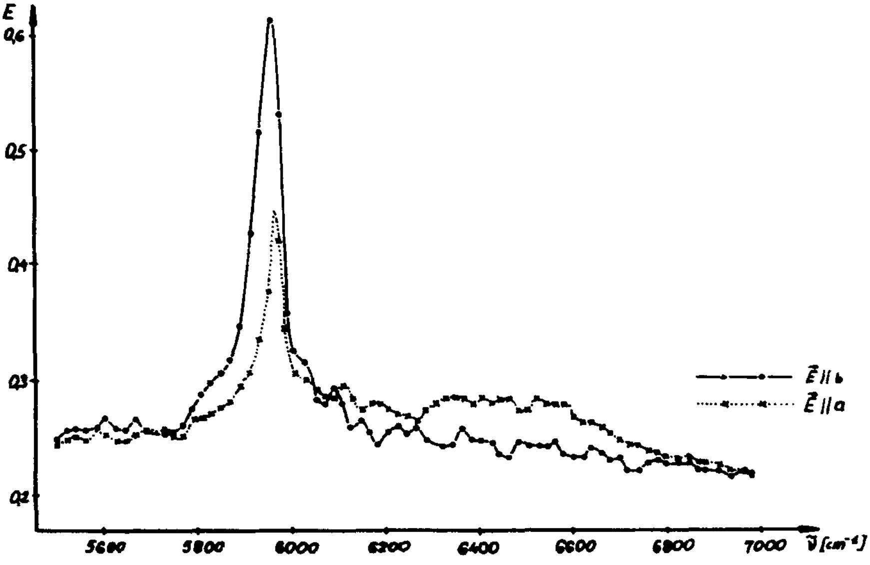

FIGURE 1 Near infrared spectrum of β-naphthol single crystal (001) ($d = 0.45$ mm) in polarized light.

ASSIGNMENTS

Infrared spectra of β-naphthol have been investigated in a number of papers.[6–8] In paper[6] two frequencies in C_2Cl_4 solution have been given: $\nu_{OH} = 3621$ cm^{-1} and $\nu_{CH} = 3060$ cm^{-1}. Baumgarth *et al.* measured the spectra in the region of OH. . (or OD. .) stretching fundamentals of pure and deuterated β-naphthols in KBr pellets in order to explain structural changes occuring during phase transition near 118°C.[7] They found that the two frequencies: 3210 and 3270 cm^{-1} are due to a hydrogen bonded chain in a disordered (stable) phase of β-naphthol. According to a recent paper by Peron *et al.*[9] the two bands may originate from in-phase and out-of-phase stretching modes of vibration of the two OH bonds coupled together by hydrogen bonding. The whole IR and Raman spectrum (700–4500 cm^{-1}) of β-naphthol in KBr pellets has been reported in the paper by Sing and Singh.[8]

On the basis of papers cited above, the band with a maximum near 6000 cm^{-1} in Figure 1 is assigned to the overtone of ν_{CH} of the symmetry type A' (resulting from the molecular point group symmetry C_s) and a large diffuse band with a maximum near 6400 cm^{-1} is assigned to the overtone of the $\nu_{OH..}$ (also of A' type).

The assignments of these bands were confirmed by measuring spectra of β-naphthol single crystals in polarized light in the temperature range of 295 to 358K; while increasing the temperature the dichroic ratio of the first band was almost constant and that of the second one was clearly changed[10] as expected for hydrogen bonding.[1c]

Low intensity and the shape of the $2\nu_{OH..}$ band is in conformity with observations that in the case of hydrogen bonded chains the intensity of first overtones decreases as compared with monomer band intensity which has been stated in several papers by Sandorfy *et al.*[11]

CRYSTAL STRUCTURE AND DICHROIC RATIO CALCULATIONS

The β-naphthol crystal belongs to a monoclinic system, the space group $I_a(C_s^4)$ with 8 molecules in the unit cell. However, in this space group there are only 4 general positions and in consequence two nonequivalent sets of molecules in the unit cell. Two neighbouring and symmetrically non-equivalent molecules are linked by hydrogen bonding in such a manner that a chain of molecules is formed throughout the crystal.[4]

In the general expression for the expected dichroic ratio (1) the summation is over i molecules in a unit cell which are symmetrically equivalent (Eq. (9)

from Ref. 1a).

$$R^K_{y/x} = \frac{I_y^{\text{theor}}}{I_x^{\text{theor}}} = \frac{n_x}{n_y \cos\zeta} \frac{\sum_i \cos^2(\mathbf{K}_i, \mathbf{y})}{\sum_i [\cos\zeta \cos(\mathbf{K}_i, \mathbf{x}) \pm \sin\xi \cos(\mathbf{K}_i, \mathbf{z})]^2} \tag{1}$$

where I_x, I_y = integrated intensities of bands measured for electric vector $\mathbf{E}_i$, of the electromagnetic wave polarized along the x and y direction in the crystal

n_x, n_y = refractive indices along the x, y directions in the crystal

$(\mathbf{K}_i, \mathbf{y})(\mathbf{K}_i, \mathbf{x})$ = angles between the transition moment $\mathbf{K}_i$ and vectors $\mathbf{E}_y$, $\mathbf{E}_x$

ζ = angle between the electric vector **E** and the electric displacement vector **D** within the crystal.

According to the statement by Dows[12] the sum of the intensities of the various unit cell transitions is seen to be equal to the intensity of transition in the isolated molecule.

In the case of β-naphthol we consider the two non-equivalent molecules as a single entity. Because the two molecules can vibrate in phase and out of phase, two types of motion are taken into account for each mode of vibration; the vector sum (**S**) of transition moments in question for both molecules corresponds to the in-phase vibration and their difference (**D**) to the out-of-phase vibration.

As the symmetry of β-naphthol molecule is low (C_s) only two symmetry species of vibration are possible: A' and A''. The species A'' have a direction of transition moment normal to the molecular plane and the species A' have a transition moment direction lying within the molecular plane without precise orientation. For such a case Rohleder and Luty[1a,1b] have proposed to calculate the dichroic ratio by means of directional cosines of the molecular plane. In order to find the directions in question the equations of average planes of the two non-equivalent molecules have been calculated by the mean squares method.[13] The directional cosines of the normal to planes, $\mathbf{N}_i$, and these of the molecular planes, $\mathbf{P}_i$, are given in Table I.

According to the assignments given in the previous section in the investigated region two bands occur: those of $2\nu_{\text{CH}}$ vibration and of $2\nu_{\text{OH}\ldots}$. For the first band we calculate the dichroic ratio as for the vibration of symmetry A'. In the case of the $2\nu_{\text{OH}\ldots}$ band we take the direction of OH stretching as lying along the OH bond. However, the positions of H atoms in a crystal are unknown so we assume they lie on the O ... O lines. This is equivalent to a suggestion that the hydrogen bonding in β-naphthol is linear as already stated by Gangakhedar *et al.*[14]

TABLE I

Directional cosines in a β-naphthol crystal with respect to othogonalized crystallographic axes system *a*, *b*, c^* (explanations in the text)

Direction	a	b	c^*
$\mathbf{N}_1$	0.6899	0.2468	−0.6806
$\mathbf{N}_2$	0.7294	−0.3202	−0.6045
$\mathbf{P}_1$	−0.7239	−0.9691	0.7326
$\mathbf{P}_2$	−0.6841	0.9473	0.7966
$\mathbf{S}_{\mathrm{CH}}$	−0.6773	−0.0105	0.7356
$\mathbf{D}_{\mathrm{CH}}$	−0.0208	−0.9992	−0.0334
$\mathbf{O}_1\text{—}\mathbf{O}_2$	0.9237	0.1717	−0.3443
$\mathbf{O}_1\text{—}\mathbf{O}_2'$	−0.5563	0.7517	−0.3547
$\mathbf{S}_{\mathrm{OH}}$	0.3024	0.7600	−0.5753
$\mathbf{D}_{\mathrm{OH}}$	0.9308	−0.3648	0.0065

The directional cosines of the $\mathbf{O}_1\mathbf{O}_2$ and $\mathbf{O}_1\mathbf{O}_2'$ vectors and those of their sum, $\mathbf{S}_{\mathrm{OH}}$, and difference, $\mathbf{D}_{\mathrm{OH}}$, and also $\mathbf{S}_{\mathrm{CH}}$ and $\mathbf{D}_{\mathrm{CH}}$ are also presented together in Table I.

Taking into account the considerations above and the results of paper[3] the dichroic ratio of the bands in question can be expressed by the following formula:

$$R^k_{b/a} = \frac{n_a}{n_b \cos\zeta} \times \frac{\cos^2(\mathbf{S}_k, \mathbf{b}) + \cos^2(\mathbf{D}_k, \mathbf{b})}{[\cos(\mathbf{S}_k, \mathbf{a})\cos\zeta + \cos(\mathbf{S}_k, \mathbf{c}^*)\sin\xi]^2 + [\cos(\mathbf{D}_k, \mathbf{a})\cos\zeta + \cos(\mathbf{D}_k, \mathbf{c}^*)\sin\zeta]^2} \tag{2}$$

where a, b = polarization directions of the electric vector $\mathbf{E}$ for (001) plate; also directions of the measurement of spectra
k = C—H or O—H oscillators

We made use, in (2), of the hypothesis that the intensity of a group of bands measured in one direction of polarized light can be expressed as a sum of the dipole moment projections of the in-phase and out-of-phase vibrations along these directions. As before,[3] we assumed that coefficients of the intensity of normal vibrations, $k(\partial\mu/\partial q)^2$, for the same oscillator are equal. This seems to be justified by the concept of the effective charge model[15] and will be discussed in the next section.

The refractive indices n_a and n_b determined by the immersion method and the angle ζ determined by the method described in Ref. 1a are as follows:

$$n_a = 1.561$$

$$n_b = 1.725$$

$$\zeta = 7^\circ\, 48' \pm 7.5'$$

Experimental intensities I_a and I_b have been determined by integrating the areas under the absorption curves measured for polarisation directions $E \parallel a$ and $E \parallel b$, respectively, in the frequency region 5700–6100 cm^{-1} for $2\nu_{CH}$ band and in 6100–6800 cm^{-1} for $2\nu_{OH..}$ band or in whole region 5700–6800 cm^{-1} for the group of the bands. Integration was carried out by weighting the diagrams. The zero-lines were taken as parallel to the absorption lines beyond the absorption region (6800–7000 cm^{-1}—Figure 1). The dichroic ratios have been calculated by dividing the average values of corresponding intensities obtained for six platelets of β-naphthol. The values obtained for the calculated and experimental dichroic ratios are presented together in Table II.

TABLE II

Calculated and experimental values of dichroic ratios of the (001) plates of β-naphthol in a near infrared

Band	$R^{\text{calc.}}_{b/a}$	$R^{\text{exp.}}_{b/a}$
$2\nu_{CH}$	1.79	1.87 ± 0.14
$2\nu_{OH..}$	0.68	0.52 ± 0.06
$2\nu_{CH} + 2\nu_{OH..}$	1.26	1.2 ± 0.1

Because the $2\nu_{CH}$ and $2\nu_{OH..}$ bands overlap and their separation is a quite arbitrary procedure we tried to calculate and measure the dichroic ratio of the whole group of bands in the 5700–6800 cm^{-1} region. For a first approximation equality of proportionality factors in the intensity of normal vibrations of different oscillators were assumed. Thus in the formula for dichroic ratio of the band group instead of the sum of two factors in (2) a sum of four factors appears, corresponding to the contributions of two vibration of C—H bonds (**S** and **D**) and of two vibrations of OH bonds (also **S** and **D**). These results are also given in Table II.

DISCUSSION

The agreement between the values of calculated and experimental dichroic ratios of the $2\nu_{CH}$ band is quite good. The greatest difference is in the case of $2\nu_{OH..}$ where the intensity is small and, threrefore, the error due to arbitrary separation of two overlapping bands is greater. However, considering the third result from Table II, it seems that the assumption of linearity of hydrogen bonding holds to the limit of experimental error.

On the basis of the above results and those concerning polarized infrared spectra of pentaerythritol crystals[16] and of ethyl alcohol single crystals[17] it seems we can assume stronger molecular interactions in the oriented gas model. Even in the presence of such interactions an X-ray structure gives their results and the oriented gas approximation can be used.

As far as the intensity of overtones is concerned, according to Herzberg[18] it is proportional to $\partial^2\mu/\partial q^2$ and the application of an oriented gas model to overtones may seem doubtful. Nevertheless, considerations of Di Paolo *et al.*[11b] suggest that in the case of a "polymer" consisting of hydrogen bonded chains a weak intensity of the first overtone of $\nu_{OH..}$ is due to the greater contribution of $\partial\mu/\partial q$ than those of $\partial^2\mu/\partial q^2$ in the complete expression of intensity of overtones. Our results and those of[1] reveal the fact that this can also be true for overtones of vibrations which do not participate in hydrogen bonding.

The most interesting result is an unexpected conformity between calculated and experimental values of dichroic ratios of the group of overlapping bands $2\nu_{CH}$ and $2\nu_{OH...}$. This may be understood in terms of the effective atomic charge model.[15] If $(\partial\mu/\partial q)^2$ is the measure of the effective charge on oscillating atoms it is clear that we can sum contributions of the transition moment vectors of the same oscillator (cases reported in Ref. 3 and Eq. (2)). Further, if the concept of effective charge model holds, the additivity of contributions of transition moments of different oscillators in dichroic ratio of β-naphthol may be explained by assuming that the shares of stretching vibrations CH and OH in effective charges on the hydrogen atoms, carbon atoms and oxygen atoms are equal or nearly equal. Only in this case the coefficients $k(\partial\mu/\partial q)^2$ which precede geometrical factors in the expression for dichroic ratio of the group of overlapping bands may be canceled.

Even the equality of whole effective charges on hydrogen and carbon atoms seems to be probable in the light of results of Person and Newton.[15b] They note that: "effective charge on the carbon atom—ξ_C—may be expected to be equal to $n\xi_H$ for a hydrocarbon, where n is the number of H atoms attached to the carbon atom". Therefore a new question appears: β-naphthol is not a hydrocarbon! But let us compare some of its properties with whose of naphthalene: β-naphthol forms solid solutions with napthalene not only as a metastable phase[7] but also as the stable one;[19] this is evidence of their quasi-isomorphism. Also optical properties are quite similar—the same optic plane (010), similar values of the angle ζ (7.5° and 8.3°). Furthermore, the most important feature is that the electronic absorption spectra of β-naphthol and naphthalene molecules are similar because the electron lone pair of the oxygen atom in β-naphthol molecule interacts with naphthalene nucleus (intramolecular charge transfer).[20] Also the Raman spectra of naphthalene and β-naphthol single crystals resemble each other.[21] Thus, in the first approximation, β-naphthol may be treated as a hydrocarbon and if the share of bending fundamentals is small in comparison with that of stretching vibrations as in paper,[22] the equality of effective charges on atoms may be likely.

CONCLUSIONS

The agreement between calculated and experimental dichroic ratios of $2\nu_{\mathrm{OH}..}$ band confirms that the hydrogen bridge in β-naphthol is linear. This reveals also that an oriented gas model may be useful even in the case of rather strong hydrogen bonding.

The conformity between calculated and experimental values of dichroic ratios of the group of the bands in the whole measured region may be explained by the treatment of β-naphthol as a hydrocarbon. The equality of effective charges on different atoms then seems probable and this fact quarantees the additivity of contributions of different oscillators in the total intensity of a group of overlapping bands.

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