Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

# The "Oriented Gas Model" and its Application to the Infrared Spectroscopy of Molecular Crystals

Józef W. Rohleder [a] & Tadeusz Luty [a]
[a] Laboratory of Chemical Physics at the Department of Physical Chemistry, Technical University, Wrochaw, Poland

To cite this article: Józef W. Rohleder & Tadeusz Luty (1968): The "Oriented Gas Model" and its Application to the Infrared Spectroscopy of Molecular Crystals, Molecular Crystals, 5:2, 145-163

To link to this article: http://dx.doi.org/10.1080/15421406808082936

*Molecular Crystals.* 1968. Vol. 5, pp. 145–163

Printed in Great Britain

# The "Oriented Gas Model" and its Application to the Infrared Spectroscopy of Molecular Crystals

JÓZEF W. ROHLEDER and TADEUSZ LUTY

Laboratory of Chemical Physics at the Department of Physical Chemistry, Technical University, Wrocław, Poland

*Received May* 29, 1968; *Revised July* 8, 1968

**Abstract**—The real path of the polarized radiation in passing throughout an anisotropic crystal essentially depends on the orientation of the principal dielectric tensor axes with respect to the cleavage plane of the sample. Proper elucidation of this fact leads to new expressions for the dichroic ratio of a molecular crystal which contains terms connected both with the orientation of molecular transition moments and with the dielectric tensor axes as well. The agreement of the theory with experiment is illustrated in several examples.

The molecular crystal is a three-dimensional periodic array of molecules weakly interacting with one another. The energy of the intermolecular interactions depends, in general, on respective orientations of the molecules in the crystalline lattice, and on their distances, and is very small in comparison with the binding energy of the atoms constituting the molecule. Therefore, in many cases or at least in separated spectral regions the infrared spectrum of the crystal closely resembles that of a solution in an inert solvent. In these circumstances the crystal can be treated as being composed of non-interacting molecules which are arranged in a manner corresponding to the symmetry of the crystal structure, i.e. it can be replaced by an "oriented gas". If a polarized electromagnetic wave with the electric vector $\vec{E}$ properly oriented with respect to the crystallographic directions falls on the crystal its absorption intensity will depend on the orientation of $\vec{E}$ with respect to the molecular transition moments, $\vec{P}_i^{(n)}$. We have assumed that to each of the $r$ molecules contained within the unit cell (subscript "$i$") a spectroscopic transition moment $\vec{P}$ can be assigned, separately for each normal vibration (superscript "$n$"). This is the principal idea of the so-called "oriented gas model" which was first introduced by Pimentel and McClellan[1] and by Ambrose, Elliott and Temple.[2] It constitutes the theoretical basis for the interpretation of the experimentally determined intensities of the infrared absorption bands of molecular crystals.

There is one point requiring some further explanation. The transition moments, $\vec{P}_i^{(n)}$, do not need exactly to be those of the free molecule. The symmetry properties of the free molecule after placing it into the crystal become somewhat modified by the surrounding molecules and, according to Halford,[3] can be represented by the symmetry point group of the lattice site actually occupied by the molecule. In general, the site symmetry is lower or at most equal to the symmetry of the free molecule. Therefore, the selection rules for the molecular transition moments $\vec{P}_i^{(n)}$ are governed by the site symmetry point group and it may happen that some frequencies which are inactive in the free molecule become allowed in the crystalline state.

From the experimental point of view, two values of the "true" integrated absorption intensity of an absorption band, $A_x^{(t)}$ and $A_y^{(t)}$, measured with the electric vector $\vec{E}$ parallel in turn to two perpendicular crystal directions $x$ and $y$, respectively, give what is called the "dichroic ratio" of the absorption band:

$$R_{y/x}^{(exp)} = \frac{A_y^{(t)}}{A_x^{(t)}} \tag{1}$$

By the true intensities we mean values corrected for finite slit width of the monochromating device which can be made by the methods described in the literature.[4] The directions $x$ and $y$ along which spectroscopic measurements are being made cannot be chosen arbitrarily but must correspond to the optical directions of the crystal.

According to the oriented gas model the absorption intensity of the crystal should be proportional to the square of the dot product, $[\vec{P}_i^{(n)}.\vec{E}]^2 = (P_i^{(n)}E)^2.\cos^2(\vec{P}_i^{(n)},\vec{E})$, and for the expected dichroic ratio we have:

$$R_{x/y}^{(\mathrm{theor})} = \frac{\sum_{i=1}^{r} \cos^2(\vec{P}_i^{(n)},\vec{E}_y)}{\sum_{i=1}^{r} \cos^2(\vec{P}_i^{(n)},\vec{E}_x)} \tag{2}$$

If the unit cell is occupied by only one molecule we have:

$$R_{y/x}^{(\mathrm{theor})} = \cot^2\Phi \tag{2a}$$

where $\Phi$ denotes the angle between $\vec{P}^{(n)}$ and the $y$ direction. Expressions (2) and (2a) are based on "pure geometrical" theory of the dichroism. $R > 1$ means that the band is polarized along the $y$ direction of the crystal whereas for $R < 1$ the polarization is along $x$.

The comparison between theory and experiment shows that the observed and predicted polarization directions are in general in agreement. This fact greatly facilitates the assignments of the bands in the spectroscopy of crystalline oriented solids and is commonly used. However, numerous discrepancies have been found between the numerical values of the observed dichroic ratios and those calculated according to (2) or (2a).[1, 5, 6] The inadequacy of the model in quantitative problems was obvious since experiments have been made on solid solutions of naphthalene in anthracene,[7] where the interactions between naphthalene molecules are in fact negligibly small. For these reasons the model was also criticized by the authors, and was believed to hold only approximately. It is of interest to note that Pimentel[1] and Mathieu[8] pointed out that the examination of optical properties of crystals might contribute to the understanding of the above discrepancies.

Nonetheless, many authors have used (2) or (2a) to determine the direction of the transition moment, most frequently of an isolated group of atoms of a molecule. It has frequently been found that the spectroscopically determined direction of $\vec{P}$ does not coincide with the direction of corresponding chemical bond known from the X-ray structure. The discrepancies sometimes amount to as much as 20°. From this information particular orientation of the groups in crystalline state was deduced.[9–12] However, such conclusions cannot be considered as reliable ones because of principal disagreement between the theory and experiment.

Hexter showed on an example of crystalline iodoform that more accurate results for the orientation of $\vec{P}$ are obtained from the analysis of the full absorption anisotropy curve taken for a plane normal to the six-fold axis.[13] In this special orientation the plate is isotropic and in such a case the corrections connected with optical properties of the crystal are unnecessary. By the analysis of similar curves made for the cleavage plane of $\beta$-$p$-nitrophenol the position of the OH bond has been found whereby the non-linearity of the hydrogen bridge of the type OH···O has been proved.[14]

The exact introduction of the optical properties of crystals into the theory of dichroism was made first by Ward.[15] Considering the problem of propagation of electromagnetic waves in anisotropic media on the basis of general electromagnetic theory Ward arrived at a result which for the most simple case with one molecule in the unit cell has the form:

$$R_{y/x}^{(\text{theor})} = \cot^2 \Phi \cdot \left(\frac{\mathscr{E}_x}{\mathscr{E}_y}\right)^{1/2} \tag{3}$$

where $\mathscr{E}_x$ and $\mathscr{E}_y$ denote half of the length of the two principal axes of the tensor of the dielectric constant and they lie within the plane of the sample. In a case of $r$ molecules in the unit cell we can combine (3) and (2) to get a more general expression:

$$R_{x/y}^{(\text{theor})} = \frac{\sum_{i=1}^{r} \cos^2(\vec{P}_i^{(n)}, \vec{E}_y)}{\sum_{i=1}^{r} \cos^2(\vec{P}_i^{(n)}, \vec{E}_x)} \cdot \left(\frac{\mathscr{E}_x}{\mathscr{E}_y}\right)^{1/2} \tag{3a}$$

In this treatment attention is given to the significance of the dielectric tensor axes but their orientation is not introduced explicitly. For this reason, expression (3) or (3a) gives correct results only in a particular orientation of the sample discussed above. Such a case has been examined with success by Susi on an example of adipic acid[16] and by Rohleder and Luty on durene crystals.[17] In a more general orientation of the sample in respect to the dielectric tensor axes expressions (3) and (3a) cease to hold, and this is caused according to our view by a change of the direction of vector $\vec{E}$ in passing the interface air/crystal.

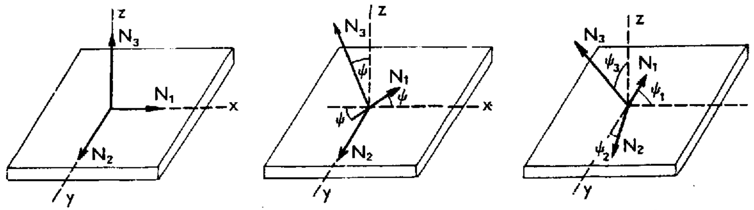
In this paper we will try to show that the proper elucidation of this effect leads to the results which are in reasonably good agreement with experimental data even in those cases in which the preceding treatment gave discrepancies qualitative in nature, i.e. the observed polarization directions were opposite to the predicted ones. For this purpose let us consider first some details of the optics of non-magnetic and non-conducting media.

## 1. The optical properties of crystals and the radiation paths

The optical properties of organic crystals which are for the most part anisotropic substances can conveniently be illustrated by means of a surface called an indicatrix. This surface has the form of an ellipsoid possessing three mutually perpendicular principal axes which we shall denote by 1, 2, 3, and the refractive indices along them by $N_1$, $N_2$, and $N_3$, respectively. For a non-magnetic and non-conducting crystal the directions of these axes coincide with the principal axes of the dielectric tensor, and $\mathscr{E}_i = N_i^2$, $i = 1, 2, 3$. The particular shape and orientation of the indicatrix with respect to the crystallographic directions are symmetry related with the crystallographic class of the crystal.[18] Cutting or cleaving a plate from a larger block of single crystal, we can meet three optically different orientations of the plate within the plane of which there are contained two, one or none of the axes of the indicatrix, Fig. 1a, b, and c, respectively. These orientations can be distinguished by means of the polarizing microscope in viewing the plate mounted on an universal stage.[19]

In the first case, corresponding to Fig. 1a, there are two planes of optical symmetry perpendicular to the crystal surface, the third being parallel to it. If a beam of polarized radiation falls on crystal surface at normal incidence and with the electric vector $\vec{E}$ directed toward $N_1$ or $N_2$ it does not suffer any change in its direction as the wave intersects the interface air/crystal. In this case the measured absorption intensity depends only on the geometrical arrangement of the absorbing oscillators according to the equation (3a).

In the third orientation shown in Fig. 1c there is no one optical symmetry plane perpendicular to the crystal surface. In this case the radiation beam divides at normal incidence into two rays which are both extraordinary in nature and are absorbed differently when travelling throughout the crystal. It will be clear from what follows that it is possible, at least in principle, to choose an orientation of the plate proper for making the measurements but this would require the use of a kind of universal stage which is hardly possible to be realized in practice. Instead of this, the orientation 1c may rather be adjusted to the case 1b by means of polishing methods.



1a 1b 1c

Figure 1. Orientation of the principal axes of the indicatrix with respect to the plane of the sample.

According to our experience the orientation most frequently met in practice corresponds to Fig. 1b. Let us introduce a rectangular coordinate axes system $x$, $y$, and $z$, attached to the sample, where $y \| N_2$ and $z \perp x, y$. The orientation $\vec{E} \| y$ is identical with the case 1a and needs no further consideration. For the second orientation, $\vec{E} \| x$, the radiation path is more complicated even at normal incidence and it is shown in detail in Fig. 2. In this case two types of effects occur:

(i) The radiation path in the crystal is in general longer than the thickness of the sample;

(ii) The cosines of the angles between $\vec{P}_i^{(n)}$ and $\vec{E}$ have to be corrected for the actual orientation of $\vec{E}$ within the crystal.

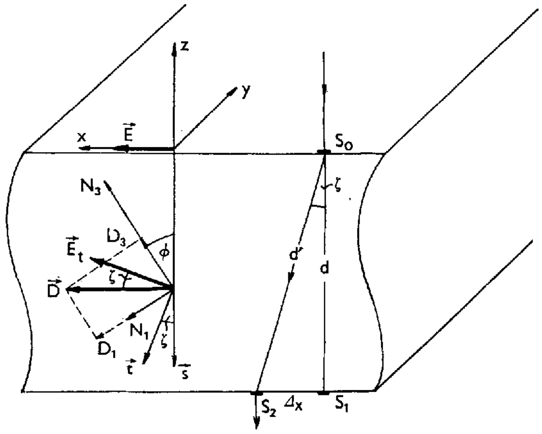


Figure 2. Orientation of the $\vec{D}$ and $\vec{E}_t$ vectors within the crystal.

From the Fig. 2 we see that the direction of $\vec{E}$ (in vacuum) changes to $\vec{E}_t$ (in crystal), and the angle between them or between $\vec{D}$ and $\vec{E}_t$ is $\xi$. $\vec{D}$ is the vector of the electric displacement. Exactly the same angle occurs between the unit vector, $\vec{t}$, of the ray-vector (Poynting vector $\vec{S}$) and the unit vector of the wave-normal, $\vec{s}$, because of $\vec{t} \perp \vec{E}_t$ and $\vec{s} \perp \vec{D}$. Hence, the direction of the ray in the crystal is parallel to $\vec{t}$ and the real path length of the ray is $d' = d/\cos\xi$, instead of $d$. The angle $\xi$ can be calculated from the definition of the dot product of $\vec{D}$ and $\vec{E}_t$:

$$\vec{D}.\vec{E}_t = |\vec{D}|.|\vec{E}_t|\cos\xi \tag{4}$$

The components of $\vec{D}$ in its own coordinate axes system, $\mathscr{E}_1$, $\mathscr{E}_2$, and $\mathscr{E}_3$, are $[|\vec{D}|\sin(90-\phi),\ 0,\ |\vec{D}|\cos(90-\phi)]$, or $[|\vec{D}|\cos\phi, 0, |\vec{D}|\sin\phi]$, and thus the components of $\vec{E}_t$ are

$$\left[\frac{1}{\mathscr{E}_1}|\vec{D}|\cos\phi, 0, \frac{1}{\mathscr{E}_3}|\vec{D}|\sin\phi\right].$$

Inserting it into (4) we obtain:

$$\cos\xi = \frac{\frac{1}{\mathscr{E}_1}\cos^2\phi + \frac{1}{\mathscr{E}_3}\sin^2\phi}{\sqrt{\frac{1}{\mathscr{E}_1^2}\cos^2\phi + \frac{1}{\mathscr{E}_3^2}\sin^2\phi}}$$

or

$$\tan\xi = \frac{\left(\frac{1}{\mathscr{E}_1} - \frac{1}{\mathscr{E}_2}\right)\sin 2\phi}{\left(\frac{1}{\mathscr{E}_1} + \frac{1}{\mathscr{E}_3}\right) + \left(\frac{1}{\mathscr{E}_1} - \frac{1}{\mathscr{E}_3}\right)\cos 2\phi} \tag{5a}$$

It is easily seen from (5a) that $\xi$ can either be positive or negative depending on actual length of $N_1$ and $N_3$ axes. The angle $\phi$ is always meant to be positive and $\phi \leqslant (\pi/4)$, so that $\sin 2\phi \geqslant 0$. The sign of the angle $\xi$ will be of some importance in further considerations.

The result (5a) can be immediately verified by experiment. For this purpose the crystal plate is set over a small hole made in a sheet of thin opaque foil and viewed in a polarizing microscope in parallel light beam with the analyzer removed. In the first orientation, $\vec{E}\|y$, only one spot is seen and in the second, $\vec{E}\|x$, two spots are visible separated by $\Delta x$ (Fig. 2). In a 45° position both spots have equal intensities and $\Delta x$ can easily be measured. We have:

$$\tan\xi_{\text{exp}} = \frac{\Delta x}{d} \tag{6}$$

Experimental and calculated values of $\xi$ are found to be in reasonably good agreement and are collected in Table 1 for a number of cases. Refractive indices and their orientation were taken either

TABLE 1

| Substance | Crystallographic system | Principal refractive indices, $N_i$ | $\phi$ | $\xi_{\text{theor}}$ | $\xi_{\text{exp}}$ |
|---|---|---|---|---|---|
| Naphthalene | Monoclinic | $N_1 = 1.525$, $N_2 = 1.722$, $N_3 = 1.945^a$ | 23.2° | + 8.5° | 8.3° |
| *p*-Nitroaniline | Monoclinic | $N_1' = 1.556$, $N_2 = 1.777$, $N_3 = 2.005^b$ | 1.0° | + 1.0° | 1.3° |
| Acetanilide | Orthorhombic | $N_1 = 1.510$, $N_2 = 1.620$, $N_3 = 1.730^a$ | 0 | 0 | 0 |
| Benzamide | Monoclinic | $N_1 = 1.541$, $N_2 = 1.666$, $N_3 = 1.830^a$ | 39.3° | + 9.3° | 8.6° |
| 1,2,4,5-Tetra-methylbenzene (durene) | Monoclinic | $N_1' = 1.584$, $N_2 = 1.619$, $N_3 = ?^c$ | 0.9° | 0.3° | 0 |

[a] According to Ref. 20.

[b] According to Ref. 21.

[c] According to Ref. 17.

from Winchell,[20] if available, or measured by means of the immersion method.

## 2. Theory of the dichroic ratio

Let us confine the considerations to the case shown in Fig. 1b for reasons which were outlined earlier. For the orientation $\vec{E}\|y$ the integrated absorption intensity of the unit cell can be written as follows:

$$A_y^{(\text{theor})} = \frac{k}{N_2 . d}\sum_i \cos^2(\vec{P}_i^{(n)}, y) \tag{7}$$

where $N_2$ is the refractive index along $y$, $d$ is the thickness of the crystal, and $k$ denotes a numerical factor which is of no significance for further developments. The directional cosines of $\vec{P}_i^{(n)}$ can be expressed more exactly by introducing the orthogonal set of molecular axes $K, L$, and $M$. The direction of $\vec{P}_i^{(n)}$ for a non-degenerate vibration in symmetry point groups of order higher than two can either be parallel to $K$, or $L$, or $M$. Other possibilities will be discussed later. For a transition moment directed along the $K$ axis we have: $\cos(\vec{P}_i^{(n)}, y) = \cos(K, y)$, and similarly for the other axes. Values of the directional cosines can be taken immediately from the structural data.

In the second orientation, $\vec{E}\|x$, first we have to write down the cosines of angles between $\vec{E}_t$ and $K$, $L$, and $M$. This is easily done by means of Table 2 in which the cosines are given of $\vec{E}_t$ and $K$, $L$, $M$

Table 2 Directional cosines of molecular axes

| | $x$ | $y$ | $z$ | |
|---|---|---|---|---|
| $K_i$ | $\cos(K_i, x)$ | $\cos(K_i, y)$ | $\cos(K_i, z)$ | |
| $L_i$ | $\cos(L_i, x)$ | $\cos(L_i, y)$ | $\cos(L_i, z)$ | |
| $M_i$ | $\cos(M_i, x)$ | $\cos(M_i, y)$ | $\cos(M_i, z)$ | |
| $\vec{E}_t$ | $\cos\xi$ | 0 | $\pm\sin\xi$ | $(\vec{E}\|x)$ |
| $\vec{E}_t$ | 0 | 1 | 0 | $(\vec{E}\|y)$ |

with respect to the $x$, $y$, $z$ axes system. From the Table we find, for instance, that for a vibration with the transition moment directed along $L$ the cosines between $\vec{E}_t$ and $L$ will be:

$$\cos(\vec{E}_t, L_i) = \cos\xi . \cos(L_i, x) \pm \sin\xi . \cos(L_i, z),$$

for the "$i$"-th molecule in the unit cell. The ± sign is connected with the sign of $\xi$. Hence, the integrated absorption intensity in the direction $\vec{E}\|x$ for the molecular axis $K$ is expected to be:

$$A_x^{(\text{theor})} = \frac{k.\cos\xi}{N_x . d} \sum_i [\cos\xi \cos(K_i, x) \pm \sin\xi \cos(K_i, z)]^2 \tag{8}$$

where $N_x$ is the refraction index along $x$ and

$$\frac{1}{N_x} = \left(\frac{1}{N_3^2}\cos^2\phi + \frac{1}{N_1^2}\sin^2\phi\right)^{1/2}$$

Thus, for the expected dichroic ratio of a vibration with the transition moment directed along $K$ we have:

$$R_{y/x}^{(K)} \equiv \frac{A_y^{(\text{theor})}}{A_x^{(\text{theor})}} = \frac{N_x}{N_y \cos\xi} \cdot \frac{\sum_i \cos^2(K_i, y)}{\sum_i [\cos\xi \cos(K_i, x) \pm \sin\xi \cos(K_i, z)]^2} \tag{9}$$

Similar expressions can be given for the molecular $L$ and $M$ axes and for other orientations of the indicatrix. Summation over "$i$" extends over all molecules contained within the unit cell. If the crystal possesses a symmetry axis, certain $K_i$ are symmetry related and the sums reduce significantly. In a case where two principal axes of the indicatrix are lying in the plane of the sample, i.e. $\phi = 0$, we have $\xi = 0$, and (9) reduces to an expression identical with (3a). In a more general orientation of the indicatrix it can be seen from (9) that the denominator contains at least two terms which can be of equal or different signs. This greatly influences the result obtained for dichroic ratio.

By introducing the unit vectors $\vec{k}$, $\vec{l}$, $\vec{m}$, corresponding to the axes

$K$, $L$, $M$, and unit vectors $\vec{e}_x$, $\vec{e}_y$, $\vec{e}_z$, corresponding to the axes $x$, $y$, and $z$, we can write (9) in a more compact form:

$$R^{(K)}_{y/x} = \frac{N_x}{N_y \cdot \cos\xi} \cdot \frac{\sum_i (\vec{k}_i \cdot \vec{e}_y)^2}{\sum_i (\vec{k}_i \cdot \vec{e}_x \cos\xi \pm \vec{k}_i \cdot \vec{e}_z \sin\xi)^2} \qquad (10a)$$

Similarly

$$R^{(L)}_{y/x} = \frac{N_x}{N_y \cdot \cos\xi} \cdot \frac{\sum_i (\vec{l}_i \cdot \vec{e}_y)^2}{\sum_i (\vec{l}_i \cdot \vec{e}_x \cos\xi \pm \vec{l}_i \cdot \vec{e}_z \sin\xi)^2} \qquad (10b)$$

and

$$R^{(M)}_{y/x} = \frac{N_x}{N_y \cdot \cos\xi} \cdot \frac{\sum_i (\vec{m}_i \cdot \vec{e}_y)^2}{\sum_i (\vec{m}_i \cdot \vec{e}_x \cos\xi \pm \vec{m}_i \cdot \vec{e}_z \cdot \sin\xi)^2} \qquad (10c)$$

The application of (9) and (10) will now be illustrated in several examples.

## 3. Comparison with experiment

### (A) CASES WITH AXIAL TRANSITION MOMENTS

In these cases the molecular transition moment is directed along one of the principal molecular axes $K$, $L$, or $M$. For the purposes of illustration we have chosen two C–H combination vibrations observed in the near infra-red region in naphthalene crystals and the well-separated first overtone of $NH_2$ antisymmetric vibrations in *p*-nitroaniline crystal.

### (a) *Naphthalene*

Naphthalene crystallizes in the monoclinic crystallographic system, space group $P2_1/c$, with two molecules in the unit cell. According to Winchell[20] the crystal exhibits a perfect (001) cleavage. In this orientation of the sample the direction of $N_3$ makes an angle of 9.5° with the crystallographic $c$-axis and an angle of $\phi = \beta - 90 - 9.5 = 23.3°$ with the plate normal. At this angle the direction of $N_1$ deviates from $x$, whereas $N_2 \| b$ lies in (001). According to this a large birefringence is observed across the plate causing a marked value of $\xi_{\text{exp}} = 8.3°$ (Table 1).

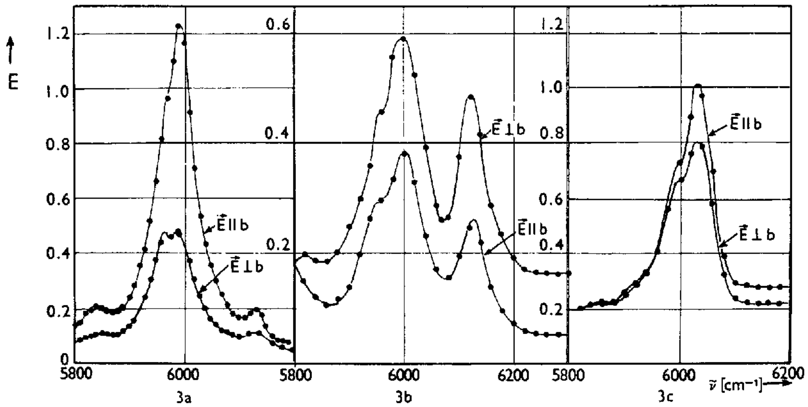
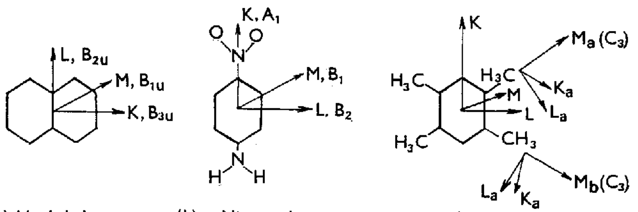


Figure 3. Polarized absorption spectra of crystal plates: (a) naphthalene, (b) acetanilide, (c) benzamide.

The combination bands, $\nu_{\text{CH}}^{(1)} + \nu_{\text{CH}}^{(2)}$ and $\nu_{\text{CH}}^{(1)} + \nu_{\text{CH}}^{(3)}$, measured for $\vec{E} \| b$ and $\vec{E} \perp b$ are shown in Fig. 3a. Their assignments and symmetry types are based on those given in [21] for fundamental



(a) Naphthalene (b) p-Nitroaniline (c) Durene

Figure 4. System of $K$, $L$, $M$ molecular axes.

transitions in naphthalene crystals. The band of higher frequency, 5995 cm$^{-1}$, corresponding to a symmetry type $(b_{1g})(b_{3u}) = B_{2u}$, has the transition moment lying along the molecular $L$-axis (Fig. 4). Similar arguments applied for the second band leads to the result that $(a_g)(b_{3u}) = B_{3u}$ has the transition moment directed along $K$. Taking the directional cosines of $K$, $L$, and $M$ axes from structural data[22] we can calculate the dichroic ratio for these two transitions by means of expressions (2), (3a) and (10a–10c). The results are shown in Table 3 in columns 4, 5, and 6, respectively, and the experimental values in column 7. For the $B_{2u}$ type the values 7.60 and 6.94, given by earlier theories, are too high in comparison with experiment, whereas for the $B_{3u}$ type the values 0.19 and 0.17 are too low. This is due to the orientation of the indicatrix which has not been introduced into expressions (2) and (3a). We believe that the agreement between columns 6 and 7 could even be improved if an exact resolution of the overlapping bands had been introduced. Such a procedure is now being in progress by means of an electronic computer and the results will be reported in a separate paper.

### (b) p-*nitroaniline*

The crystal of *p*-nitroaniline belongs to the monoclinic system, the space group being P $2_1/n$, with four molecules in the unit cell. A crystal of larger volume easily divides along (101)[23] into thin plates of excellent transparency. According to this our reference axes system for dichroic ratios will be the $b$ axis and $a' = [101]$.

The refined crystal structure has been reported by Trueblood and collaborators[24] and the absorption spectra in the $-NH_2$ overtone region by Rohleder and Szostak.[25] Among the observed absorption bands, of which nearly all show a marked splitting caused by strong crystal field, the overtone of antisymmetrical $NH_2$ vibrations is a well isolated band and its anisotropy can serve as a proof of our theory. The refractive indices are given after Tanaka[23] in Table 1. $N_2 \| b$ lies in (101) and $\sphericalangle N_1$, $x = \sphericalangle N_3$, $z = \phi = 1.0°$. Nevertheless, the birefringence is very high so that $\xi_{obs} = 1.3°$. The values of dichroic ratios are given in Table 3 and it can be seen that the value given in column 6 is nearest to the experimental value.

### (B) CASES WITH THE TRANSITION MOMENT LYING IN A PLANE

If a molecule possesses as the only symmetry element a symmetry plane, $\sigma_h$, only two types of symmetry can result: $A'$ and $A''$, i.e.

TABLE 3

| Substance | Vibration type and symmetry | $\nu_{max}$, cm$^{-1}$ | $R_{b/a}^{(calc)}$ (acc. to [6]) | $R_{b/a}^{(calc)}$ (acc. to [15,16]) | $R_{b/a}^{(calc)}$ (present work) | $R_{b/a}^{(exp)}$ (present work) |
|---|---|---|---|---|---|---|
| Naphthalene | $\nu_{CH}^{(1)} + \nu_{CH}^{(2)}$, $B_{2u}$ | 5995 | 7.60 | 6.94 | 4.80 | $4.51 \pm 0.28$ |
|  | $\nu_{CH}^{(1)} + \nu_{CH}^{(3)}$, $B_{3u}$ | 5965 | 0.19 | 0.17 | 0.45 | $0.47 \pm 0.06$ |
| *p*-Nitroaniline* | $2\nu_{NH_2}^{as}$, $A_1$ | 6901 | 0.37 | 0.41 | 0.45 | $0.46 \pm 0.02$ |
| Acetanilide | $2\nu_{CH}$, $A'$ | 5980 | 0.74 | 0.69 | 0.69 | $0.70 \pm 0.02$ |
| Benzamide | $2\nu_{CH}$, $A'$ | 6030 | 0.93 | 0.91 | 1.28 | $1.18 \pm 0.01$ |
| 1,2,4,5-Tetra-methylbenzene (durene) | $\nu_4 + 2\nu_5$, $E$ | 5670 | 0.88 | 0.85 | 0.85 | $0.82 \pm 0.04$ |

* Dichroic ratio in respect to the $b$ and $a' = [101]$ axes system.

the vibrations of the molecule can either be symmetrical or antisymmetrical with respect to $\sigma_h$. The symmetrical vibration cannot be represented by a vector because the displacements of the atoms are all lying in a plane. We believe, therefore, that the anisotropic properties of such absorption bands should be treated by means of the position of the $\sigma_h$ plane, i.e. the directional cosines of a vector should be replaced in (9) by cosines of the $\sigma_h$ plane, or by the sines of its normal, $n$, because of:

$$\cos(\sigma_h, x) = -\sin(n, x),$$

and similarly for $y$, $z$. Therefore, eq. (9) becomes:

$$R^{(\sigma_h)}_{y/x} = \frac{N_x}{N_y \cos\xi} \frac{\sum_i \sin^2(n_i, y)}{\sum_i [\cos\xi \sin(n_i, x) \pm \sin\xi \sin(n_i, z)]^2} \qquad (11)$$

The application of (11) will now be discussed with reference to three examples.

### (a) *Acetanilide*

Acetanilide belongs to the orthorhombic crystallographic system and cleaves perfectly along (001).[20] In this orientation $\phi = 0$, and $\xi = 0$, and the conformity with the simpler theory of Ward and Susi can be anticipated. This is, indeed, the case as is seen from Table 3, columns 5 and 6. The dichroic ratios are given for a $2\nu_{\mathrm{CH}}$ overtone band shown in Fig. 3b. Both values, 0.69 and 0.69, equal each other and are quite close to the experimental value, 0.70. Owing to the fact that $N_1 = 1.510$ does not differ much from $N_2 = 1.620$ the correction $N_2/N_1$ is very close to unity and the result obtained from pure geometrical theory, given in column 4, does not deviate significantly from the correct value.

### (b) *Benzamide*

Benzamide crystallizes in two polymorphic forms. Phase *I*, stable at room temperature, is monoclinic, space group $C^5_{2h}$ with four molecules in the unit cell.[26] The lattice parameters are as follows:[26]

$$a = 5.59, \quad b = 5.01, \quad c = 21.93\ \text{Å}, \quad \beta = 90°45'.$$

The molecules are asymmetric but are not far from planarity so that to each molecule a symmetry of the $C_s$ point group can be assigned. This is especially true in the benzene ring for the C–H vibrations which we can divide into the planar ($A'$) and non-planar ($A''$) modes. The crystalline plates used in experiments were tested for the type of polymorphic form and for the orientation of the cleavage plane by means of X-ray method. The rotation photographs gave two periods of the following lengths:

$$a = 5.62, \quad \text{and} \quad b = 5.04\ \text{Å}.$$

This means that the samples examined were of the form $I$, and simultaneously, that the cleavage plane was (001).

The optic plane is in this case (010) and $\sphericalangle N_3, z = \phi = 39°15'$[20] which leads to an appreciable value of $\xi_{\text{exp}} = 8.6°$ (Table 1). The polarized absorption spectrum is shown in Fig. 3c and according to the results of Mann and Thompson[27] the higher peak corresponds to a $2\nu_{\text{CH}}$ overtone of the symmetry $A'$. The observed and calculated dichroic ratios are given in Table 3. It is worthwhile to note that according to earlier theories (columns 4 and 5) the calculated dichroic ratio, $R_{b/a}$, is smaller than unity which leads to erronous conclusions.

### (c) 1,2,4,5-*Tetramethylbenzene* (*durene*)

In durene crystals the exact value of $N_3$ is unknown but it is very unlikely to exceed 2.0. Assuming this figure, and $\phi = 0.9°$, we get from (5a) that $\xi_{\text{theor}} = 0.3°$. Experimentally, $\xi$ is near to zero, and is too small to be measured exactly. Thus the optical properties of durene crystal correspond to a pseudo-orthorhombic crystal. In this case the corrections are of little influence on the numerical values of the dichroic ratio. As an example we consider an absorption transition, $\nu_4 + 2\nu_5$, which is a $CH_3$– combination tone of the $E$-type.[17] The transition moment lies in the plane perpendicular to the $C_3$ axis of the methyl group. Taking into consideration that to each molecule four methyl groups are attached the dichroism of an in-plane transition moment can be calculated in a manner similar to that used in previous examples. The results shown in Table 3 point out to a satisfactory agreement between calculated and experimental values.

## 4. Concluding remarks

The examples discussed above clearly show that the introduction of the orientation of the indicatrix in the outlined manner leads to results which are in reasonably good agreement with experiment even in cases so far controversial. We feel that the oriented gas model can be supposed to hold exactly whereby the interpretation of absorption spectra of molecular crystals of unknown structure gains a more reliable basis.

### REFERENCES

1. Pimentel, G. C. and McClellan, A. L., *J. Chem. Phys.* **20**, 270 (1952); Pimentel, G. C. and Person, W. C., Schnepp, O., *J. Chem. Phys.* **23**, 234 (1955).
2. Ambrose, E. J., Elliott, A. and Temple, R. B., *Proc. Roy. Soc. London* **A206**, 192 (1951).
3. Halford, R. S., *J. Chem. Phys.* **14**, 8 (1946).
4. Ramsay, D. A., *J. Amer. Chem. Soc.* **74**, 72 (1952); Fray, S. J., Goodwin, A. R., Johnson, F. A. and Quarrington, J. E., *J. Sci. Instr.* **40**, 387 (1963); Vincent-Geisse, J. and Cohen de Lara-Benzaquen, E., *Compt. rend.* **260**, 6319 (1965); Roeseler, A., *Monatsber. Deut. Akad. Wiss. Berlin* **7**, 146 (1965); Kabiel, A. M. and Tera, F. M., *Z. Physik. Chem.* **232**, 402 (1966); **233**, 403 (1966); Jones, R. N., Venkataraghavan, R. and Hopkins, J. W., *Spectrochim. Acta* **A23**, 925, 941 (1967).
5. Person, W. C., Pimentel, G. C. and Schnepp, O., *J. Chem. Phys.* **23**, 230 (1955).
6. Bruhn, W. and Mecke, R., *Z. Elektrochem.* **65**, 543 (1961).
7. Pimentel, G. C., *J. Chem. Phys.* **19**, 1536 (1951).
8. Mathieu, J. P., *J. Phys. Radium* **16**, 219 (1955).
9. Mann, J. and Thompson, H. W., *Proc. Roy. Soc.* **A211**, 168 (1952).
10. Francel, R. J., *J. Amer. Chem. Soc.* **74**, 1265 (1952); cf also *Technique of Organic Chemistry*, Ed. A. Weissberger, Intersc. Publ. Inc., New York 1956, Vol. IX, Chap. IVE.
11. Sandemann, J., *Proc. Roy. Soc.* **A232**, 105 (1956).
12. Abbott, N. B. and Elliott, A., *Proc. Roy. Soc.* **A234**, 247 (1956).
13. Hexter, R. M. and Cheung, H., *J. Chem. Phys.* **24**, 1186 (1956).
14. Rohleder, J. W., *Spectrochim. Acta* **17**, 1275 (1961).
15. Ward, J. C., *Proc. Roy. Soc.* **A228**, 205 (1955).
16. Susi, H., *Spectrochim. Acta.* **17**, 1257 (1961).

17. Rohleder, J. W. and Luty, T., *Acta Phys. Polon.* **31**, 653 (1967).
18. Nye, J. F., *Physical Properties of Crystals*, Clarendon Press, Oxford 1957.
19. Hartshorne, N. H. and Stuart, A., *Crystals and the Polarising Microscope*, 3rd Ed. Arnold Ltd., London 1960.
20. Winchell, A. N., *The Optical Properties of Organic Compounds*, Academic Press Inc., New York, 1954.
21. McClellan, A. L., Pimentel, G. C., *J. Chem. Phys.* **23**, 245 (1955).
22. Cruickshank, D. W. J., *Acta Cryst.* **10**, 504 (1957).
23. Tanaka, J., *Bull. Chem. Soc. Japan* **36**, 833 (1963).
24. Trueblood, K. N., Goldish, E. and Donohue, J., *Acta Cryst.* **14**, 1009 (1961).
25. Rohleder, J. W. and Szostak, M., *Acta Phys. Polon.* **30**, 187 (1966).
26. Penfold, B. R. and White, J. C. B., *Acta Cryst.* **12**, 130 (1959).
27. Mann, J. and Thompson, H. W., *Proc. Roy. Soc.* **A192**, 489 (1948).