

PROGRESS IN  
INFRARED SPECTROSCOPY

Volume 2

Based on lectures from the  
Sixth and Seventh Annual Infrared Spectroscopy Institutes  
held at Canisius College, Buffalo, New York, 1962 and 1963

*edited by* Herman A. Szymanski

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# Polarized Infrared Spectroscopy

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## INTRODUCTION

Any fundamental mode of motion that is accompanied by an oscillating electric moment leads to the absorption of electromagnetic radiation. Since the oscillating electric moment (transition moment) is a vector quantity, it can only interact with electromagnetic radiation that has an electric-field component in its direction. Therefore, if we wish to obtain information about the direction of the transition moment most conveniently, we must have it fixed in space, and must use plane polarized radiation. Since the transition moment must be fixed in space, we necessarily deal with solids in the study of polarized infrared spectra. These solids can be single crystals, oriented polycrystalline layers, or oriented polymer films.

The significance of polarized infrared spectra lies in the possibility of identifying the characteristic direction associated with a given infrared absorption. If we know the direction of the transition moment in space, it becomes easier to correlate the absorption with a mode of motion of the molecular or crystalline structure. In the study of the vibrational spectrum of larger molecules, where individual band identification is difficult, polarized infrared spectra aid in segregating the observed bands into the appropriate symmetry classes, to allow the selection of the fundamentals from a smaller number of frequencies. The same type of information can also be

obtained from the measurement of the depolarization of Raman-active lines and the investigation of infrared band contours in the vapor phase.

Polarized infrared spectra of crystals offer a useful method of attack, since each infrared-active band can be characterized according to its symmetry. A study of polarized infrared spectra can help us in the following ways: If the structure of the molecule and the direction of transition moments in space are known, this will help in assigning various fundamental modes of motion to infrared absorptions; or if the assignments are known, the polarized infrared spectra will yield directions of transition moments in space and information about the structure of the system under study. Sometimes these results do not agree with other structural determinations. In such cases changes in the previously proposed structure often result in good agreement with the infrared spectral interpretation.

The following subjects will be considered in this section: the means of obtaining polarized infrared radiation; the means of obtaining a suitable sample for our study; the interpretation of results and development of the necessary theoretical background; and discussion of the type of results which can be obtained by the study of polarized infrared spectra.

## POLARIZERS

In the visible and ultraviolet regions transmission polarizers are quite easy to obtain. However, there are no such transmission polarizers available for the general infrared region. Therefore, to obtain polarized infrared radiation, we have to resort to the principle of polarization by reflection.

For radiation with the electric vector vibrating perpendicular to the plane of incidence, the intensity of radiation reflected from a dielectric is given by the formula

$$(I_{\sigma})_r = I_{\sigma} \frac{\sin^2 (i - r)}{\sin^2 (i + r)}$$

and for radiation with the electric vector vibrating parallel to the plane of incidence, the intensity of radiation reflected is given by

$$(I_{\pi})_r = I_{\pi} \frac{\tan^2 (i - r)}{\tan^2 (i + r)}$$

where  $I_{\sigma}$  and  $I_{\pi}$  are the intensities of the two polarized beams before reflection,  $i$  is the angle between the direction of the incident light and the normal to the interface, and  $r$  is the angle between the direction of the refracted light in the medium and the normal.\* The dielectric constants of the two media determine an angle,  $\tan i = n'/n$ , at which the reflection of the parallel electric vector is 0. At the same angle, called Brewster's angle, there is considerable reflection of the perpendicular electric vector. In Fig. 1 an illustration of reflection in the case of an air-selenium interface is given [26]. It can be seen that at Brewster's angle (which is about  $68^{\circ}$  in this case) the reflected radiation is entirely perpendicular. Thus we have obtained pure polarized radiation by reflection. However, using a polarizer made of a reflecting surface is rather inconvenient, since we require one that can be easily inserted into and removed from a spectrometer, without upsetting the optical path. If we now consider the transmitted radiation at Brewster's angle, all of the parallel radiation goes through while the major portion of the perpendicular radiation is lost. The perpendicular radiation can be decreased by using several reflections at the same angle, until the transmitted beam consists of parallel radiation only.

The most commonly used polarizer is made up of six silver chloride plates which are held in a frame at the required angle to the incoming beam [46]. This polarizer can be used for radiation of approximately  $2-20\mu$ . Another commonly used polarizer is made up of selenium films [26]. These selenium layers are only  $4\mu$  thick, and because of this extreme thinness are very fragile.

N. J. Harrick [33] has developed an infrared polarizer depending on reflections at a germanium-mercury interface with which two reflections are sufficient. This polarizer can be used with wavelengths ranging from  $2\mu$  all the way out into the far infrared. Such a polarizer is described in Harrick's article, but as far as I now know, it is not available commercially.

An infrared polarizer made of pyrolytic graphite, which could be called a true transmission polarizer, has also been described [53]. The optical anisotropy of pyrographite, resulting from its electrical anisotropy, causes light falling on this polarizer to become

\*According to common usage the plane of polarization is defined as the plane containing the *magnetic* vector; however, in the present article we are concerned with the direction of the *electric* vector, so that throughout this discussion the direction of the latter will be pointed out.

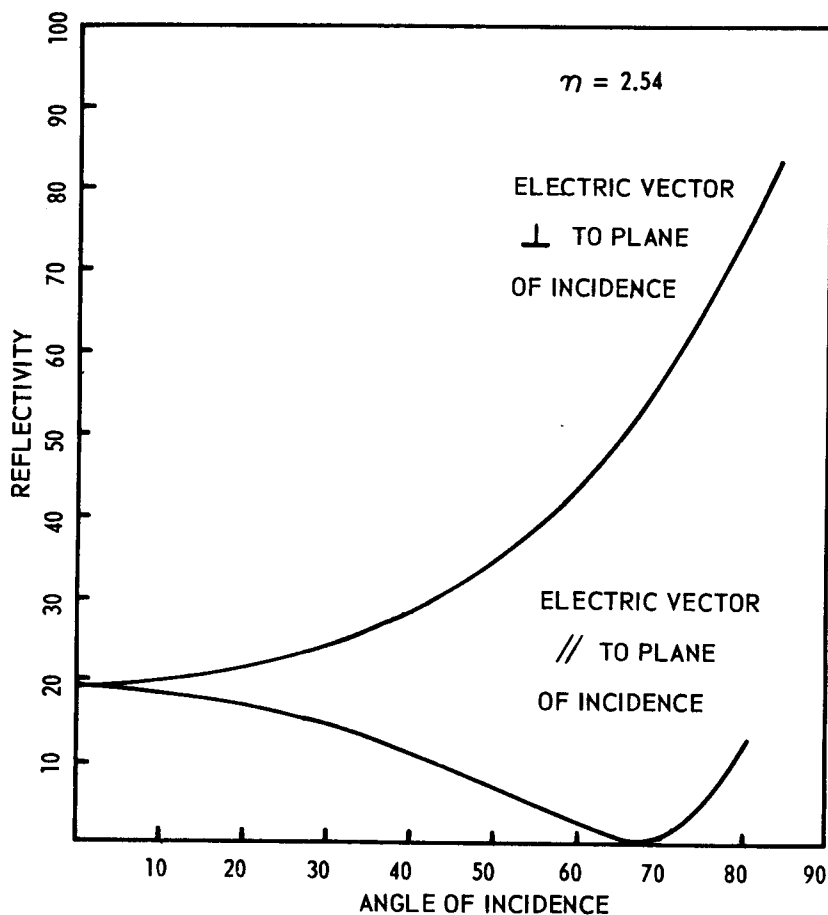


Fig. 1. Reflection at an air-selenium interface.  
[Reprinted by permission from *J. Opt. Soc. Am.* 38:213 (1948).]

polarized, since the absorption coefficient has a maximum if the electric field is in the  $c$  direction of pyrographite, while it has a minimum perpendicular to the  $c$  direction. This polarizer made of pyrolytic graphite can be used with wavelengths from  $10\mu$  out to the far infrared region.

Bird and Shurcliff [13] discussed an improvement in the design of pile-of-plate polarizers, describing one made of silver chloride plates. They found that if the silver chloride plates are of uniform



thickness and are exactly parallel, a number of undesired reflected rays can get through the plates, and thereby decrease the degree of polarization attained. Thus they describe a scheme (illustrated in Fig. 2) whereby the silver chloride plates used are thinned down at one end (wedging) and lined up not completely parallel to each other (fanning). The actual wedging and fanning angles required for improved performance are very small, and rolled plates of silver chloride intended to be parallel-faced will usually yield smaller sections that have the required thickness difference, so that they can be used for making up silver chloride polarizers.

### SAMPLE PREPARATION

The preparation of a suitable sample is probably the most difficult part in the practice of polarized infrared spectroscopy. The study of the infrared spectrum of any material in the condensed phase requires a very thin ( $4-30\mu$ ) layer. At the same time, to cover the spectrometer slit a sample as large as  $\frac{1}{2}$  in.  $\times$  1 in. might be needed. The preparation of a single crystal of these dimensions would be just about impossible. However, methods have been used in which single crystals prepared by the usual crystallographic means have either been cleaved or polished down to the required dimensions. Polishing is used in most of these cases since the thickness of the sample can then be reasonably well controlled.

In order to realize the possibilities of using single crystals for polarized infrared spectra, it is extremely important to keep in mind the limitations imposed on this method by the complicated manner

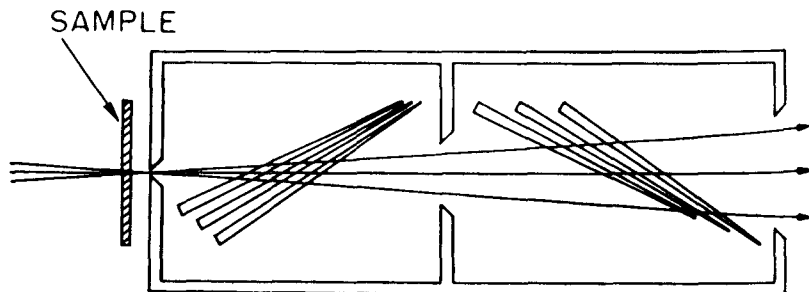


Fig. 2. Schematic diagram of six-plate polarizer employing fanning and wedging.  
[Reprinted by permission from *J. Opt. Soc. Am.* 49:236 (1959).]

in which light is propagated through a crystal. The structurally significant directions are defined inside the medium, whereas the plane of polarization and the direction of propagation of the radiation are identified only outside the medium. If we are to use the latter directions to obtain knowledge about the former ones, we must select orientations for the crystal such that plane polarized radiation may traverse it without suffering either refraction or change of polarization character. Otherwise the incident radiation will suffer refraction according to no simple law, and the electric vector will be resolved in the medium depending on the direction of propagation and the frequency of the light.

For many crystals, the directions of the polarization axes are fixed by symmetry and become independent of the frequency of light. In uniaxial crystals of the hexagonal, trigonal, and tetragonal systems, and for biaxial crystals of the orthorhombic system, all the distinguishable polarization axes are fixed by symmetry along the crystallographic axes. For monoclinic crystals, one axis is fixed by symmetry while the other two are unrestricted. There are no restrictions upon the axes of a triclinic crystal.

Therefore, one should always remember that spectra observed along or perpendicular to polarization axes fixed by symmetry will assume a fundamental significance, while spectra taken in other directions can lead to erroneous interpretations, unless the light-transmitting properties of the crystal under study are fully taken into account.

If a single crystal is not available, then a polycrystalline mass in which the microcrystals are all uniformly oriented in one direction can be used. Such layers can be grown either from a solution by evaporation of the solvent, or from a melt by controlled cooling or by sublimation. Such polycrystalline oriented layers have the disadvantage that the layer thickness is not uniform and the orientation not always exact, but in many cases they have given satisfactory results.

Large molecules, such as long-chain polymers, proteins, or other natural long-chain molecules, can usually be oriented in thin films by depositing them from solution in certain ways, by cold or hot drawing, or by some suitable treatment. These layers usually also suffer from a lack of uniformity in thickness and orientation. In cases of naturally occurring polymers, especially proteins, samples often can be found that are well oriented in one direction.

A quantitative treatment of such partially oriented polymers will be given in a later section.

Instead of giving generalized instructions for the preparation of samples for the study of infrared dichroism, we shall give the method of sample preparation separately for each example discussed.

## MEASUREMENT

The quantity we endeavor to measure in the study of polarized infrared spectra is the dichroic ratio, i.e., the ratio of band intensity when the electric vector in the radiation falling on the oriented sample is in such a direction as to give maximum intensity to band intensity when the electric vector is perpendicular to this direction.

Ambrose, Elliott, and Temple [2] give a quantitative treatment of the method for locating the direction of a transition moment in space by the measurement of polarized infrared spectra along the three major axes of the crystal. They point out that, in general, a unique direction of transition moment could only occur in crystals with one molecule per unit cell. When there is more than one molecule in the unit cell, calculations of transition-moment direction will lead to two values of either or both of the angles defining the transition moment in the crystal. In the case of acetanilide [1] four directions of the N—H transition moment were found; two of them could be eliminated as incompatible with the x-ray data, but the ambiguity concerning the other two could be removed only by comparison with other related molecules.

In order to obtain all the experimental data needed, two samples are necessary, one containing two of the crystal axes in the plane of the sample, and the other containing the third axis. If these samples are not obtainable then one crystal can be used, for example, in the following way: If the  $a$  and  $b$  axes are included in the plane of the sample, we can obtain polarized spectra along the  $a$  and  $b$  axes; if the sample is then tilted around the  $b$  axis, with the light falling on the sample perpendicular to the  $b$  axis, we can observe bands arising from spectra along the third axis. Usually the angle of tilt cannot be very large, but tilts up to  $15-20^\circ$  have been used in various experiments.

A number of experimental errors can occur in the measure-

ment of dichroic ratios. In addition to imperfect orientation of samples, we would like to mention imperfections of the polarizer and the polarization of the spectrometer itself. This last error originates mainly from reflections at the prism face, and gives rise to the fact that the infrared beam going through the spectrometer is already partially polarized. An article by Charney [20] quantitatively discusses these two errors, and suggests methods of evaluation of possible errors in the dichroic ratio measurements due to these factors.

We have already mentioned the difficulty of preparing samples large enough for polarized infrared studies. When only very small samples can be obtained, a reflecting microscope can be used. A number of such reflecting microscopes have been described, and Fig. 3 is a general diagram of one. In this case the useful area at the illuminated spot at the microscope stage is about  $1\text{ mm} \times 0.13\text{ mm}$ . Many satisfactory spectra reported in the literature have been obtained on the reflecting microscope with both polarized and unpolarized infrared radiation. Nevertheless, a number of difficulties do arise. One of them is the strong heating effect of the concentrated radiation at the microscope stage. Cole and Jones [21] have presented a table to show that when the sample is supported on a sodium chloride plate, a compound with melting point of approximately  $40^\circ\text{C}$  is stable, but a compound melting around  $30^\circ\text{C}$  will melt. The other difficulty is due to the large convergence angle of the beam at the microscope stage. The effect of convergence on polarized infrared spectra was treated in an article by Wood and Mitra [62]. They have shown that when a uniaxial crystal has absorbing dipoles perpendicular to the plane of the sample, these dipoles can absorb convergent radiation that is falling on the sample along the unique axis. No such absorption occurs with parallel radiation. In the case of calcite the out-of-plane deformation vibration of the carbonate ion at  $881\text{ cm}^{-1}$  can show as much as 50% absorption depending on the degree of convergence and sample thickness.

## THEORY

The method described by Ambrose *et al.* [2] and Pimentel and his co-workers [51, 52] at about the same time is known as the oriented gas model. It assumes that the behavior of the sample is that

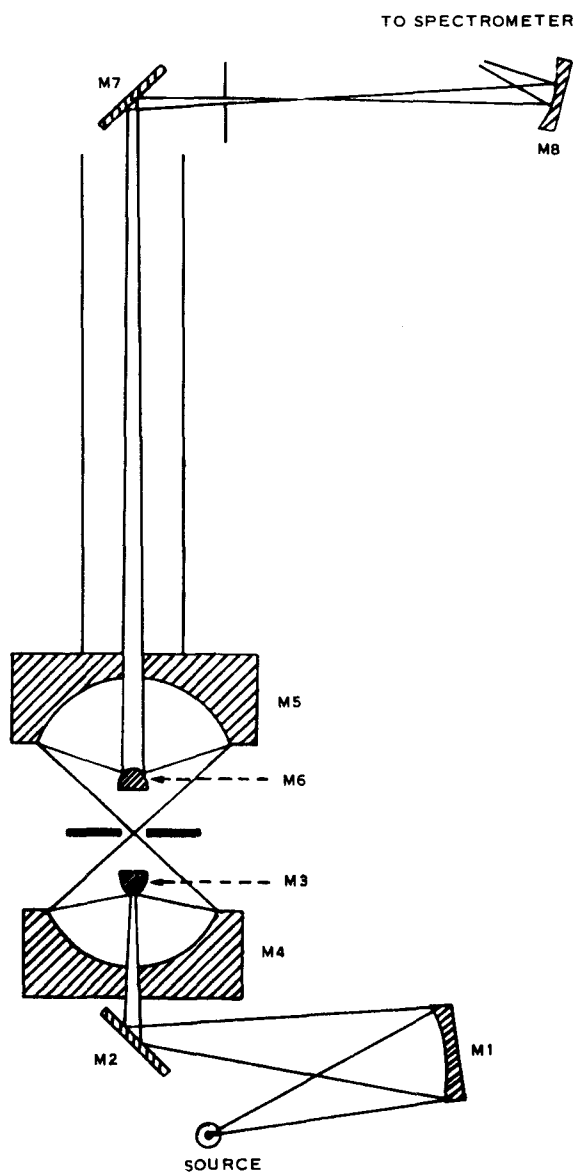


Fig. 3. Optical system of a microilluminator. [Reprinted by permission from Chemical Applications of Spectroscopy, Interscience Publishers, Inc., New York, 1956, p. 314.]

of a gas whose molecules remain perfectly oriented in space but do not interact at all. This assumption is only approximate since there are interactions in the crystal. These give rise to two different effects: the splitting of bands in consequence of the interaction between molecules having the same structure; and the violation of the gas selection rules, inactive vibrations becoming active again because of interaction of neighboring molecules. The magnitude of this interaction can usually be evaluated from the size of the shift of bands from the gas phase to the crystalline spectrum, and the size of the splitting of bands. In the case of naphthalene, for example, there are very small shifts from the gas phase spectrum to the crystalline spectrum and the splittings, where found, are very small ( $2-3\text{ cm}^{-1}$  only). In this case, therefore, we can assume that the interaction between neighboring molecules is very small, and as a first-order approximation we can treat the molecules as oriented gas molecules.

More rigorous treatments of the selection rules for molecular crystals have been developed by Halford [32], Hornig [35], and Winston and Halford [61]. Since recent reviews on this subject are available [44, 59], in this paper we shall present only an outline of the general principles involved.

Of the two procedures for determining the selection rules for vibrational spectra in crystals, the first (factor group analysis) proposes that all the spectroscopic frequencies can be discovered and classified by examination of the isolated crystallographic unit cell. The second method (site group analysis) assumes that one can deal with the motions of one molecule moving in a potential field that has the symmetry of the surrounding crystal. This assumption is strongly supported by experimental findings, the coupling between molecular motions in different molecules in a crystal being extremely weak in most cases.

A suitable knowledge of the crystal structure is necessary for both procedures. This usually consists of the *space group* designation along with the number of molecules per unit cell. The space group (*S*) is characteristic of the total crystal structure, which can be constructed from the unit cell by the translations which carry any unit cell into any other. The *unit cell group* or *factor group* (*U*) is characteristic of the internal crystal structure, i.e., the symmetry properties of the unit cell, if we define the translations

which carry a point in a unit cell into the equivalent point in another cell as identity. The two are related by

$$(S) = (U) \times (T)$$

where  $(T)$  is the group consisting of pure translations.

About any point in the crystal there is a local symmetry. For most points this will consist only of the identity operation. However, if the point is located on some elements of symmetry, the corresponding operations leave that point invariant. Such a point is called a site. Usually a unit cell has several different kinds of sites, and sometimes it has several definite sets of the same kind. The symmetry of a site is described by the *site group*, which is a subgroup of the factor group.

The center of mass of a molecule does not change under the operations of the molecular group. Its equilibrium position in the crystal is usually situated on a site. This is only possible if the site group is a subgroup of the molecular group. The site group, in general, will be of lower order than the molecular group, although this is not necessarily so. When it is true, the selection rules for the crystal will be less strict than for the isolated molecule and, therefore, the spectrum of the crystal will be richer in bands than that of the gas phase.

When the site group has been identified, the selection rules can be deduced in the usual way. The relation between the vibrations of an isolated molecule and one in the crystal can be easily established by comparing character tables for the molecular group and the site group.

To identify the site group, one has to remember that an acceptable site group must be a subgroup of both the factor group and the molecular group. Sometimes only one common subgroup exists, but if there are more than one, a further distinction can be made on the basis of the number of molecules in the unit cell. In order to employ this procedure, it is important to have the table given at the end of Halford's article at hand. It lists the site groups for each of the 230 space groups, the numbers of equivalent sites per set, and the multiplicities of sets.

We can paraphrase Halford's summary [14] of these matters as follows: the selection rules that pertain to an *isolated* molecule are determined by the symmetry of the molecule itself, described

by the *molecular group*. The selection rules that govern the molecule in the crystal are determined by the *static* symmetry of the field caused by its surroundings, described by the *site group*. The most complete selection rules, which involve the *dynamic* interactions of the molecule with its neighbors, are determined by the symmetry of the complete unit cell, described by the *factor group*.

At this stage we would like to present a few examples which illustrate a number of points discussed in the preceding sections.

In the case of urea, the question arose as to whether the molecule is completely planar, i.e., whether the hydrogen atoms are in the same plane as the heavy atoms. Ordinary infrared and Raman spectra did not give sufficient information to resolve this problem. However, work by Waldron and Badger [60] on a single microcrystal of urea in the reflecting microscope has given conclusive evidence for the planarity of urea.

Urea would have  $C_{2v}$  symmetry regardless whether the hydrogen atoms are all planar or above and below the plane of the heavy atoms. However, the selection rules are different in the two cases. In the first case, one would expect four N—H stretching vibrations, while in the second case only three of these would be infrared active. Waldron and Badger located four of these bands, two each in the respective polarized spectra, and thereby have shown that there are indeed four infrared-active N—H vibrations.

Polarized spectra were of considerable help in the completion of the total vibrational assignment of urea. The crystal structure of urea [17] is tetragonal and belongs to the space group  $V_4^3$ ; there are two molecules in the unit cell, with the C—O bonds pointing in opposite directions and the planes of the molecules at right angles to each other.

Angell [3] has prepared an oriented microcrystalline mass of urea by melting a small amount of urea on a sodium chloride plate and then cooling it at one end. The crystals started growing at that end and were completely oriented in one direction, as could be observed under a polarizing microscope.

Figure 4 gives the polarized infrared spectrum of this oriented microcrystalline layer, along with the spectrum in a KBr pellet and the spectrum of the oriented layer using nonpolarized radiation. It can be seen that the bands at 1680, 1600, 1160, 1010, and 546  $\text{cm}^{-1}$  are polarized parallel and the bands at 1625, 1470, 788, 714, and 600  $\text{cm}^{-1}$  are polarized perpendicular, while the broad band



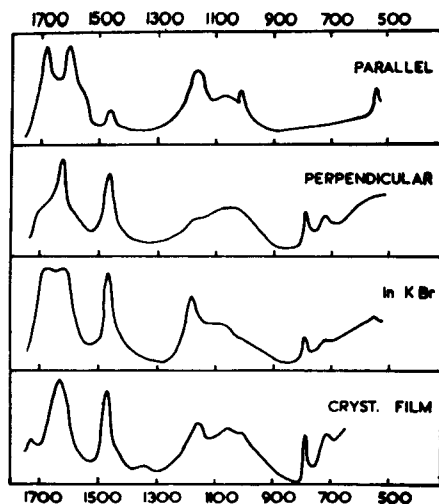


Fig. 4. Infrared spectra of crystalline urea.

extending from 1150 to 900  $\text{cm}^{-1}$  seems to have the same intensity in both polarizations. In the polarized spectra, bands at 1625 and 1600  $\text{cm}^{-1}$ , which previously could not be separately identified, were resolved. In this way the polarized spectra served as additional information for the assignment of fundamental vibrations. The last spectrum is of interest because it shows the effect of the polarization of the spectrometer. This spectrum taken with nonpolarized radiation shows great resemblance to the spectrum described as perpendicular, showing that the radiation going through the spectrometer had at least a partially perpendicular character.

The oriented gas model has been used by Pimentel and McClellan [51] in their interpretation of the naphthalene spectrum. A single crystal of naphthalene was grown and then polished to the required thickness. Naphthalene crystallizes in space group  $C_{2h}^s$ , and the principal cleavage plane is the  $ab$  plane. Spectra of the crystals were recorded at normal incidence for the  $b$  axis both perpendicular and parallel to the plane of polarization. Other spectra were taken at  $\pm 15^\circ$  from normal incidence, for the perpendicular orientation of the  $b$  axis.

The molecular symmetry of naphthalene is  $D_{2h}$ , while the site symmetry is  $C_i$  and the factor symmetry is  $C_{2h}$ . The factor group analysis predicts that each vibration of gaseous naphthalene will