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Optical Properties of Highly Absorbing Crystals†

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Abstract—Methods of obtaining polarized single crystal absorption spectra and other closely related spectral data for highly absorbing substances in the ultraviolet and visible regions are discussed. Specular reflection spectroscopy is treated in some detail, both experimental and interpretive techniques being covered, direct absorption methods are discussed, with emphasis being placed on possible sources of difficulty that can arise in crystal measurements involving high optical densities, and the importance of considering the use of other techniques to confirm the results of absorption and reflection studies is brought out. The presentation is illustrated by examples drawn from the author's current research activities.

Introduction

The variety of motivations that exist for single crystal absorptive studies may be grouped roughly into those related to the investigation of solid state phenomena as such and those concerned with using the crystal as a convenient medium for the study of molecular properties. Among the former are included the investigation of solid state spectral effects, such as those that may be understood in terms of exciton theory, and the correlation of absorptive and other solid state properties, while an important example of the latter is the determination of the polarization of molecular absorption bands. Unfortunately, a great many crystals, including many composed of molecules whose investigation in the solid would be of theoretical interest or would potentially lead to results of significance in other areas, as well as those which possess some of the most

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striking solid state properties, are so highly absorbing that their study by direct absorption requires the preparation of extremely thin samples. The net results have been that, on the one hand, many areas of study have largely been neglected and, on the other, when studies have been made, the resulting spectra have often been relatively uninformative or simply incorrect.

The results that have been obtained over the years on nickel dimethylglyoxime (NiDMG),† an inorganic complex whose crystal spectra have been the object of considerable study,[1-4] serve to illustrate well the difficulties that can surround absorption measurements on even moderately highly absorbing crystals. In the top two panels of Fig. 1 are replotted versions of polarized NiDMG spectra that have appeared in the literature,[1,2] while the lower panel presents the same spectra as they were recently determined in our laboratories,[5] the $\perp$ and $\parallel$ labelling of the curves indicating whether they were obtained with the incident radiation having its electric vector polarized perpendicular or parallel to the molecular planes.† For reasons that will be brought out later, the more recent set of data is thought to be a reasonably accurate representation of the true absorption spectra for NiDMG. A comparison of the three pairs of curves shown in Fig. 1 indicates that the earlier results reveal very little reliable information other than the general region of the onset of total absorption in the samples being studied.‡ Such data can, of course, be useful, especially for the cautious comparison of several compounds, if one is cognizant of their nature and limitations, but can be highly misleading if proper care is not

† By way of background, it may be noted that interest in this compound stems in part from the fact that a strong visible absorption occurs in the solid that has no obvious counterpart in solution. The NiDMG crystal structure is such that the molecules stack in columns, the nickel atoms falling one above the other and forming essentially infinite chains, and thus it has been speculated that the low-lying single crystal band, as well as this compound's low solubility, is associated with metal–metal interaction in the solid.

‡ Although the fact that the $\perp$ curve rises sharply before that for the $\parallel$ direction seems to be associated in this case with the out-of-plane polarization of the lowest energy band, work on other substances indicates that one must exercise caution in drawing such conclusions.

exercised in their interpretation. In this latter regard, it will be noted in Fig. 1 that the wide differences in the absorption spectra for the two crystal directions are completely lost in the previously reported curves, a circumstance that has led to incorrect inferences being drawn regarding the nature of the polarization of the low energy transition. Similarly, the discrepancies (amounting to a

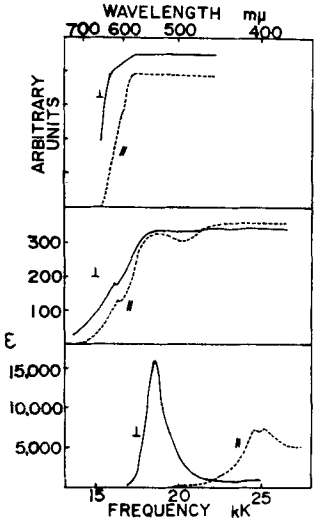


Figure 1. Polarized single crystal absorption spectra of nickel dimethylglyoxime. The upper two panels present previously reported results,[2, 1] while the lower panel reports spectra recently determined in our laboratories.[5] In each instance the $\perp$ curve is that obtained with the electric vector of the incident radiation polarized perpendicular to the molecular planes and the $\parallel$ curve is that for the in-plane polarization.

factor of about 50) in the molar extinction coefficients shown in the lower two panels should also be noted, since quantitative errors of this magnitude can lead to the misassignment of transitions.

In any case, regardless of the nature of the valid conclusions that one may draw from the other curves, the spectra shown in the lower panel clearly bring out much more detail of the absorption than was previously available and are of the type necessary if the experimental situation is to be characterized adequately. Thus, the

recent study of a series of NiDMG-type complexes ranging from the situation where the nickel atoms are highly separated in the solid, and therefore crystal effects are minimal, to one where the crystal perturbation is relatively great, has allowed the identification of the "single-molecule" band that gives rise to the low-lying NiDMG crystal band.[5] This work also indicated that the associated transition is other than *d–d* in nature, and has revealed much detail concerning the total array of spectral changes that can accompany the solid formation in these complexes.

The data of Fig. 1 have been selected as a result of the author's familiarity with the NiDMG problem, but the situation illustrated is quite common in that many published spectra, and doubtlessly many that have never been published, show in varying extents the characteristics possessed by earlier NiDMG spectra reproduced here.† Thus, during the past several years the author and his coworkers have been developing a series of techniques that allow one to obtain reliable absorptive information for those crystals that are sufficiently highly absorbing to make their study non-routine. Although these methods have evolved within the context of problems having intrinsic scientific interest in themselves, such as the NiDMG work discussed above, the current widespread interest in single crystal spectroscopy in many areas of chemistry, physics, and biology and the confusion that appears to exist as to what constitute reasonable spectra, seem to make advisable a discussion that centers attention on the experimental approaches involved as such. The following will be such a presentation, the illustrations contained in it being drawn from work currently in progress in these laboratories. It should be pointed out, however, that no attempt will be made here to give an all-inclusive treatment of the topic, but rather,

† To cite just a limited number of additional examples, other NiDMG spectra similar to those shown in the upper panels of Fig. 1 have been reported,[3] the situation for quinhydrone has been shown to be quite analogous to that for NiDMG,[6] and Day *et al.*[7] have recently shown evidence that earlier spectra for Magnus's green salts were badly attenuated. Of course, if such effects are less obvious than in these rather extreme cases, they become more difficult to detect and thus in some respects are more likely to cause interpretive problems.

largely as a result of the author's background and interests, emphasis will be placed on single crystal reflection and absorption spectroscopy and other methods touched upon very briefly. Moreover, of the major areas dealt with, reflection studies will be discussed in most depth, in the belief that most workers interested in visible and ultraviolet spectra of molecular crystals, from whose point of view this is written, are least familiar with this approach.

Reflection Spectroscopy

The Basis of the Method

A powerful tool for the study of the absorptive properties of crystals possessing relatively high extinction coefficients is specular (i.e. mirror-like) reflection spectroscopy.† The usefulness of this approach rests on the fact that near a region of absorption the variation in the index of refraction is roughly paralleled by the reflection coefficient, R, the fraction of the incident radiation that is reflected by the crystal surface. The reflectivity thus generally rises to a maximum value and then falls to a minimum as one moves through an absorption band from the low energy side.‡ The relationship of the extinction coefficient (k),§ the index of refraction (n), and the reflection coefficient (R) to each other for a typical

† This technique, in which the surface reflectivity is measured, is not to be confused with diffuse reflection spectroscopy, where the light detected is attenuated in regions of absorption by actual absorption in the sample.[8]

‡ Since a major contribution is made to the reflection coefficient by the difference in the indices of refraction of the reflecting medium and the medium through which the radiation is incident, this description of the reflection band may not be strictly correct if the experimental conditions are such that radiation is incident through a material whose refractive index is significantly different from one.[9]

§ k is not identical with the usual molar extinction coefficient ϵ, being the "imaginary part of the complex index of refraction", but may be related to it through

$$\epsilon = (4\pi k)/(2.303\lambda C)$$

where C is the molar concentration of absorber in the crystal and λ is the wavelength to which ϵ and k refer. The specific dependence of the reflection coefficient on n, the index of refraction, and k is given by Eq. (4) and the complex index of refraction defined by Eq. (3).

absorption spectrum of moderately, but not extremely, high intensity is shown in Fig. 2. It will be noted that the n and R curves possess the expected shape in the vicinity of the low energy absorption that occurs at about 390 mμ, whose crystal molar extinction coefficient here is about 39,000. Moreover, both of these curves also show the expected peaks corresponding to the higher energy transitions even though the absorptions are not particularly

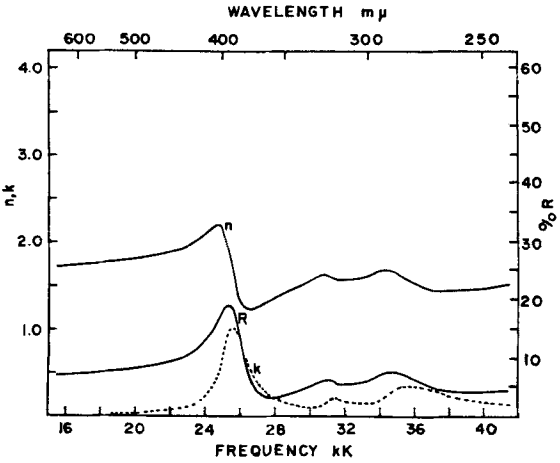


Figure 2. The reflection coefficient (R), index of refraction (n), and the extinction coefficient (k) for, in the terms of Ref. 10, the R_{min} principal direction of Face 1 of auramine perchlorate. The n and k curves were derived through a Kramers-Kronig analysis of the reflection data.

well resolved. Thus merely by visual inspection of the reflection curve one may infer the general nature of the absorptive properties, as was done for this very example before the analysis that led to the k and n curves of Fig. 2 was carried out.[10]

The above example suggests the utility of using the study of the reflection coefficient as a function of wavelength as a means of investigating the absorptive properties of solids and illustrates the fact that, since the more intense transitions usually have a greater effect on the refractive index, the sensitivity of reflectivity studies increases as does the intensity of the transitions involved. In fact,

it appears that reflection and absorption are complementary in the sense that the regions of applicability of the two methods in general overlap, and usually direct absorption can be used for those bands too weak for reflection studies, while reflection can be used in most cases where absorption studies become difficult due to high intensity. Before citing further examples of the use of reflection and discussing the various methods available for the interpretation of the spectra thus obtained, however, it would seem appropriate to give some details of the experimental equipment and procedures that have been developed in connection with these studies.

Reflection Measurements

Figure 3 presents a schematic diagram of the instrument used to obtain the reflection spectrum of Fig. 2 and the other spectra of auramine perchlorate shown in later figures. This double-beam

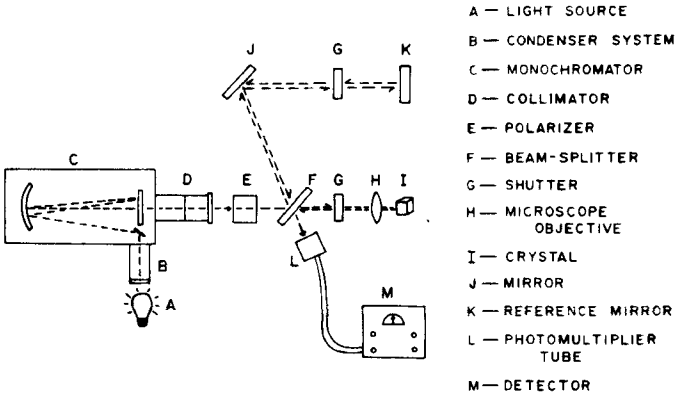


Figure 3. Schematic diagram of the original reflection microspectrophotometer used in these laboratories.

instrument, whose construction and operation have been discussed in some detail elsewhere,[10] is relatively inexpensive and easily constructed and allows one to obtain accurate data for even relatively small crystal faces. It will be noted that the spectrophotometer is so designed that the spectra are taken at normal incidence (except for any convergency introduced by the objectives),

a feature which greatly simplifies their subsequent analysis in terms of electromagnetic theory. Obtaining a reflection spectrum on this instrument consists of first taking a spectrum of the crystal face under study (I in Fig. 3) relative to the reference mirror (K), and then obtaining a spectrum under exactly the same conditions of an aluminum mirror that has been substituted for the crystal. After correcting these measurements for "stray light",[10] the appropriate division of one set of data by the other leads to a reflection spectrum for the crystal relative to the substituted aluminum mirror. This spectrum may then be made absolute from a knowledge of the reflectivity of the substituted mirror.

After this instrument had been in use for a time it became clear that it incorporated many of the features found in commercial microscopes, and consequently a second microspectrophotometer has been constructed which has at its heart a Leitz "Ortholux" microscope. One may thus take advantage of the provisions made in microscope design for the accurate and reproducible positioning and rotation of a specimen, and through the use of a trinocular head examine visually the exact area of the crystal surface being studied before and during the course of a run. Moreover, it has been possible to modify this instrument so as to allow ready interconversion between reflection and direct absorption measurements, thus allowing the two types of studies to be made, if desired, on precisely the same areas. This extremely adaptable microspectrophotometer has also been converted to a spectrofluorimeter to measure single crystal fluorescence when the occasion demanded.[11] The advantages that this instrument has over that diagrammed in Fig. 3 are thus essentially its greater versatility and adaptability, but it is in turn somewhat more expensive and complex to set up.

In this newer spectrometer light from an appropriate source is again passed through a Bausch and Lamb monochromator of the type used in the spectrophotometer of Fig. 3 (or through two such monochromators if the spectral distribution of the light source and spectral purity demands of the experiment require it), collimated, and rendered plane polarized by a Glan-type prism. The monochromatic polarized beam then passes, in the case of reflection

studies, directly to the vertical illuminator supplied by the microscope manufacturer, which has been stripped down and converted into what amounts to a quartz substrate beam splitter, the deflected portion of the beam being focused on the crystal at essentially normal incidence by an appropriate objective. The reflected radiation then traverses the beam splitter and, if desired, another Glan prism, and falls on a detector, which is generally a photomultiplier tube whose output is monitored by an Eldorado Model 201 photometer. This instrument also has a double-beam arrangement built into it, but in practice the light sources and the detection system used have been found sufficiently stable to allow one to operate in single-beam mode.

The positioning, alignment, and rotation of the crystal are achieved by using standard microscope stages augmented, as necessary, by special goniometric modifications. Actually obtaining a spectrum here involves essentially the same sequence of measurements as is employed when the formerly described instrument is used, in that the techniques of calibrating the whole apparatus by replacing the crystal with a mirror of known reflectivity and obtaining a second set of data, and of securing a set a "stray light" corrections while having nothing before the lens, are followed here also. One minor modification of the procedure outlined previously[10] is that principal directions for a given face have on occasion been found by taking advantage of the fact that if the polarizer and the analyzer prisms are crossed, these directions appear as "extinctions" as the crystal is rotated, just as in absorption work.

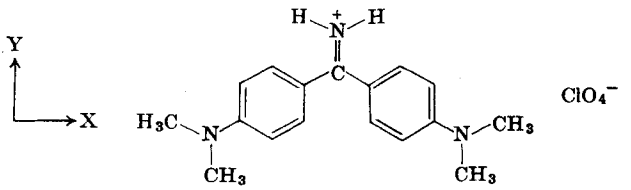
Interpretation of Spectra

Visual Analysis

In some instances the information that one may wish to obtain from a set of reflection spectra may be derived by simple inspection of the experimental curves. Such a situation may arise, for instance, when one wishes to assign the polarization of a band and is dealing with a sufficiently simple crystal structure and a sufficiently high molecular symmetry that the appearance or non-appearance of

the band along a series of principal directions will allow one to make the assignment. An example of such a case is provided by recent work on $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (TPP),[12] where the lowest energy band in the visible spectrum was found to appear prominently in the spectrum obtained with polarized light whose electric vector vibrated parallel to one principal direction of the (010) face of the triclinic modification and to be almost unobservable for radiation polarized along the other principal direction in this face. A consideration of the projections onto the principal directions of a set of orthogonal axes appropriate to the approximate D_{2h} symmetry exhibited by the porphine nucleus of TPP, and the spectrum obtained for a principal direction of a second face that corresponded to almost purely out-of-plane absorption, allowed one to conclude that the low energy band in this substance is polarized along the in-plane axis passing through the hydrogen-bearing pyrrole nitrogens.

An excellent example of the great amount of material that one may in favourable cases derive by simple inspection of reflectivity curves is provided by auramine perchlorate,[10] a diphenylmethane dye one of whose resonance structures may be represented by:



The well-characterized solution spectral properties of this substance[13] combined with the fact that high quality crystals with very stable surfaces can be fairly easily prepared has made "auramine" the material on which many of the reflection techniques discussed here have first been explored in our laboratory. Auramine is also attractive from the point of view that its absorption spectrum is rather typical, in both its level of complexity and the molar extinction coefficients encountered, of many of the substances that one might wish to study by these methods, and that its crystal

spectra have rather interesting characteristics from a purely solid-state point of view.[10]

Figure 4 shows the solution absorption spectrum of auramine. Adam,[13] on the basis of his solution and rigid glass studies and non-empirical arguments, assigned the low energy 440 mμ band of Fig. 4 as "x", in terms of the in-plane axes defined on the molecular diagram above, the 372 mμ and weak 316 mμ bands as "y", and the high energy band as being the result of two electronic

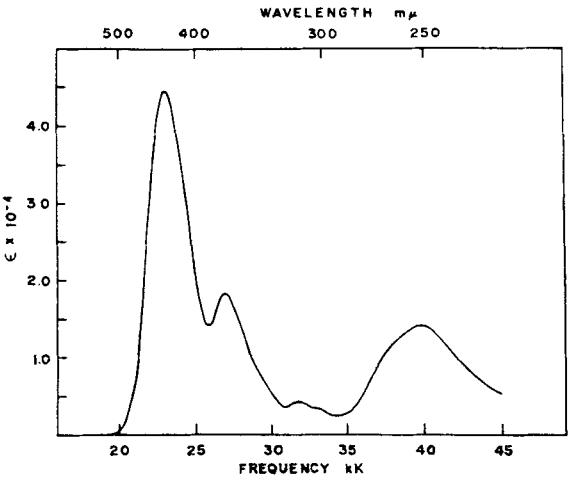


Figure 4. Absorption spectrum of an aqueous solution of auramine perchlorate.

transitions, that of lower energy being "y" and that of higher "x". Thus if one had a sample made up of a collection of fixed, similarly oriented auramine "molecules" and examined it with polarized radiation, one would expect to obtain an "x-system" consisting of a low energy transition of relatively high intensity and a high energy band of lower intensity† when the electric vector vibrated parallel to the x-axis, and a "y-system" between these two x

† Adam's[13] polarization studies also indicate a very weak transition of "x" polarization occurs at 328 mμ, which is so feeble as to be unresolved in the solution spectrum and is not considered here.

transitions consisting of three bands of lower intensity when the radiation had a y-polarization.

In Fig. 5 the polarized reflection spectra obtained for one face of the auramine crystal are presented. One clearly sees that the bands present in the R_{max} curve are those expected for the x-system, while those present in the R_{min} direction are those expected for the y-system. Thus the qualitative interpretation of the spectra presented

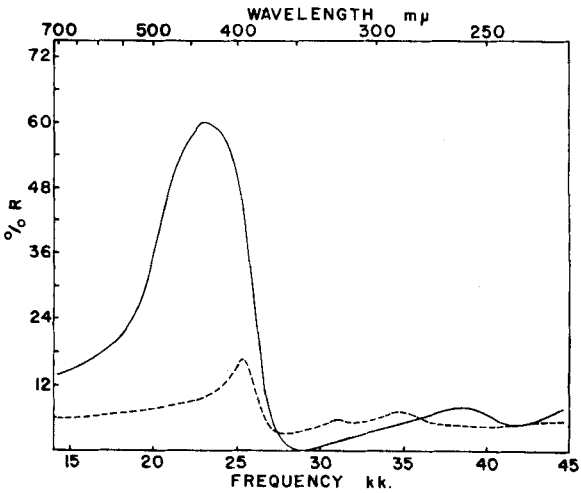


Figure 5. Reflection spectra for Face 4 of the auramine perchlorate single crystal: (——) spectrum obtained with polarized radiation whose electric vector vibrates parallel to the R_{max} principal direction; (– – –) spectrum obtained for radiation polarized parallel to the R_{min} principal direction. (From Ref. 10.)

in Fig. 5 leads one to most of the conclusions that one can obtain from a polarized fluorescence study of a rigid glass solution of this material—namely that the second, third, and fourth transitions observed here are perpendicular to, and the fifth is parallel to, the lowest energy transition and that the high energy solution band is actually related to two transitions of opposite polarization. It should be noted that this information is available without reference to a detailed crystal structure, a point of possible importance in

connection with assigning relative polarizations of transitions in compounds that do not emit.

The crystal structure for auramine is in fact not known in detail at the present time. It is fairly clear on the basis of its reflection spectra, however, that the auramine crystal possesses a structure such that all the cationic chromophoric units are spectroscopically equivalent. This fact has allowed the spectral characteristics of three of the principal directions of this crystal to be used to develop a crystal model in terms of which all eight available crystal spectra may be understood.[10]† The procedure followed entailed accepting Adam's polarization assignments and then using the spectral data to develop a gross picture of some aspects of the crystal structure, but clearly once the structure is known the process can be altered to use it in conjunction with the spectra to obtain the absolute polarizations on a strictly empirical basis. Thus one here has a demonstration of the utility of making polarization assignments through polarized reflection studies, and also the potential usefulness of using the data accumulated in optical studies to orient chromophoric groups in the initial stages of X-ray crystallographic structure determinations. The latter procedure, whose practicality has already been demonstrated by recently completed work on 1,5-*bis*-(dimethylamino)pentamethium perchlorate (BDP)[14]‡ might prove particularly useful in situations where heavy atom techniques cannot be applied.

Other examples of polarization assignment by inspection include those made of the lowest energy transition in the polyene-related β-ionylidene crotonic acid[18] and the charge-transfer band of the quinhydrone crystal.[6] The latter case is of special interest here

† The type of reasoning involved in setting up the crystal model can be exemplified by noting that the conclusions drawn in regard to the spectra of Fig. 5 imply that the projections of the **x** and **y** axes on this face are respectively parallel to the R_{max} and R_{min} principal directions.

‡ X-ray crystallographic studies which it is hoped will further illustrate such application of spectral studies are currently in progress on auramine.[15] It is also worthy of note in this regard that the main orientational features of the recently reported triclinic modification of quinhydrone[16] were independently predicted on the basis of spectral evidence.[17]

since previous direct absorption studies had resulted in a widely quoted assignment that was in fact in error by some 34°. It was this situation that led to the rather careful analysis of the problems that can arise in absorption studies on such substances in our laboratories in order to allay our fears that the reflection work might in some way be giving spurious results.

Kramers-Kronig Analysis

In many cases one wishes to have available detailed absorption spectra for the crystal at hand. This is obviously the case if one's prime interest is the study of crystal absorptive effects as such, but it is also true that as the crystal structure becomes more complex than those involved in the examples cited above, the need for crystal absorptive information rapidly becomes more acute even for the assignment and resolution of molecular transitions. Perhaps the most general method for obtaining the desired information in such cases is through a "Kramers-Kronig analysis" of the reflection spectra, an approach based on a very general theorem that has found application in a wide variety of physical situations. In the present case, this theorem states that at a specific circular frequency, ω_i, one may compute the phase change on reflection, $\theta(\omega_i)$, through the evaluation of the following integral expression[19]

$$\theta(\omega_i) = \frac{\omega_i}{\pi} \int_0^\infty \frac{\ln R}{\omega^2 - \omega_i^2} \, d\omega. \tag{1}$$

Once one has available $\theta(\omega_i)$ the optical constants at ω_i may be evaluated by a consideration of Fresnel's equation for the intensity of normal incidence reflectivity which, when written in terms of the complex amplitude of the reflected wave, becomes

$$R^{1/2} e^{i\theta} = (\mathbf{n} - 1)/(\mathbf{n} + 1) \tag{2}$$

where $\mathbf{n}$, the complex index of refraction, is defined as

$$\mathbf{n} = n - ik. \tag{3}$$

Multiplying each side of Eq. (2) by its complex conjugate of course yields the more familiar form of Fresnel's equation for the measured reflectivity in terms of n and k

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \tag{4}$$

but expanding both sides and equating the real and imaginary parts leads to a pair of simultaneous equations that may be solved to give

$$n = \frac{1-R}{1-2R^{1/2}\cos\theta+R}, \tag{5}$$

and

$$k = \frac{-2R^{1/2}\sin\theta}{1-2R^{1/2}\cos\theta+R}. \tag{6}$$

Thus, having measured R and computed θ for a given frequency, one may compute both n and k at this frequency.†

An IBM-7094 program has been developed in our laboratories which,‡ utilizing the calculative scheme outlined by Gottlieb,[19c, 20] carries out the integration of Eq. (1). The high-energy and low-energy regions for which reflection data are not explicitly provided as input are approximated as having constant reflectivities, the reflection coefficients being set respectively equal to those of the last high energy and the last low energy points for which values are provided. The integration is then carried out analytically in these two regions and numerically, using Simpson's rule and appropriately taking into account the singularity that occurs for $\omega=\omega_0$, in the interval for which explicit data are provided. Equations (5) and (6) are then employed to compute n and k, k is

† The above expressions are appropriate to the situation where one considers the time-dependent part of the wave equation that results from the solution of Maxwell's equations to have the form $e^{i\omega t}$. If one instead writes $e^{-i\omega t}$, then the right-hand side of Eq. (1) becomes negative, the complex index of refraction must be written $\mathbf{n}=n+ik$, and the right-hand side of Eq. (6) becomes positive.

‡ This program was originally written by Mr. F. K. Krist and subsequently modified by Dr. A. V. Fratini.

converted to a quantity equal to the product of ϵ† and the molar concentration of the absorbing species present in the crystal, and, optionally, ϵ itself computed when the crystal concentration is available.

The Kramers-Kronig analysis of reflection spectra has been practiced in recent years by infrared spectroscopists and physicists concerned with the optical properties of inorganic materials or metals, but has been little exploited by workers interested in the electronic spectra of molecular crystals of the type under discussion here. Aside from the somewhat general lack of awareness of the power of reflection spectroscopy among chemists, the reason for this circumstance may lie in the difficulties that can arise from Eq. (1)'s requiring a knowledge of the reflection coefficient over the entire frequency range, when in practice one of necessity is restricted to a limited experimental interval. The "resonance denominator" term in Eq. (1), however, weights favorably the data near ω_0 and gives little weight to those from regions remote from ω_0, and thus one can in some cases obtain satisfactory optical constants using just the experimental data. Such situations are much more likely to arise in the infrared,‡ where relatively well-isolated bands may be encountered, than in the visible and ultraviolet, where one can generally be assured that strong bands occur in the vacuum ultraviolet for which, in many instances, data are not readily available.

The occurrence of physically unreasonable negative extinction coefficients in the derived absorption spectra is the most common, and often a highly discouraging, symptom that the reflection data obtained experimentally are not adequate for a completely satisfactory analysis using merely the straight-line approximation described above for the high and low energy extrapolations of the experimental data. This circumstance occurs when the phase change computed from Eq. (1) is positive (when one uses the

† See footnote on page 5 for the relationship between k and ϵ.

‡ Difficulties can also arise in the infrared as a result of the effect of inaccessible reflectivity data, however, as has been demonstrated by Schatz *et al.*[21] (see also Ref. 19f) and is apparent from various published spectra.

conventions adopted here, then the true θ must fall in the range $-\pi \leq \theta \leq 0$) and thus leads to a negative k-value when used in Eq. (6). A number of procedures for correcting the calculated phase and thus obtaining more reliable optical constants have appeared in the literature.[19b, d, 21–25] These generally involve adjusting the calculated phase in some way so that it, or the optical constants derived from it, fulfill some predetermined criteria which reflect known properties of the substance under study. In the investigations thus far carried out in our laboratories a convenient and apparently successful approach has been to place an "effective" peak in the vacuum ultraviolet and vary its characteristics until an extinction coefficient of zero is obtained in the long wavelength region, where the crystals in question may be assumed to be essentially transparent. Reasonable optical constants have then been obtained throughout the region of interest and the resulting molar extinction coefficients have compared well to those measured directly when such were available for comparison. Moreover, the integrated intensities for the crystal absorption bands thus derived have approximated those for the corresponding molecular transitions when they could be expected to do so.

As an example of the difficulties described above and the effectiveness of the suggested approach to overcoming them, Fig. 6 shows in various stages of refinement the absorption spectrum obtained from the Kramers-Kronig analysis of the R_{max} curve of Fig. 5. A considerable portion of the spectrum derived using the simple "straight-line" extrapolation of the measured reflectivity is seen to be negative. It is in fact as if one had a baseline that sloped downward as one moved to higher energies, and that the effect of the refinement of the analysis was the rotation of this baseline upward, a situation that reflects the increasing importance of the vacuum ultraviolet phase contribution as one moves to higher energies. The curve that is finally obtained has very much the appearance that one expects for the x-system absorption previously described, and integration of the low energy band of this final curve gives an intensity that is approximately 0.9 of that expected on the basis of the solution transition moment and the

projection of the x-axis of a molecule oriented as suggested by the proposed crystal model onto the principal direction in question.† The insensitivity of the positions of both absorption bands dealt with in Fig. 6 to the nature of the high energy approximation used is also worthy of note, as it thus appears that even for cases where the absolute k-values are quite poor the positions of the absorptions can be determined with some confidence from the results of a Kramers-Kronig analysis. In the case of the intense, low energy band, moreover, the intensity can even be obtained moderately well from the unrefined curve,‡ reflecting the fact that the phase is strongly dominated by this transition in its immediate vicinity.

The final results obtained in these analyses seem to be surprisingly free of dependence on the exact form of the high energy approximations used, and in one case the use of a "rectangular" vacuum ultraviolet band even led to reasonable results. Nevertheless, a description of the procedure used in connection with the derivation of the curves shown in Fig. (6) may be of some interest. The high energy reflectivity was here approximated by a curve that gradually rose from the last measured point to a peak value at about 170 mμ and then decreased rather rapidly to about 1.5% at 150 mμ, which value the program then used in its straight-line extrapolation. Refinement consisted of first varying the 170 mμ peak value until considerable improvement in the k's had been obtained, and then making still further improvement by changing slightly the minimum value in the 150 mμ region. The final curve is that obtained with maximal and minimal values of 15 and 1.4% respectively,

† Some loss of intensity in the crystal, compared to that in solution, appears to occur along each principal direction,[26] and may in fact be a real effect rather than any artifact of the analysis. In any case, quantitative agreement of this nature is certainly gratifying and encouraging if one notes that direct absorption measurements on a sample of auramine with $\epsilon = 10^5$ would require a sample of thickness of the order of 500 Å, if one had an instrument on which reliable optical densities of, say, 2 could be obtained. The errors in the absolute intensities from such a measurement, even if a sample of such a thickness could be prepared, would almost surely exceed 10%.

‡ Clearly problems arise here regarding proper choice of baseline, however, as they have in other, similar, situations.[27]

while the intermediate curve is that obtained when the 170 mμ peak has a reflectivity of 50%. As indicated in the caption for Fig. 6, the reflection spectra from which the refined curves are obtained also involve a low energy extrapolation based on a classical dispersion fit of the experimental data, but in this case and the

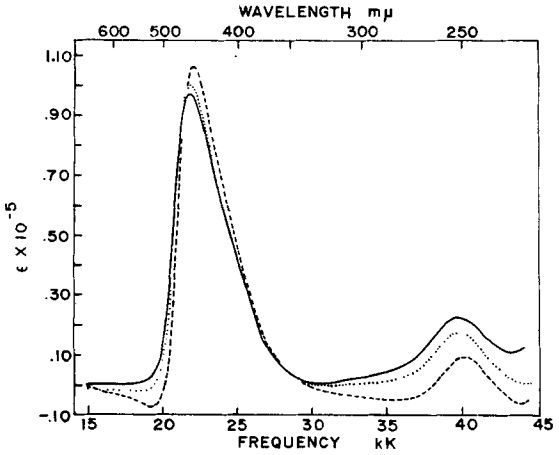


Figure 6. The absorption spectrum, in various stages of "refinement", derived through a Kramers-Kronig analysis of the reflection data for the R_{max} principal direction of Face 4 of auramine perchlorate: (– – –) curve obtained using just the experimental data and the straight line high and low energy approximations discussed in the text; (....) partially refined curve obtained using a low energy extrapolation (to 1700 mμ) based on the classical dispersion theory analysis of Ref. 10 and an "effective" vacuum ultraviolet transition, in addition to the straight line extrapolations; (——) final curve obtained by varying the nature of the "effective" vacuum ultraviolet reflectivity to obtain zero extinction coefficients in the long wavelength region.

others examined here such extrapolation has not been found to be a necessity. The classical dispersion theory data were included in the auramine studies as a result of the requisite parameters being readily available from previous work.[10]

Classical Dispersion Theory

Since the reflection coefficient is determined by the complex index of refraction, classical dispersion theory, which in principle

allows one to compute the index of refraction of a crystal from molecular properties, provides a convenient method for the analysis of reflection spectra. As it has been applied in our laboratories this approach involves the use of the expression for **n** that one obtains from the damped harmonic oscillator model for the solid with the inclusion of an internal field correction appropriate to cubic symmetry.† The explicit expression used to compute the complex index of refraction has been given and its application to the reflection spectra of auramine and BDP recounted elsewhere.[10, 28, 29] It will be sufficient to note here that the utility of classical dispersion theory lies in its ability to provide rather ready insights into the molecular origin, at least on one level of sophistication, of the effects one has encountered in a given study[28, 29] and, as in the case of auramine,[10] rationalize observed effects quantitatively whose reasonableness is not at all obvious from a simple qualitative examination.

The detailed fitting of a reflection spectrum through the application of classical dispersion theory results in a set of n's and k's calculated on the basis of those dispersion parameters that give the best fit to the observed reflection spectrum. Figure 7 illustrates the amazingly close correspondence that can exist between these optical constants and those obtained from the Kramers-Kronig analysis. The largest differences seem to be those associated with the high intensity bands and, on the basis of rather limited observation, it would appear that such deviations are more severe the stronger the band with which one is dealing.[11, 26] For the more weakly absorbing, relatively speaking, directions of auramine, the two sets of optical constants are essentially identical. This situation suggests that dispersion theory can also provide a useful link between reflection spectra and detailed absorptive curves. It would appear, however, that the Kramers-Kronig method, which does not assume a specific model for the solid, is the most direct and

† Although one should in principle use the form of the internal field that is appropriate to the crystal structure at hand, the cubic correction has been found to give parameters that could be reasonably related to molecular properties.[10, 28, 29]

generally useful approach in this regard. It should be recalled that the dispersion analysis requires considerable trial and error computational effort in finding the proper parameters with which to fit the data and involves, just as does the Kramers-Kronig method, recognition of the effects of high energy transitions. Moreover those applications of classical dispersion theory analysis made here

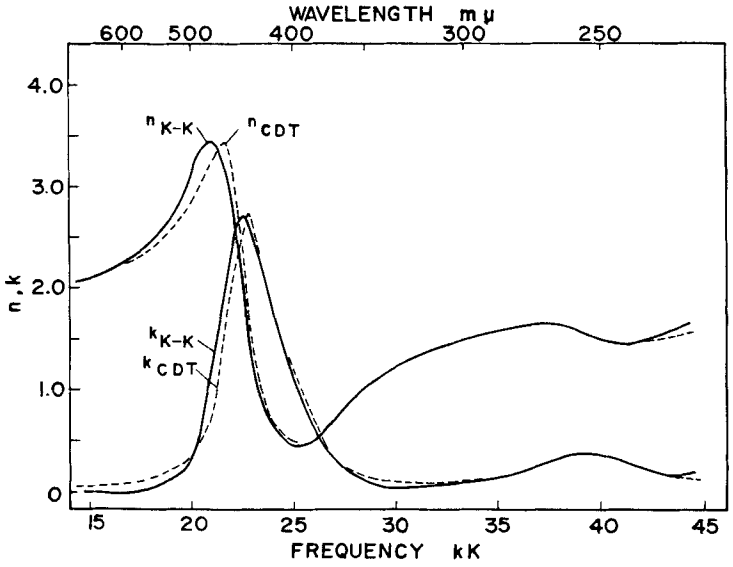


Figure 7. The optical constants obtained through a Kramers-Kronig analysis (n_{K-K} and k_{K-K}) and a classical dispersion curve-fit (n_{CDT} and k_{CDT}) for the R_{max} principal direction of Face 3 of auramine perchlorate.

to date have involved situations in which the vibronic fine structure of the electronic transitions is not resolved, and thus the whole vibronic envelope for a given transition may be appropriately represented by a single term in the dispersion equation [Eq. (1) of Ref. 10]. If considerable vibronic structure were observed, the detailed fitting of the reflection curve could become extremely complex.

The foregoing remarks should not be construed as discounting

the value of classical dispersion analyses, but merely constitute an attempt to place them in context in comparison with the Kramers-Kronig method in regard to the derivation of absorption spectra. The two methods should be evaluated in each instance in the light of circumstances that surround, and the goals of, a given study.†

Possible Experimental Problems

In carrying out polarized reflection studies one must of course consider most of the experimental factors, such as the spectral purity and degree of polarization of the incident radiation, that are of importance in analogous absorptive work. Since most workers are reasonably cognizant of these more general aspects of spectroscopic technique, some of which will be treated below in the section on absorption spectrophotometry, those that will be emphasized at this point are more or less uniquely related to reflectivity measurements. It is worthy of note, however, that the two specific factors mentioned above often are in fact not so important in reflection as in direct absorption studies, since in the former case an increase in the absorption reveals itself as an increase, and not a decrease, in the signal.

When reflection measurements, which actually involve the study of the surface layers of a crystal, are expected to provide information concerning bulk optical properties, it is clearly required that the sample be free of surface defects and contamination which could cause the observed spectra to be unrepresentative of the true crystal reflectivity. A common difficulty in this regard is the formation of an amorphous layer on the surfaces of many organic crystals if the mother liquor that adheres to them on filtration is merely allowed to evaporate. The severity of this problem varies greatly from compound to compound, however, as is illustrated by the fact that it was not encountered at all in the case of auramine, while azobenzene crystals grown from petroleum ether and simply

† The dispersion approach has been applied also in the analysis of infrared reflectivities to give quantitative absorptive information.[30] Here again the spectra so analyzed present rather simple structural features.

filtered and allowed to dry yield reflection spectra more representative of a randomly oriented film than of the crystal itself.[31] These problems often may be overcome by an appropriate series of washings of the crystal designed to flush away the adhering mother liquor and material dissolved in it.

Another difficulty which has been encountered on occasion[18, 28, 31] and which is similar in nature to that described above is the time dependent decay of the crystal reflectivity associated with exposure of the crystal surface to radiation. This decay could have a number of causes, including various types of physical surface damage and randomization, as well as actual molecular photo-reactions. It appears to occur more commonly in crystals whose surfaces are subject to the amorphous surface layer described above, and on occasion has also been associated with the rise of what appear to be interference peaks in the reflectivity spectrum.

Another common occurrence in these studies is the observation of spurious peaks in the reflection spectra at the point, on the long wavelength side of the spectrum in the studies carried out here, where the crystal becomes non-absorbing. This phenomenon is not understood in complete detail, but is almost assuredly associated with part of the radiation that is transmitted through the crystal surface suffering some form of internal scattering† and reaching the detector as part of the signal that is taken as a measure of the reflected intensity. In absorbing regions one may expect that all the radiation that penetrates into these strong absorbers will essentially be absorbed totally within a very short path-length and thus the "back scattered" component will only be significant when the crystal becomes transparent. There is evidence that reflection from a parallel "back" face relatively close to that under study can make a substantial contribution to the effect.‡

Figure 8 shows a rather mild example of the results of this back-scattering in some of the spectra that have been obtained for BDP.

† Crystal emission and absorption studies provide independent evidence that internal scattering in these materials can be very appreciable.

‡ See, for instance, Ref. 10 and the example that follows.

Both sets of spectra were obtained on faces on which the long-axis (the polarization direction of the transition that gives rise to the reflection band of Fig. 8) of the molecule projects essentially fully on the R_{max} principal direction,[14] and thus one anticipates almost identical spectra in each case. This expectation is certainly fulfilled

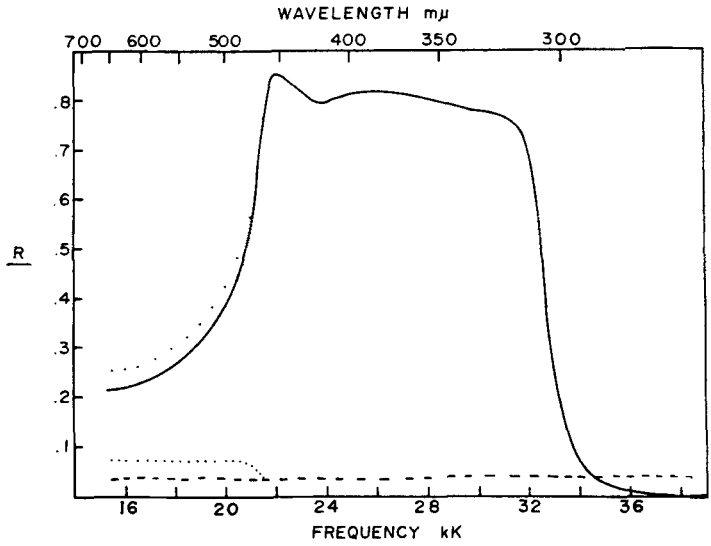


Figure 8. Reflection spectra of two faces of 1,5-*bis*-(dimethylamino)-pentamethinium perchlorate which should be essentially spectroscopically equivalent: (---) and (——) reflection spectra for what has been termed Face 3;[14] (....) reflection spectra for Face 1[14, 29] in regions where they differ from those for Face 3.

in the absorbing region, but as one moves to lower energies Face 1 shows a pronounced increase in its reflectivity relative to that of fact that these faces differ greatly in their relationship to the crystal morphology. In particular, the normal to Face 1 is parallel to the shortest crystal axis and this face has a parallel counterpart lying relatively close to it. Interestingly, the anomoly occurs even in the R_{min} direction of Face 1, which one would expect to be non-

absorbing,† and one can reduce the long wavelength portion of the Face 1 R_{max} curve to the corresponding Face 3 curve by subtracting the low energy "shelf" of the Face 1 R_{min} curve from it.

Visual analysis of the BDP curves or their discussion in terms of classical dispersion theory has not been greatly hampered by the anomalies illustrated in Fig. 8, but the effect varies greatly from compound to compound and crystal to crystal of the same compound, and on occasion it has seemed that a new transition has appeared in the solid.‡ Difficulties can arise, however, when one subjects data containing even the subtle errors shown in Fig. 8 to a Kramers-Kronig analysis, and in this instance such an analysis of the Face 1 R_{max} curve resulted in negative extinction coefficients on the low energy side of the absorption similar to those shown in Fig. 6. A similar analysis of the Face 3 data, however, led to a totally positive extinction curve whose integrated intensity compared very favorably with that which one expects on the basis of solution studies.[11]§ Thus, as one might expect, unreasonable Kramers-Kronig extinction coefficients may be a result of inaccurate reflection measurements as well as the use of data for a restricted spectral range, a point that has also been illustrated by the work of Philipp and Taft on the optical constants of diamond.[24]

Figure 8 also provides an example of one of the interesting solid state effects that have been encountered in these studies—"metallic reflection" from molecular crystals, in which an intense molecular band gives rise to an extended region of high reflectivity. This phenomenon will not be discussed in detail here,[32] but it should be observed that the correlation between the position of the reflection and the associated absorption that one often sees quoted

† It would appear that the absorption of the scattered component at shorter wavelengths arises here from a change in polarization on scattering and/or a small, but appreciable at these thicknesses, R_{min} absorption.

‡ When the sample is of appropriate thickness, interference peaks can also occur in these anomalous regions if an appreciable "back face" reflectance is involved.

§ No attempt was made to augment the experimental data with any approximation other than the straight-line extrapolation of the high and low energy regions on both faces.

—namely, that the reflection peaks to the low energy side of the absorption—breaks down for intense bands at the approximate point where metallic reflection sets in. A typical situation is illustrated by Fig. 9, which gives the reflection spectrum and derived optical constants for a highly absorbing direction of auramine. Comparison of Figs. 2 and 9 shows that in each instance the n-curve peaks to the red of the low energy absorption, as expected, but the R curve only peaks to the red of this absorption in the more weakly absorbing case.† It is thus clear that as the

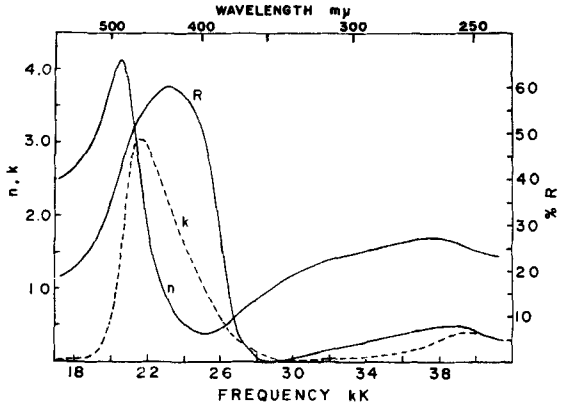


Figure 9. The optical constants obtained from a Kramers-Kronig analysis of the R_{max} curve of Fig. 5. The reflection curve (R) is also shown here.

absorption becomes stronger one may not, as may usually be done in situations such as are typified by Fig. 2, place the associated absorption at the approximate point where the reflection band has, on its high energy side, fallen to its half-height.‡

One aspect of the experiments that are discussed here that one might find troublesome is that the use of microscope objectives as focusing devices introduces convergency and thus one is not working at truly normal incidence. This might be considered

† Wood[9] discusses some of the difficulties associated with locating the position of the region of absorption by inspection of reflection spectra.

‡ It appears, however, that the location of this half-height is still a convenient and useful convention for positioning reflection bands.

disadvantageous from at least two points of view, in that (1) Fresnel's equation for normal incidence is used in the analysis of the spectra, and (2) the spectra obtained are usually discussed in terms of the molecular projections on the face in question. If one wishes to take an optimistic view, however, it may be pointed out that a convergent polarized beam consists of components polarized both in and perpendicular to the plane of incidence, and the effects of convergency on these components tend to cancel up to rather large angles of incidence.† One might thus expect the measurements made with convergent light to approximate the normal incident results so long as one did not use very strong convergency. The possible difficulties related to the anisotropic nature of the crystal, which is really the point of item (2), are more difficult to evaluate quantitatively, but are somewhat mitigated by the fact that over much of the spectrum the light is much less convergent within the crystal than without due to refractive effects. In any event, experiments carried out on auramine using lenses of various convergencies, and others in which the convergency was varied by the use of beam stops, indicated that, within the limits of the precision of our present studies, the effects of convergency are not significant. As an added precaution, however, it is common practice in our laboratories to operate with the smallest possible convergency, as regulated by appropriate beam stops, that is consistent with the desired light levels. Of course, when using microscopic techniques one should always be alert to possible effects of convergency and keep them in mind when evaluating any unusual features of the spectra obtained.

In concluding this section, it is probably well to note that, as in the case of absorption studies, one must be aware of the possibility that dispersion of principal directions may occur if these directions

† Bennett and Koehler[33] have shown the reflectivities of the two components for a series of handbook values of optical constants are almost identical up to an angle of incidence of 10° and their Fig. 10 illustrates the nature of the cancellation that one can expect at higher angles. Calculations carried out in these laboratories using optical constants typical of those encountered in the work described here lead one to similar conclusions. (F. K. Krist, private communication.)

are not determined in the face in question by the crystal symmetry involved. Although such variation of the principal directions with wavelength can be bothersome it can also lead to additional information or confirm conclusions already drawn from other evidence, as has also been illustrated by the auramine studies already reported.[10]

Absorption Studies

In many instances a combination of reflection and absorption studies is desirable, in that direct absorption can often permit one to confirm conclusions drawn from reflection spectra, and the availability of reflectivity data allows one to evaluate the correctness of absorption results. Moreover, absorption studies may lead to detail in the weakly absorbing regions that has been missed in reflection. An example of the interplay of the two techniques that may turn out to be typical of one of the more fruitful ways of applying reflection spectroscopy is provided by azobenzene.[31, 34] Here direct absorption studies have only been possible on one crystal face, but the crystal and molecular geometries are such that data from at least two faces are required for a unique assignment of the in-plane polarizations.[35] The resulting ambiguity has been resolved by examining the reflection spectra for several faces of the crystal and checking their analysis through a consideration of the results for the face for which direct absorption data are available. In addition to allowing one to make the desired polarization assignments, this study has also resulted in a great deal of additional detail becoming available concerning the nature of the azobenzene absorption spectra.

It has already been mentioned that the second microspectrophotometer described above has been designed to allow absorption studies to be carried out on very small specimens.† Even with the

† Instruments built around microscopes and designed to allow essentially the same type of absorption measurements made here have been described previously.[7, 36] A more detailed accounting of the instrument used in the work reported by Day *et al.* is intended. (A. J. Thomson, private communication.)

availability of such equipment, one of the most severe difficulties that arises here is, as has been pointed out above and by Stewart and Davidson[37] in connection with their elegant method of preparing thin crystal sections, the obtaining of suitable samples. Each substance studied presents a unique problem in this respect and thus any generalization is difficult, but the most simple and commonly applied methods of sample preparation for direct absorption work in our laboratories have involved melting the sample under pressure between two quartz plates or allowing a solution to evaporate directly on a quartz slide. The use of both these approaches is facilitated by the fact that the microspectrophotometer allows one to study areas of rather limited cross-section and to examine specimens visually in some detail in selecting an area for study.

In view of the problems illustrated by Fig. 1 it becomes clear that extreme care must be exercised in such measurements. The possible sources of error that one may encounter thus are of some interest, and although one cannot compile an exhaustive catalogue here, some of those that appear to be the most critical for high absorbers will be discussed. In light of the rather lengthy section on reflection that is included above, perhaps the most appropriate of such errors to mention first are those that may result from reflection losses. Figures 5 and 8 demonstrate that a considerable fraction of the incident radiation can be reflected and thus never enter the crystal, and in such cases a correction should be made. The actual significance of such corrections depends on the relative magnitudes of the optical densities and reflectivities involved, and their importance can often be estimated from a knowledgeable guess at the reflection to be expected in a given situation even if detailed measurements have not been made.

The spectra recorded in Fig. 1 indicate that the difficulties here involve both highly absorbing directions appearing more transparent than is actually the case and weakly absorbing directions being more opaque than they should. In highly dichroic crystals such effects can clearly result from failure to align the principal directions properly relative to the polarization vector of the incident light or from the failure of the incident radiation to have a sufficiently

high degree of polarization. It should also be noted, however, that a less obvious source of these effects is scattering within the crystal of initially highly polarized and properly aligned radiation resulting in its depolarization. In the study of quinhydrone single crystals,[17] for instance, it was found that if a large crystal was illuminated with radiation polarized along its highly absorbing direction, one could observe transmitted radiation even though the crystal was so thick as surely to be totally absorbing in this direction. Upon examination with polaroid this transmitted radiation was found to be polarized perpendicularly to its original direction. One means of evaluating and eliminating many of the practical consequences of this scattering for a highly absorbing direction is to take the spectra through a second polarizer, aligned parallel to the first and placed before the detector.

Another source of apparent transmission for a sample that should be totally absorbing is spectral impurity of the incident radiation. For example, an optical density of 3 implies that only 0.001 of the radiation originally entering the crystal is transmitted. If the fraction of the incident radiation that differs from the nominal wavelength and falls in a transmitting region is also of this magnitude, then clearly one will not be able to measure the true optical density.† The importance of this "impurity" radiation will depend strongly on the interaction of such details of the experimental situation as detector response, spectral distribution of the light source, and the nature of the absorption spectrum under study. When the possibility of such problems arises their importance may often be evaluated by obtaining spectra on samples of varying thicknesses and making quantitative comparisons of the relative optical densities within and between these spectra.

Most authors discussing microspectrophotometric work are careful to point out the importance of properly focusing the crystal image on the slit of the spectrograph or the diaphragm of the detector employed, but it would appear that it is at least equally

† If a considerable fraction of the light incident on the crystal is actually lost by reflection, then the impure component becomes an even more important limiting factor.

important to give consideration to the proper illumination of the crystal. Considering once again the studies carried out on quinhydrone, it was found that if one used a condenser image that was larger than the crystal, so that some of the incident radiation actually spilled around the crystal, a sample that was thick enough to be totally opaque would be visually observable and photometrically appear to be transmitting, even though a photomultiplier

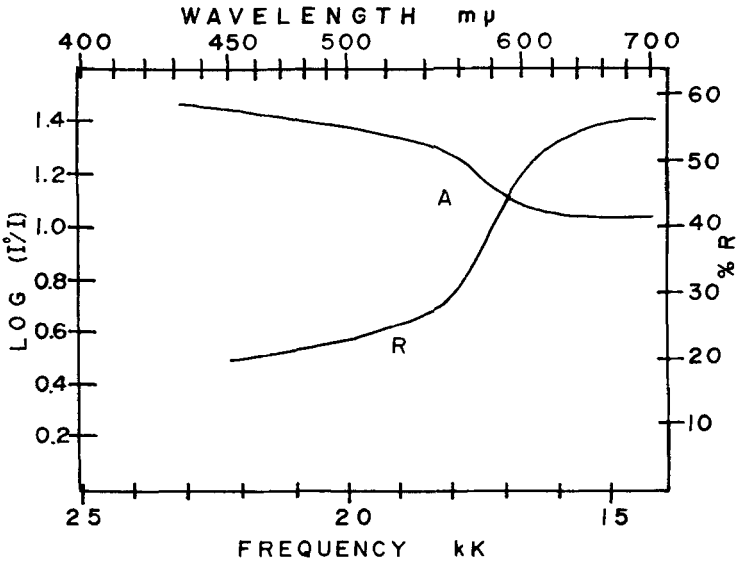


Figure 10. Reflection (R) and "absorption" (A) spectra for a copper bar 0.036 mm thick. The "absorption" spectrum is that obtained when the incident radiation is allowed to "spill around" the sample (see text).

tube iris was closed down so that the crystal image completely filled it. It appears that these observations are a consequence of the light that passes around the crystal striking the microscope objective, being reflected from it to the crystal, and hence through the objective to the detector. That such effects can make an appreciable contribution to the "transmitted" signal is demonstrated by Fig. 10, which shows the reflection spectrum for a flattened copper wire 0.036 mm thick and the apparent "absorption"

spectrum obtained when the incident radiation is allowed to spill around the sample, but the phototube iris is appropriately closed down. It will be observed that the "optical density" is strongly correlated with the reflectivity and falls noticeably in the region where the reflectivity increases. When properly illuminated, the bar is totally opaque, as it should be. It would thus appear that one can obtain spectra that are mixtures of reflection and absorption if one does not properly focus the beam on the crystal, place the sample on a pinhole, or otherwise avoid "spillage" around the crystal.

Concluding Remarks

As was mentioned in the introduction, this paper is not intended to be a complete discussion of all methods of studying the optical properties of highly absorbing solids, but deals rather exclusively with single crystal reflectivity and absorption. Since, however, the difficulties surrounding work in this area are such that one may raise questions about the results of studies involving almost any single mode of investigation, it would certainly seem advisable to attack each problem with a number of techniques in order to build up a set of mutually confirming and complementary data. Thus at least mention of some of the other methods currently available for gaining absorptive information regarding high absorbers is appropriate in this concluding section. This group of techniques includes diffuse reflection spectroscopy,[8] alkali halide pellet absorption spectroscopy,[1,4] and colloid absorption studies.[2,5] Although these methods lead to non-polarized results, the spectra thus obtained should in general be characteristic of the solid and interpretable in terms of any polarized single crystal data available. If any disparity arises, one or the other or both sets of results should be considered suspect until it is resolved.

"Stretched film" techniques[38] appear to provide a fruitful avenue to information on the anisotropic nature of molecular absorption which, although it may not be so detailed as that obtained from single crystal studies, can be free of crystal effects.

Thus one has a chance to evaluate the effects of crystal environment on the measured crystal dichroic ratios and, once again, would hope to be able to rationalize the supporting evidence, if one chooses to view it as such, in terms of the conclusions drawn from the crystal studies. (Photoselection methods[39] can of course play a similar role.)

The importance of this collateral evidence may be gathered from considering once again the NiDMG work outlined in the introduction. In this instance the spectra reported in the lower panel of Fig. 1 are thought to be essentially correct as a consequence of their being quantitatively confirmed by the absorption spectra of low-temperature colloidal suspensions and the Kramers-Kronig absorption curves obtained through analysis of the single crystal reflection spectra.[5] Moreover, a warning signal that the spectra shown in the top two panels of Fig. 1 are in fact not representative of the detailed crystal absorption is contained in the observation that these spectra differ markedly from those reported for KBr pellets containing NiDMG and for colloidal suspensions of NiDMG.† One in fact may conclude in both the NiDMG and the quinhydrone cases, simply by observing the crystal reflectivity visually through a piece of sheet polaroid, that the published absorption spectra grossly fail to depict the true dichroism.

It should have become clear in the course of this discussion that the study of a substance, or a series of substances, by the techniques outlined here is a major undertaking if it is to be done thoroughly. Equally clear, however, is the fact that experimental data that are not completely correct, especially in an area such as this where anything approaching "exact" theoretical work is still far from being achieved, can easily be misleading and result in considerable wasted effort on the part of other workers, while well-characterized results for carefully selected compounds can form a sound basis for further experimental and theoretical work. The effort involved in obtaining truly representative data for these high absorbers is thus generally well rewarded.

† These differences have been noted previously,[1,2] but it appears their true significance has not been comprehended.

Acknowledgement

The references and citations included in this paper indicate the author's indebtedness to the students who have collaborated with him, and are presently doing so, for very substantial contributions to this research program. I should especially like to acknowledge the efforts of my first group of graduate students, who did much to bring our laboratory into being. These include Drs. A. V. Fratini, S. C. Neely, L. J. Parkhurst, and Mr. F. K. Krist. In addition to the work reported here that has already been specifically noted as being connected with their efforts, Dr. Fratini did much of the developmental work on our first microspectrophotometer, and Dr. Parkhurst had a similar role with respect to our second instrument and also collected data on and evaluated many of the possible sources of error that can arise in these studies. Figures 2–7 and 9 are from the thesis of Dr. Fratini, Fig. 8 from that of Dr. Neely, and Fig. 10 from that of Dr. Parkhurst.

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