

Infrared Spectroscopy at High Pressures: Polarized Spectra of Single Crystals of Acetonitrile

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Single crystals of three polymorphs of acetonitrile and acetonitrile- d_3 have been grown under pressure in a diamond anvil cell. While still under pressure polarized mid-infrared spectra of these three single crystals have been obtained. In addition, low temperature far-infrared spectra have been recorded for polycrystals of two of the polymorphs. These data have been used to predict likely crystal structures for the three crystalline phases.

Introduction

One of the advantages of the commercially available diamond-window high pressure cell is the ease and speed of growing single crystals. Using pressure to grow such single crystals means that the sample can be monitored under a microscope for possible phase changes, and ir spectra can be obtained at any point in the pressurization process. Because of these advantages we are now engaged in a continuing study of the polarized ir spectra of single crystals of organic molecules. Acetonitrile is one such molecule and was selected because we wanted to determine if the strong dipole in acetonitrile affected orientation in the crystal structure.

Background

Vapor and liquid spectra of acetonitrile and acetonitrile- d_3 have been reported by several authors.¹⁻⁸ As a result of these investigations, all of the fundamentals of acetonitrile have been satisfactorily assigned with the exception of $\delta_a\text{CH}_3$, the CH_3 degenerate deformation. Two absorption bands were observed between 1400 cm^{-1} and 1500 cm^{-1} and the various authors¹⁻³ do not agree as to which band was $\delta_a\text{CH}_3$ and which was a combination band. Milligan and Jacox⁹ obtained the solid state spectrum (low temperature) of

both acetonitrile and acetonitrile- d_3 in hope of clarifying this point. However, they conclude that coupling through Fermi resonance makes it impossible to give a definite assignment for $\delta_a\text{CH}_3$. In addition they concluded that the ir multiplet structure of CH_3CN and CD_3CN in the solid phase indicated that the molecules had to crystallize in the orthorhombic, tetragonal, or trigonal systems.

Pace and Noe¹⁰ also studied the solid state polycrystal spectra (low temperature) of acetonitrile and acetonitrile- d_3 . They concluded that acetonitrile exists in two (α and β) polymorphic forms. They obtained powder x-ray data on one form at liquid nitrogen temperatures and from this they concluded that the α form of acetonitrile is a primitive orthorhombic crystal with eight molecules per unit cell. Coupled with the observed ir multiplet structure (which differed from that observed by Milligan and Jacox⁹), they conclude that the α form of acetonitrile had either a D_{2h} or D_{2d} space group.

Experimental

The technique for growing a single crystal in the diamond-window high pressure cell has been described previously¹¹ and will only be briefly mentioned here. Liquid acetonitrile is sealed in the pressure cell between a metal gasket and the diamond anvils. Pressure is increased on the sample until solidification to a polycrystal occurs. The pressure is then decreased until only one seed crystal remains at which point the pressure is slowly increased until the single crystal is fully grown. Acetonitrile is one of the more difficult single crystals to grow, but even so the entire process only took about 1 hr. We are not concerned in this work with the exact pressures involved, but we can estimate that the single crystal is fully grown at 20-30 kbar. As the pressure is

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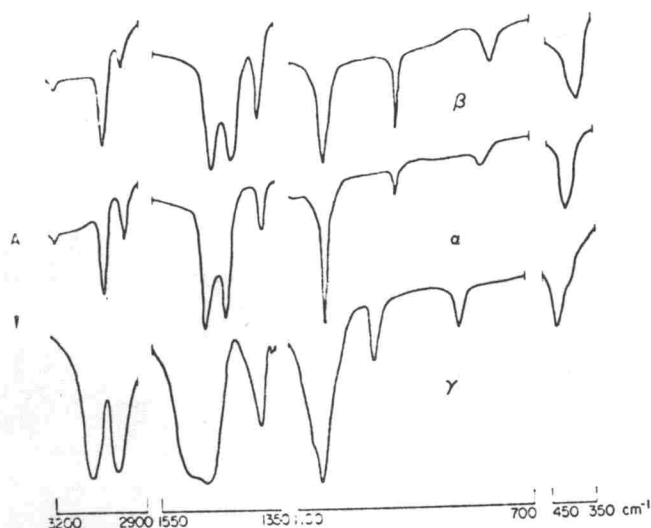


Fig. 1. Infrared spectra of single crystals of β , α , and γ forms of CH_3CN . No polarization.

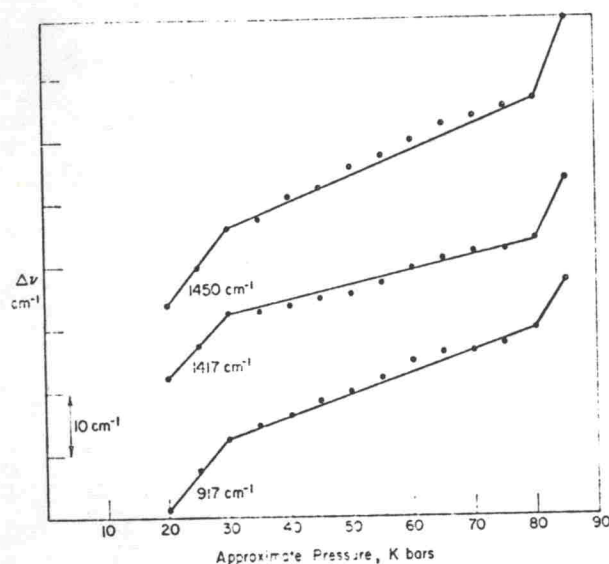


Fig. 2. Pressure vs frequency, CH_3CN .

increased on this sample, a single crystal-single crystal phase transformation takes place near 30 kbar. This phase change cannot be mistaken when viewed under a microscope. The spectra of the two phases (Fig. 1) are quite similar, but the existence of different polymorphs was even more definitely established when it was demonstrated (to be discussed later) that we could obtain spectra of two crystal faces of each polymorph.

Single crystals of the third polymorph are produced by increasing the pressure on the single crystal of the second polymorph. Near the extreme upper limit (~ 80 kbar) of our pressure range, striations appear in the crystal. This slight physical change is similar to that observed for the transition to the high pressure phase of benzene. This benzene transition has been

definitely established by x-ray data.¹² For acetonitrile the presence of a third crystalline phase can be established by the drastic spectral changes (Fig. 1) and by the change in slope of the pressure vs frequency curve (Fig. 2) at the phase transition point. At a low pressure, phase 1 (β form) changes to phase 2 (α form) which is stable over a considerable pressure range. It is only at high pressure that phase 3 (γ form) appears. The presence of a third polymorph has not been reported in any previous study.

Previously we mentioned that we had obtained spectra on two crystal faces of each polymorph. Different faces are obtained by simply melting the crystal and repeating the growing process while attempting to select a seed crystal of different physical appearance. This random process eventually will produce a crystal with a different crystal face perpendicular to the incident radiation of the spectrophotometer. This can be seen in Figs. 3 and 4 that show the polarized spectra of two crystal faces of the β crystal of acetonitrile. Figures 5 and 6 show the similar spectra for the γ crystal. The polarized spectra of two faces of the α crystal are not shown since the polarization effects here are identical to those seen for the β crystal. The polarized spectra of the β form of CD_3CN are shown in Figs. 7 and 8.* Infrared spectra were obtained for the α and γ

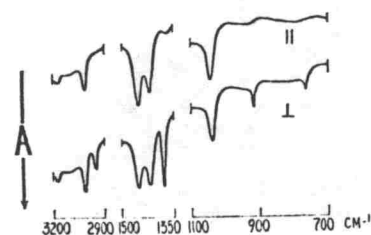


Fig. 3. Polarized ir spectra of a single crystal of the β form of CH_3CN (xz or yz crystal face perpendicular to the incident radiation). In this and Figs. 4-12, parallel ($\parallel$) and perpendicular ($\perp$) refer to the direction of the electric vector of the polarized radiation with respect to one of the crystal axes.

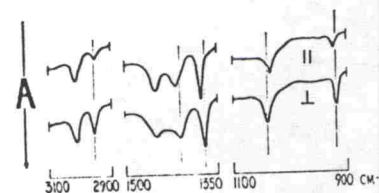


Fig. 4. Polarized ir spectra of a single crystal of the β form of CH_3CN (xy crystal face perpendicular to the incident radiation).

* For CD_3CN , the only absorption bands above 1250 cm^{-1} are the CD and CN stretching frequencies. These vibrations have frequencies near 2200 cm^{-1} , a region that is masked by diamond window absorption.

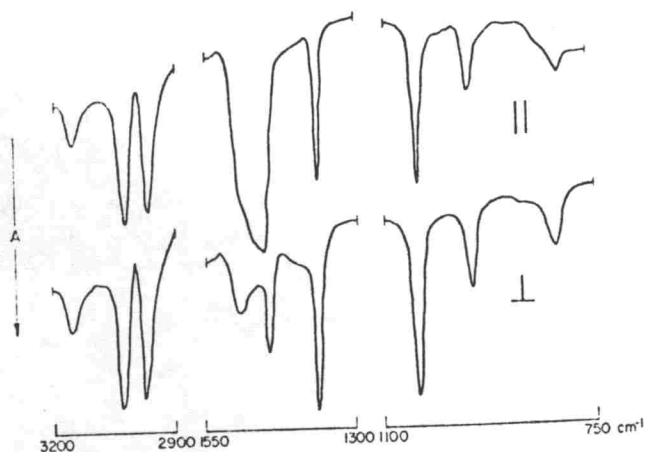


Fig. 5. Polarized ir spectra of a single crystal of the γ form of CH_3CN .

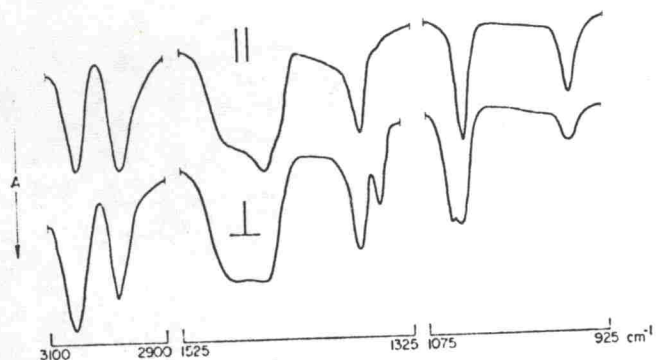


Fig. 6. Polarized ir spectra of a single crystal of the γ form of CH_3CN (second crystal face).

forms of CD_3CN on only one crystal face and are not shown here.

The samples of acetonitrile and acetonitrile- d_3 were commercial products used without further purification. The mid-infrared spectra were obtained on a Perkin-Elmer Model 521 spectrophotometer with the diamond cell mounted in a 6X beam condenser. Because of diamond window absorption, ν_{CN} , the CN stretching vibration near 2250 cm^{-1} could not be observed in the pressure measurements. A wire grid polarizer was used for the polarized spectra. The far-infrared spectra were obtained on a Perkin-Elmer Model 301 spectrophotometer using a dewar-type low temperature cell.

Results

The observed frequencies for CH_3CN and CD_3CN are listed in Tables I and II, respectively. We label the first two crystalline phases β and α , because the frequencies of the observed bands and the frequency shifts between the spectra of the two polymorphs agree roughly with those found by Pace and Noe.¹⁰ Therefore we adopt their notation for each crystalline phase. Further confirmation that we are seeing the same two phases as Pace and Noe comes from comparison of the

temperature and pressure behavior of the two crystals. Pace and Noe found that the β phase existed over only a short temperature range before changing to the α phase which was stable over a long temperature range. In Fig. 2, it can be seen that the β form only exists in a short pressure range while the α form exists over a wide pressure range.

Pace and Noe¹⁰ obtained ir spectra of the α form of acetonitrile at three temperatures: -65°C , -115°C , and -192°C . The spectrum obtained at -192°C is quite different from those run at -65°C and -115°C . At the two higher temperatures, half of the fundamentals are singlets and half are doublets. At -192°C , one fundamental is a quartet and four are triplets. The triplet splitting is quite similar to what we observe in the polarized spectra of the γ form. Thus we believe that there is a phase change between -115°C and -192°C and the spectrum at -192°C is really of the γ phase rather than the α form. This is quite important for the only x-ray data¹⁰ available was taken at -196°C and will be of the same form.

The polarized spectra of Figs. 3, 4, 7, and 8 (β form) and the frequencies of Tables I and II confirm the arguments of Milligan and Jacox⁹ concerning the assign-

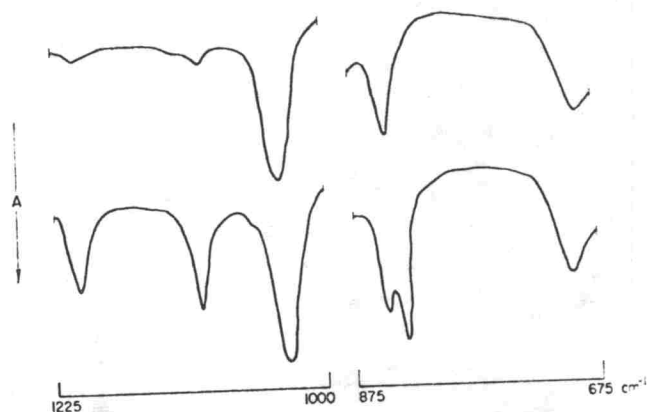


Fig. 7. Polarized ir spectra of a single crystal of the β form of CD_3CN .

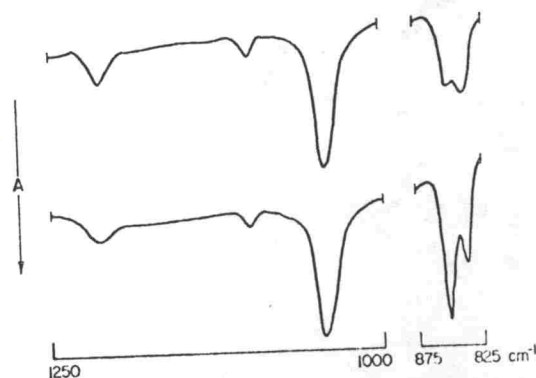


Fig. 8. Polarized ir spectra of a single crystal of the β form of CD_3CN (second crystal face).

Table I. Observed Frequencies for CH₃CN Single Crystals

<i>D</i>	Mode	β	α	γ
$B_{1g} - B_{2g}$	$\nu_{CC} + \nu_{CN}$	3178	3180	3235
B_{1g}		3016	3016	3061
B_{2g}		3013	3014	3054
B_{2g}	ν_a CH	3011	—	3052
B_{2g}		2956	2950	2985
B_{1g}	ν_s CH	2954	2948	2980
				2975
B_{1g}		1453	1461	1491
B_{2g}	δ CCN + r CH ₃	1451	1459	1483
B_{1g}		1419	1428	1456
B_{1g}		1416	1426	1443
B_{2g}	δ_a CH ₃	1412	1423	
B_{1g}		1376	1370	1370
B_{2g}	δ_s CH ₃	1369	1368	1368
				1364
B_{2g}		1045	1042	1054
B_{2g}		1043	1040	1047
B_{1g}	r CH ₃	1038	1039	1044
B_{1g}		920	926	960
B_{2g}	ν_{CC}	919	926	958
				955
B_{1g}	2 (δ CCN)	769	780	815
				810
B_{1g}		—	402	—
B_{1g}	δ CCN ^a	—	392	—

^a Polarized spectra obtained on only one crystal face.

ment of the bands in the 1400-cm⁻¹ region of the spectra. In CD₃CN, the combination band (1200 cm⁻¹, should be free of Fermi resonance coupling with δ_s CD₃ (1010 cm⁻¹). Based on the C_{3v} molecular symmetry, the combination band should be split into an A_1 and E component. We appear to be observing the A_1 component because no matter what crystal face we observe there is some direction of the polarizer which brings about complete extinction of the 1200-cm⁻¹ band. Such polarization behavior has not been observed for either of the two bands in the 1400–1450-cm⁻¹ region of CH₃CN. These differences can only be explained by a coupling through Fermi resonance of δ_s CH₃ and the combination band (δ CCN and r CH₃) leading to mixed modes for both the 1450-cm⁻¹ and 1420-cm⁻¹ absorptions.

Discussion of Crystal Structure

As can be seen in Figs. 3 and 4 and Tables I and II each vibrational mode of the β and α forms of CH₃CN is polarized into either a doublet or a triplet. Based on the molecular symmetry (C_{3v}) each A_1 mode is split into a doublet in the crystal spectra and each E mode into a triplet. All the factor groups which will give such splitting require a C_3 site group. Combining the splitting requirement with attempts to construct a unit cell of acetonitrile of the proper symmetry limit the factor group possibilities to C_{2v} , C_{3v} , D_{2d} , and D_2 . The far-

infrared frequencies for polycrystalline CH₃CN and CD₃CN are listed in Table III. The ratio of the frequency of CH₃CN to the frequency of CD₃CN can be used to identify the lattice modes as rotational or translational. This is also shown in Table III. The only reason we can visualize for not observing the weak high frequency bands (near 135 cm⁻¹ in CH₃CN) in the deuterated molecule is that they have shifted far enough to be hidden by the very strong bands near 115 cm⁻¹. If this is true these modes are also rotational modes. Three or possibly four lattice frequencies have been observed for both the α and β forms of CH₃CN. The predicted number of ir active lattice frequencies for the possible factor groups is six except for the D_2 factor group which should show fifteen lattice frequencies. While it is possible that two or three lattice modes could have frequencies below the 45-cm⁻¹ limit of our spectrophotometer, it is not possible that there are eleven or twelve frequencies below 50 cm⁻¹. Thus the possible factor groups are limited to C_{2v} , C_{3v} , and D_{2d} .

At this point, selection of a factor group must rely on chemical intuition rather than spectroscopic facts. Not only is the polarization behavior identical between the α and β forms of acetonitrile, but the frequency differences between the two forms are remarkably small. If we take spectra just before and right after the α to β phase change (at nearly equal pressures or tempera-

Table II. Observed Frequencies for CD₃CN Single Crystals

<i>D_{2d}</i>	Mode	β	α^a	γ^a
B_{3u}		1210	1222	1233
B_{2u}	δ CCN + r CD ₃	1205		
B_{2u}		1102	1105	1115
B_{3u}	δ_s CD ₃	1099		
B_{1u}		1044	1049	1054
B_{3u}		1038	1037	1051
B_{2u}	δ_a CD ₃	1034		
B_{2u}		850	853	877
B_{3u}	r CD ₃	846	852	872
B_{1u}		842		
B_{2u}		836	843	872
B_{3u}	ν_{CC}	834		
B_{2u}	2 (δ CCN)	692	711	—

^a Polarized spectra obtained on only one crystal face.

Table III. Observed Frequencies for CH₃CN and CD₃CN Polycrystals (~ -120°C)

CH ₃ CN		CD ₃ CN		CH ₃ -CN/CD ₃ -CN		Type
β	α	β	α	β	α	
134	139	—	—			<i>R</i>
116	119	112	117	1.04	1.02	<i>T</i>
73	87	62	77	1.18	1.13	<i>R</i>
50	50	50	50	1.00	1.00	<i>T</i>

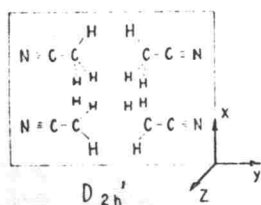


Fig. 9. Proposed crystal structure for the β form of CH_3CN .

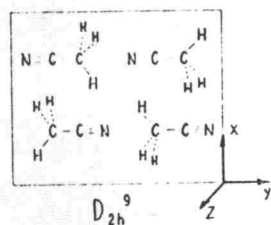


Fig. 10. Proposed crystal structure for the α form of CH_3CN . Actual crystal has eight molecules per unit cell with a plane of four molecules identical to the four shown in the figure. This second plane of four molecules is parallel to the first plane, either above it or below it.

tures) we find that only the 1420-cm^{-1} and 1370-cm^{-1} bands show significant ($>5\text{ cm}^{-1}$) frequency differences. This would seemingly indicate a minimum change in intermolecular forces as a result of the phase change. The easiest way to do this is for the phase change to be between different space groups of the same factor group (i.e., $D_{2h}^1 \leftrightarrow D_{2h}^9$) rather than between different factor groups (i.e., the two molecules of a C_{2v} unit cell going to the three molecules of a C_{3h} unit cell). However we cannot construct two crystal structures in the same factor group for any factor group but D_{2h} . The two proposed structures are shown in Figs. 9 and 10. The D_{2h}^1 crystal only requires four molecules per unit cell, but the D_{2h}^9 crystal requires eight molecules per unit cell in order to have D_{2h} symmetry. Only four molecules are shown in Fig. 10. A similar layer of four molecules is above or below the first layer and parallel to it. Transition from D_{2h}^9 to D_{2h}^1 only requires a rotation of half of the molecules in the unit cell. It is interesting to note (Table III) that the rotational lattice modes show a large frequency difference between the β and α crystals, while the translational lattice modes do not show much of a difference. Figure 11 shows the correlation diagram of a CH_3CN crystal of D_{2h} symmetry. Here it can be seen that each A_1 vibration splits into a doublet in the crystal and each E vibration into a triplet. Figure 12 shows that the direction of the transition moments of the vibrations of a D_{2h} factor group will be along the x , y , or z axis. Thus it can be deduced that in Fig. 3 we are either looking at the xz or yz crystal face and in Fig. 4 we are looking at the xy crystal face.

Therefore we feel that the α and β forms of acetonitrile are likely to have a D_{2h}^1 or D_{2h}^9 space group.

From a comparison of the two crystal structures it seems as if the CH vibrations would be less sterically hindered for vibrations of the D_{2h}^9 space group than for vibrations of the D_{2h}^1 space group. Also it can be predicted that increasing pressure would bring about bigger frequency shifts (Fig. 2) for D_{2h}^1 vibrations than for D_{2h}^9 modes. These last two statements suggest that the α crystal has a D_{2h}^9 space group while the D_{2h}^1 space group fits the β crystal.

For the δ crystal little can be said about the factor group. The splitting of both A_1 and E vibrations into three components means that the site symmetry has to be lowered from C_s to C_1 . With a C_1 site symmetry almost any factor group is possible. However, remember that the low temperature (-192°C) spectrum obtained by Pace and Noe also shows splitting into a triplet except for one band which shows four components. This fourth component could be explained as a combination band leaving only triplets. Then the low temperature spectrum is the same as our high pressure spectrum of the γ form. Pace and Noe¹⁰ also obtained x-ray powder data on CH_3CN crystals at -196°C and found this form to be a primitive orthorhombic crystal with eight molecules per unit cell. Assuming this is the γ crystal means that the factor group is limited to C_{2v} , D_2 , or D_{2h} . With the present data we have no means of limiting the factor group any further.

Conclusions

While we cannot definitely establish the crystal structures of CH_3CN , likely structures have been proposed for two of the polymorphs and limitations have been placed on the crystal structure of the third polymorph. None of the proposed structures positions the dipole of

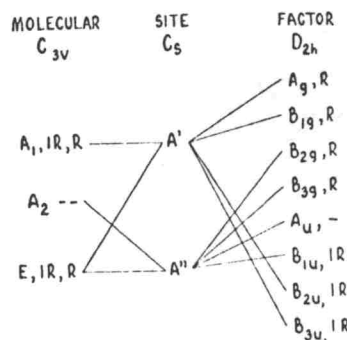


Fig. 11. CH_3CN correlation diagram.

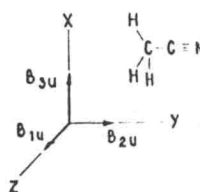


Fig. 12. Direction of transition moments for a D_{2h} crystal.

the C₂N group in a fashion that allows complexing to a dimer (or higher polymer) as has been proposed for liquid nitriles. Thus any orientational effects that exist in the liquid do not appear to carry over to the solid.

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Books continued from page 16

Introduction to Fourier Optics. By JOSEPH W. GOODMAN. McGraw-Hill Book Company, New York, 1968. 287 pp. \$13.50.

Principles of Holography. By HOWARD M. SMITH. Wiley-Interscience, New York, 1969. 239 pp. \$9.95.

Two recent books, one by Goodman and one by Smith, deal with that part of modern optics associated with optical processing and holography. They both rely on the use of spatial Fourier transforms in the description of optical fields. To a certain extent, the books tend to complement each other and it thus seems appropriate to review the books together, even though a review of Goodman has already appeared—see *Appl. Opt.* **8**, 1148 (1969).

Introduction to Fourier Optics is an excellent textbook. The reviewer used the book as a text in a graduate course during the spring of 1969 and it was very well received by the students in the course. After a brief introductory chapter, the second chapter deals with the analysis of two-dimensional linear systems. Although the book is specifically directed toward persons with electrical engineering backgrounds, it should not be limited to such people. In using the book with a cross section of engineering students, this reviewer found that some review of one-dimensional Fourier analysis was useful when studying Chap. 2. However, this poses no real problem in using the book. Two appendices in the book deal with Dirac delta functions and the derivation of several Fourier transform theorems.

Chapter 3 is devoted to the foundations of scalar diffraction theory. The Helmholtz equation is solved using Green's theorem. The derivation of the Fresnel-Kirchhoff diffraction formula using a free-space Green's function and the derivation of the Rayleigh-Sommerfeld diffraction formula using an alternate "self-consistent" Green's function are both carried out in detail. A generalization of the Rayleigh-Sommerfeld theory to nonmonochromatic waves and a treatment of diffraction in terms of an angular spectrum of plane waves are also included in Chap. 3. In Chap. 4 the Fresnel and Fraunhofer approximations are applied to the diffraction integrals and a number of Fraunhofer diffraction patterns are calculated using the two-dimensional Fourier transform techniques of Chap. 2.

Chapters 5 and 6 form the heart of the book and deal with the diffraction theory of image formation. The Fourier transforming properties of lenses are derived in Chap. 5. Although several configurations are considered they all involve plane wave illumination. While this is the simplest to consider theoretically, spherical wave illumination is often used experimentally and some discussion of this case would improve this chapter. Image formation with monochromatic illumination is also discussed in Chap. 5,

and an impulse response is derived as the Fourier transform of the pupil function. Chapter 6 is devoted to the frequency analysis of optical imaging systems. The coherent transfer function is derived and its relationship to the optical transfer function of an incoherent imaging system is carefully developed. The general treatment of nonmonochromatic illumination may seem unsatisfactory to some students. While one is certainly sympathetic to the problems associated with taking "a rather long detour through the theory of partial coherence" the insight gained by showing coherent and incoherent illumination as limiting cases of the propagation of mutual intensity might make a modest effort along these lines worthwhile. Another possible source of confusion in Chap. 6 arises from the fact that the cut-off frequency for coherent illumination is referred to the image plane. Thus in a system with magnification, this number would not be the maximum spatial frequency of the object which is transmitted by the system.

Chapters 7 and 8 deal with applications and make up the last half of the book. Spatial filtering and optical information processing are discussed in Chap. 7 using the Fourier transform methods developed in the earlier chapters. Topics covered in this chapter include photographic film characteristics, incoherent and coherent processing systems, complex spatial filtering and matched filtering, and synthetic-aperture radar data processing. Chapter 8 is devoted to holography. Both the Gabor and the Leith-Upatnieks holograms are described using the ideas of spatial frequency spectra. The effects of film characteristics, nonlinearities, and emulsion thickness are discussed along with generalizations to incoherent light and moving objects.

Goodman's book can be highly recommended as a text for a course in Fourier optics. There is an average of about ten problems at the end of each chapter, many of which are challenging and effective.

Principles of Holography by H. M. Smith is a different type of book from Goodman's. It is more of a monograph whose main purpose "is to present a unified and complete treatment (of holography) under one cover." The book is not written as a text—there are no problems—and it would be difficult to use the book as the basis for an introductory course in the field. As the author states in the preface "it is assumed that the reader has a knowledge of several aspects of optics, such as modulation transfer functions, spatial frequency, phase, coherence, diffraction, and so on." Goodman's book goes a long way toward providing this background.

Smith attempts to bring order out of the chaos in the holography literature up through 1968. To a large extent he has succeeded although the goal of a complete treatment is virtually impossible in such a rapidly growing field. The first two chapters

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