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LIPP ER61 0248

DEC 2 1966

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Microtechnique for the Infrared Study of Solids

Diamonds and Sapphires as Cell Materials

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▶ A microtechnique for obtaining the infrared spectra of solids and corrosive liquids, utilizing sample weights as low as 4 μg., is described. A cell in which diamonds or sapphires are used as window material is employed to obtain spectra in the 2- to 35-micron region. The visible and ultraviolet regions can also be studied. Spectra are obtained routinely, easily, and rapidly without many of the limitations inherent in other procedures. So far as is known, the method is applicable to all solids.

ALTHOUGH the infrared spectra of liquids and gases may be obtained by simple methods, recording the spectra of solids is sometimes difficult. Solids may be studied by several techniques, with the nature of the specimen generally suggesting the applicable method. However, each particular method has various disadvantages, either with respect to sample handling techniques or to the quality of the spectrum obtained. Accordingly, it is desirable to supplement the available techniques for solids with new ones that may increase the number and type of solid samples capable of being studied in the infrared region.

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A cell utilizing diamond or sapphire windows has been used to obtain the spectra of a wide variety of solids in the 2- to 35-micron region. As far as is known, the cell may be used in a routine manner to study infrared spectra of all solids. The method is essentially a microtechnique giving spectra on specimens weighing as little as 4 μg. (4×10^{-6} gram). The same cell can be used throughout the visible and ultraviolet regions on solids and extremely corrosive liquids in a routine manner. The cell was initially designed to study the effect of high pressures on solids (*61*), but the ease of obtaining spectra on solid specimens led to the investigation of its use as a routine method for the study of solids. The disadvantages and advantages of this technique are compared with those of other methods.

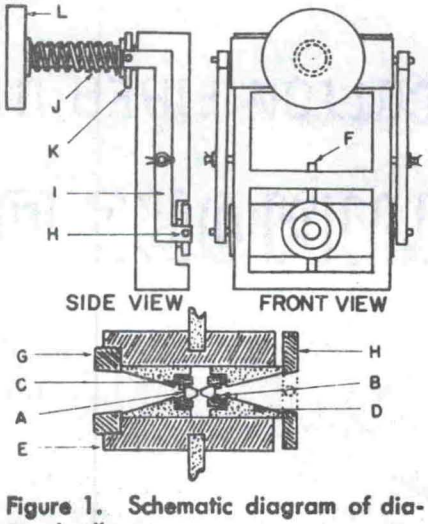


Figure 1. Schematic diagram of diamond cell

A. Diamonds or sapphires
B. Brass disk
C. Washer
D. Steel piston
E. Bearing
F. Pivot
G. Thrust bearing
H. Pivoted pressure plate
I. Lever arm
J. Calibrated spring
K. Thrust plate
L. Screw

DESCRIPTION OF CELL

The apparatus used is shown in Figure 1. Two gem-cut Type II diamonds, *A*, comprise the infrared cell proper. The culets of each diamond are ground and polished to form small irregular octagonal flat surfaces parallel to the tables. The specimen is squeezed into a thin film between these small surfaces, which have areas varying between 10^{-4} and 10^{-2} sq. inch. To eliminate axial alignment problems two diamonds having markedly different surface areas are used. Each diamond is seated on its tabular face over a small hole in a [illegible] disk *B*.

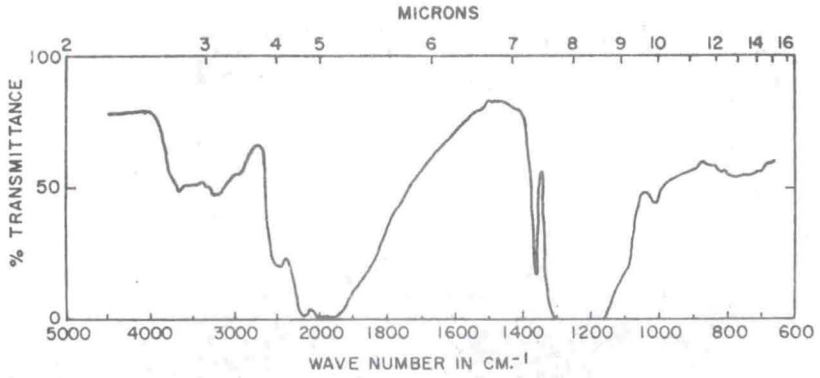


Figure 2. Infrared spectrum of typical Type I diamond, $^3/_{32}$ inch thick

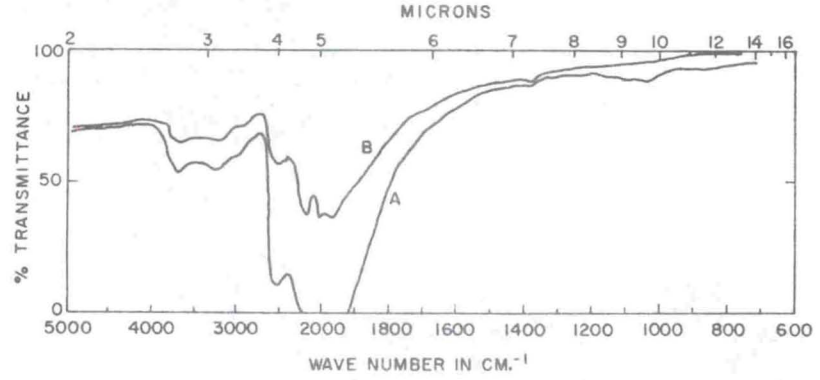


Figure 3. Infrared spectra

A. Typical Type II diamond, $^3/_{32}$ inch thick
B. Thin Type II diamond, 1 mm. thick

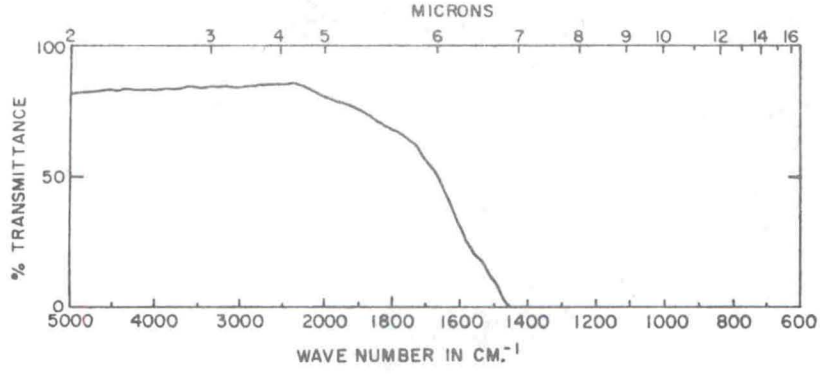


Figure 4. Infrared spectrum of sapphire, 1 mm. thick

suitable recess in a stainless steel piston, *D*. The somewhat flexible mount using rubber washers is designed to permit some alignment motion of the diamond surfaces. The stainless steel pistons are bored with a tapering hole extending to the brass seat. The taper is designed to permit acceptance of the maximum flux from a cone of radiation which passes through both pistons, both diamonds, and the specimen film between the diamond surfaces. The specimen itself is located at the focus of the beam.

The two pistons slide in a close-fitting brass bearing, *E*, which is pivoted to permit free rotation about a vertical axis. The pivots, *F*, are located in the framework carrying the pressure-generating equipment. One piston is restrained by a thrust bearing, *G*, which screws into one end of the brass bearing. At the other end of the bearing a pivoted pressure plate, *H*, bears against the exposed end of the second piston. The pivots of the presser plate are set in one end of the lever arms and permit free rotation of the plate about a horizontal axis. These two sets of pivots form a universal joint, ensuring that the stress applied by the presser plate is always directed along the axis of the pistons. The presser plate is bored out to permit entry of the radiation into the rear piston. The lever arms, *I*, are actuated by a calibrated spring, *J*, bearing against a thrust plate, *K*, which is pivoted into the upper ends of the levers. This spring is compressed by a manually operated screw, *L*. The whole unit is designed to be mounted in a commercial infrared beam condensing unit and the functional parts of the cell are only 1 inch thick to fit into the restricted focal area of the lens system.

CELL MATERIALS

Figures 2 and 3 compare the infrared spectrum of a Type I diamond with that of a Type II diamond. In the thicknesses used in our work (approximately $^1/_4$ inch) both types of diamonds show intense absorption in the 4- to 5-micron region with weaker absorption in the 3-micron region. The Type I diamond shows additional strong absorption in the 7- to 10-micron region. Both types of diamonds are transparent in the 15- to 35-micron region. For use as infrared window material the Type II diamond is required, since it is transparent in the important "fingerprint" region of the spectrum. The absorption in the 4- to 5-micron region is undesirable, but fortunately, there are relatively few characteristic group frequencies in this region. The use of thinner diamond windows (1 mm. or less) makes this region partially transparent and spectra can be obtained if care is taken to subtract the diamond absorption (Figure 3). To obtain spectra routinely in this region, the diamond windows were replaced by sapphire windows. The infrared spectrum of a 1-mm. sapphire window is given in Figure 4. Through the use of these two window materials, the spectrum of any solid may be recorded from 2 to 35 microns. The distinction between Type I and Type II diamonds is not always as definite as implied by Figures 2 and 3, in that diamond specimens of intermediate type are known corresponding to varying amounts of absorption in the 7- to 10-micron region. The cause of the different types of absorption in this region is not definitely known (*13*).

The procedures used for grinding the diamond surfaces have been described (*61*). A similar technique was used to grind and polish the sapphire windows.

INFRARED EQUIPMENT

A commercial double-beam infrared spectrophotometer equipped with NaCl and CsBr interchange units and a KBr lens beam condensing system was used in the 1- to 25-micron region. The useful range of the equipment was extended to 35 microns by replacing the KBr lenses in the beam condensing system with KRS-5 (TlBr-TlI) lenses. Since the aperture of the hole at the base of the diamond was approximately 2 mm. in diameter, essentially the full width of the focused slit was used, but only a portion of the slit length was accepted by the cell because of the loss in a[illegible]tion of the

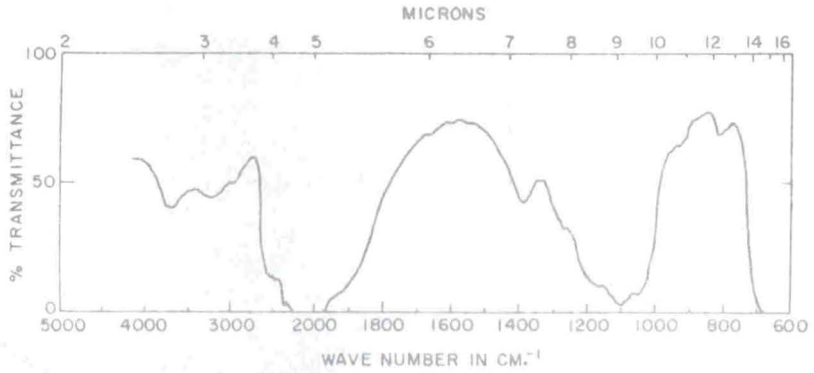


Figure 5. Infrared spectrum of cubic boron nitride

reference beam was needed so that the full scale of the instrument could be used. This was accomplished by a wire screen or a perforated sheet of aluminum. The limited amount of energy available made slow scanning speeds desirable. These were usually 0.5 or 0.2 micron per minute. The instrument settings used were: time constant 2, gain 5%, of maximum; slit 2 or 3 times standard.

SAMPLE-HANDLING TECHNIQUE

When the diamond cell is used, sample handling is very simple. No preliminary work need be done.

One of the pistons is inserted in the bearing with the unit in a horizontal position and a small quantity of the substance to be studied is placed on the diamond with a small spatula. An excess of sample on the diamond surface is usually not a problem, because any excess is readily extruded from between the diamond surfaces. The second piston is inserted and hand pressure is applied to form an even film. The thrust plate is then screwed into place and the pressure is raised to a few thousand atmospheres to obtain a clear film. Before the spectrum is recorded, the pressure is decreased to the lowest value consistent with maintaining a clear film. In practice the minimum pressure required is in the range of 1 to 100 atm. The cell is placed at the focal point of the lens system and its position adjusted in the beam to produce a maximum transmittance in a spectral region containing no strong bands.

The total amount of sample required depends on the skill of the operator in placing the material on the diamond. One-half milligram is usually more than enough, and 10 μg. (10^{-2} mg.) or less of material can be utilized by careful handling.

If absorption is too great for a given specimen, the sample may be diluted with LiF or KBr. For quantitative analysis the sample may be mixed and ground with a known weight of a suitable substance that has known absorption bands to serve as an internal standard.

Sample quantities on the order of 10 μg. require special handling. In experiments described below a hypodermic needle was employed to transfer the sample. This needle had a barbed tip which made it possible to pick up a crystal by pressing gently on the crystal with the barbed point. If a crystal could not be picked up by this method, it was scooped up with the tip of the needle.

The small crystal was transferred directly to the balance pan of a microbalance. The weight was recorded and the sample was transferred to a small Petri dish for temporary storage. The crystal was then transferred onto the diamond in the piston which was inside the bearing. The second piston was inserted gently and rotated with respect to the lower piston, while hand pressure was applied to facilitate uniform distribution of the material. If necessary, additional pressure could be applied by the screw arrangement on the cell. The spectrum was recorded in the usual manner.

EXAMPLES OF SPECTRA TAKEN WITH DIAMOND CELL

Representative spectra recorded using the diamond cell are shown in Figures 5 to 8. Except for boron nitride, all specimens were reagent grade materials available in the laboratory and used without further purification. In general, a spectrum consisting of sharp well-defined bands is obtained. In most cases the spectrum obtained compares favorably with the spectrum resulting from a melt, a mull, or a solution specimen. Usually only minor differences are evident upon comparison with good pellet spectra. The differences include variations in the resolution and intensities of certain absorptions and the presence or absence of weak bands. Some of the spectra are weak, but this is to be expected in view of the extremely small quantities of sample used.

Figure 5 shows the spectrum of cubic boron nitride, which proved impossible to obtain by ordinary means. This material, which is as hard as diamond, cannot be ground by any ordinary means without introducing impurities. Its index of refraction and/or particle size was so large that spectra could not be obtained in ordinary pellets and mulls. Solution and melting were out of the question, since retention of the cubic symmetry was important. The spectrum shown was obtained routinely on a small crystal crushed by the diamond anvils. The bands at 1400 and 810 cm.$^{-1}$ appear to be due to impurities of hexagonal boron nitride, the spectrum of which can be obtained by any convenient method. The intense band at 1100 cm.$^{-1}$ is presumably the B-N stretching mode in the cubic form, while the band starting to appear at approximately 700 cm.$^{-1}$ presumably corresponds to a bending mode.

The spectrum of 15 μg. of boric acid (Figure 6,*A*) is of higher quality than several reported mull spectra (*34*, *49*). In particular, the broad band near 800 cm.$^{-1}$ is resolved into two bands at 740 and 810 cm.$^{-1}$ The spectrum of a thin single crystal of boric acid (*25*) shows more structure than the present spectrum, while the spectrum of a pellet (*52*) is approximately the same.

The spectrum of 25 μg. of benzoic acid (Figure 6,*B*) closely resembles that obtained on a pellet (*49*), with only minor differences. The spectrum is that of the crystalline dimer, and shows no interferences from monomer bands, which can appear in the potassium bromide pellet (*20*). A pellet spectrum and a mull spectrum (*2*) are inferior to the present spectrum in general appearance and band shape. The spectrum obtained from 4 μg. of benzoic acid (Figure 6,*C*) is weak, but it can be utilized readily for qualitative analysis.

Seven micrograms of *p* - nitrophenylacetonitrile give a spectrum (Figure 7,*D*) which is similar to that resulting from a pellet sample (*49*). The present spectrum is far superior to that obtained on the mull (*49*). The latter exhibits Christiansen effects and a large amount of scattering.

A spectrum of 18 μg. of 1,3-diphenyl-1,3-propanedione (Figure 7,*E*) shows more structure than does that of a solution (*49*). In particular, several bands near 800 cm.$^{-1}$ are absent from the solution spectrum, because of the strong absorption of the solvent, CCl_4, in that region. The larger broad band near 1540 cm.$^{-1}$ is resolved into three bands in the above-recorded spectrum.

The spectrum of 13 μg. of *m*-dinitrobenzene (Figure 7,*A*) differs slightly from that of the pellet (*22*, *49*). Several bands are doublets in the pellet spectrum, and are unresolved in the present spectrum.

Twelve micrograms of cinnam[illegible] give a spectrum (Figure [illegible] strong sharp bands. Th[illegible] different from that of t[illegible]

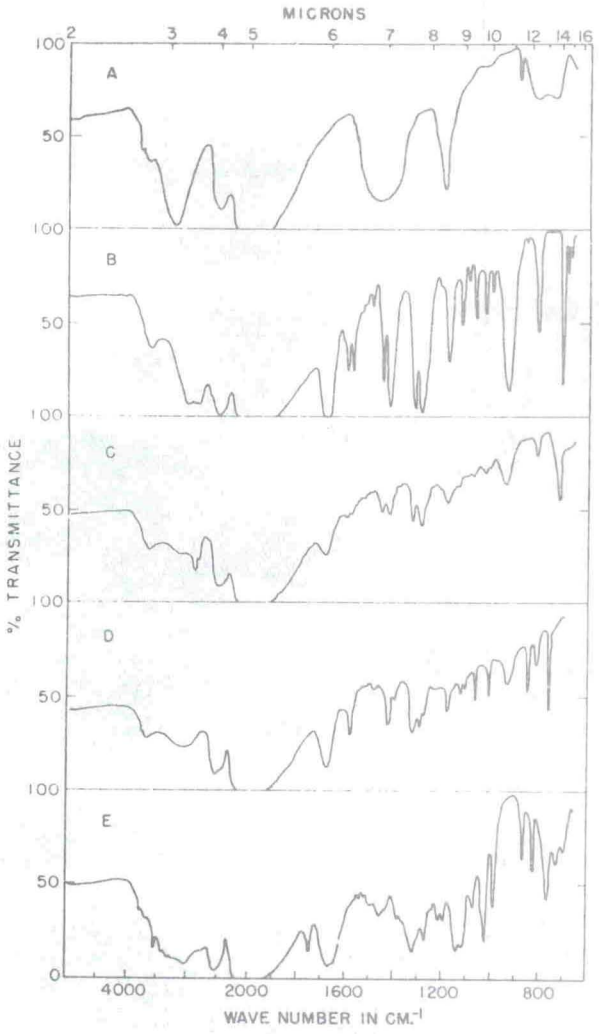


Figure 6. Infrared spectra

A. Boric acid, 15 μg.
B. Benzoic acid, 25 μg.
C. Benzoic acid, 4 μg.
D. p-Bromobenzoic acid, 7 μg.
E. l-Ascorbic acid, 88 μg.

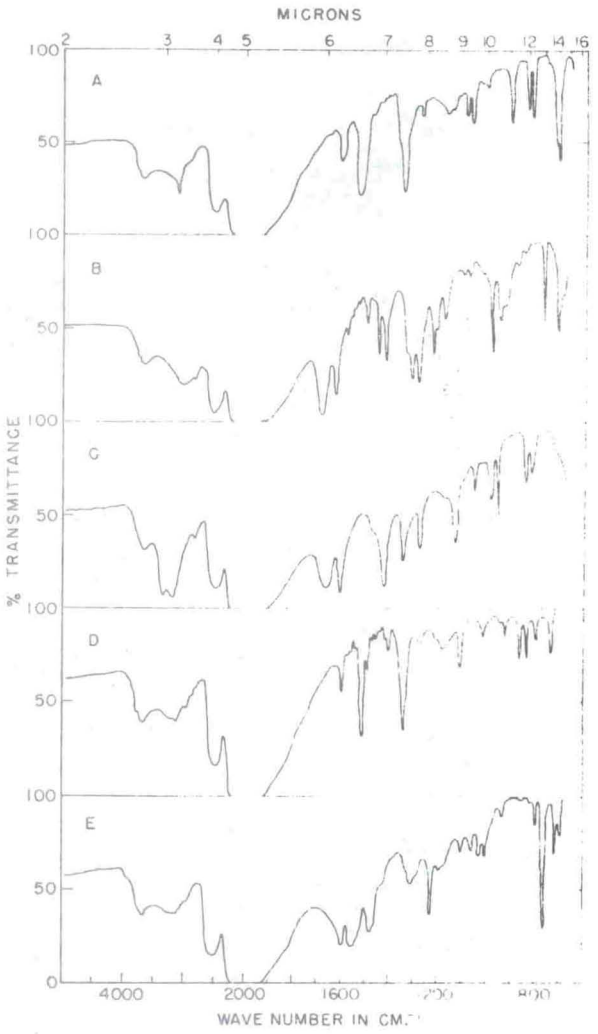


Figure 7. Infrared spectra

A. m-Dinitrobenzene, 13 μg.
B. Cinnamic acid, 12 μg.
C. Acrylamide, 39 μg.
D. p-Nitrophenylacetonitrile, 7 μg.
E. 1,3-Diphenyl-1,3-propanedione, 18 μg.

sample (*49*), with large bands and shoulders being resolved. The band shapes are somewhat sharper than those in the solution spectrum (*49*). The spectrum compares favorably with that obtained from the crystalline dimer in a potassium iodide pellet (*20*), except that the C-H stretching bands show up much better in the latter. Bands due to the absorbed monomer, which may be present in a potassium bromide pellet spectrum, do not appear in the present spectrum.

The spectrum of 39 μg. of acrylamide (Figure 7,*C*) closely resembles that obtained from a pellet (*49*) with regard to sharpness of bands and resolution. The over-all quality of the spectrum is superior to that of a melt spectrum (*49*) and a mull spectrum (*14*). In particular a band appears in the melt spectrum at 1620 cm.$^{-1}$, while two bands appear in the present spectrum, at 1610 and 1670 cm.$^{-1}$ The N-H stretching frequencies show up strongly. Minor variations are evident upon comparison with a spectrum of oriented crystals in a melt (*59*).

The spectrum of only 7 μg. of *p*-bromobenzoic acid (Figure 6,*D*) compares favorably with the pellet and the mull spectrum (*49*).

A sample of 88 μg. of *l*-ascorbic acid which was run from 300 to 5000 cm.$^{-1}$ (Figures 6,*E*, and 8) gives a definitive spectrum which is similar in quality to the pellet spectrum (*49*) but vastly superior to the mull spectrum (*49*). Another mull spectrum reported (*60*) compares well with the present spectrum.

ANALYSIS OF SPECTRAL METHODS AVAILABLE FOR SOLIDS

The usefulness of the method proposed here for obtaining infrared spectra on solid samples can best be evaluated by comparing it with the other methods in use at the present time. The general considerations of interest are: scope of applicability, quality of spectra obtained, and ease of operation. The available techniques can be summarized briefly as follows:

1. Solution in liquid solvents.
2. Mulls (Nujol, hexachlorobutadiene, perfluorokerosine).
3. Films (thin single crystals, solids crystallized from melts, deposits from solution or vapor, etc.)
4. Alkali halide disks.
5. Miscellaneous methods.

With the exception of 5, these methods are reviewed in tabular form in Table I.

Miscellaneous Methods. A technique (*54*) has been used in which solids are squeezed between salt plates containing a rectangular moat-type channel surrounding a transmittance region of 1 × 5 mm.

ADVANTAGES. It is convenient; the sample can be recovered; a useful spectrum can be obtained with small amounts of sample; there are no interfering bands; and the difficulties

Table I. Infrared Spectral Methods Useful for Solids

Method	Score of Applicability	Quality of Spectra Obtained	Ease of Operation	Ref.
Solution	Very useful within limits imposed by solubility conditions, especially in quantitative analysis. Microtechniques are available.	Characterized by broad bands with decrease in intensity with transition from crystal state to solution. Solvent spectrum may obscure bands of sample. Solvent interactions and shifts of frequencies (from those of a given crystalline state) may occur, as well as missing or new bands.	25 μg. or less of solid may be used. Sample is easy to prepare with known thickness.	(7, 28, 43, 47, 48, 51, 53)
Mull	Applicable to large number of compounds. An internal standard is necessary for quantitative analysis.	Useful if proper techniques are used. Fewer interfering bands than with most solvents. Scattering, orientation, and Christiansen effects may be observed. Polymorphic changes may appear from grinding or method of preparation.	Preparation of sample is relatively easy. Nujol is most common mulling agent. Milligram quantities are needed for sample preparation. Recovery of sample is difficult. Size of particles may be important.	(3-5, 7, 10, 11, 20, 23, 28, 36, 40-43, 47, 48, 51, 55)
Single crystals	Application possible only when single crystals can be grown.	Sharp, well defined bands with no interfering bands.	Procedure is time-consuming.	(25)
Solids crystallized from melts	Very useful for low melting solids, but structural changes or even decomposition may occur with substances of high melting points.	Sharp, well defined bands. Polymorphism can occur. No interfering bands are possible when compound is unchanged upon melting.	Preparation of sample is easy but mg. quantities are usually needed. Sample recovery is easy.	(23, 47, 48, 53)
Deposits from solution or vapor	Special techniques (unusual solvents, low temperature cells, etc.) may be needed to obtain wide application.	No interfering bands. Scattering, polymorphism, and Christiansen effects are sometimes observed.	Preparation is laborious. Optical reproducibility sometimes is difficult. Size of particle is important.	(7, 17, 23, 43, 47)
Alkali halide disks	Useful for a large number of compounds. Quantitative methods can be used. Micro quantities can be studied with beam condensers.	No interfering bands. Scattering usually is not observed. Spectra can differ greatly from those recorded by other methods because of interaction of substance with polar alkali halide matrix. Spectra may differ because of polymorphism, difference in grinding and preparation conditions, or use of different matrix materials. Particle size effects are observed on some samples.	Pressed disk techniques are needed. Adsorbed water may be troublesome. Disks may be stored if sample is inert to matrix and nonvolatile. Distribution of sample can be uniform.	(1, 2, 5, 6, 9, 12, 15, 16, 19-21, 24, 26, 27, 29-31, 33, 35-41, 44, 51, 54-58, 62, 63)
Miscellaneous methods		See text		

associated with the potassium bromide disk method are avoided.

Disadvantages. The procedure is limited to relatively soft solids; and a beam condenser is needed.

Solids have been laminated with thin sheets of mica or silver chloride. Polyethylene sheets can be impregnated with various solid materials (*50*). An advantage is that impregnation is effective with insoluble or nonplastic materials. The technique has only limited applicability, because of the polyethylene and mica bands which interfere with the spectrum of the sample.

A number of solids have been run by suspension in suitable liquid media using small amounts of emulsifying agents (*18*).

Bacteriological specimens have been studied by means of dried films mounted on a silver chloride window (*46*).

A matrix isolation technique has been used by a number of workers, using low temperature Dewar systems with liquid He, H_2, Ar, N_2, CO_2, etc. The matrix isolation method requires special techniques and equipment (*8*).

ANALYSIS OF DIAMOND CELL TECHNIQUE

In common with the techniques currently available the diamond cell inherently possesses certain advantages as well as disadvantages.

Advantages. The method seems applicable to all solid materials in a purely routine manner. Spectra are obtained rapidly and easily in as short a time as required by the most rapid method available. Preparation of the specimen is extremely easy and in most cases no preliminary work is necessary. Prolonged grinding, freeze-drying, or other time-consuming procedures are eliminated. Since the diamonds are inert, reactive and relatively unstable materials can be studied routinely. In fact, highly corrosive liquids such as fuming sulfuric and concentrated phosphoric acid have been studied using the diamond cell.

The technique is essentially a micromethod, requiring very small quantities of material, with no modifications being required as the quantity of specimen available varies. The specimen is unaffected by the experiment and can be recovered routinely if desired.

High quality spectra are obtained. Sharp strong bands are observed and bands may often be resolved by this technique which are not resolved by other methods. No major interfering bands are present below 1900 cm.$^{-1}$, so that the important fingerprint region is free of interference. If desired, a sapphire cell will permit observation of the region above 1900 cm.$^{-1}$ with[illegible] interferences.

As with most other methods [illegible]

ling solids directly, problems of preferential orientation may be expected with this technique. However, microscopic observation shows that the specimens are polycrystalline in nature with no apparent preferential orientation. If desired, the cell can be used without modification in the visible or ultraviolet ranges.

Disadvantages. As now constituted, the small surface areas of the diamonds necessitate the use of a beam condensing unit. All diamonds have a strong band that obscures the region from approximately 2700 to 1800 cm.$^{-1}$ Medium bands near 3000 and 3500 cm.$^{-1}$ can mask weak C-H and N-H frequencies. However, all or part of both of these interferences can be eliminated by using thinner diamonds or sapphires. Spectra should be run under a nominal pressure, since pressure transitions which may occur in some materials might cause unpredictable changes in the spectra. Transitions of this type are not widespread, and the effects of transitions on the spectra are not very marked in most instances and have been reversible to the low pressure form (*32*). Other pressure effects such as shifts and intensity changes are of such small magnitude at low pressures as to be negligible (*32*).

At present, quantitative work requires an internal standard. However, if an accurate method for measuring the specimen film thickness were available, quantitative work could be performed without such standards. Normal specimen thickness may be such that weak bands do not appear or strong bands do show 100% absorption. This purely experimental problem appears with all techniques. If bands are too strong, an alkali halide diluent may be employed. Under these circumstances spectra may be affected by some of the factors enumerated under the pellet techniques. However, the difficulties are not as serious, since a 1 to 1 or 1 to 2 dilution using LiF as a diluent is generally sufficient to reduce the intensities of most strong bands. Increasing the intensities of weak bands is more difficult, but can be accomplished in some instances by repeatedly building up the film thickness, reducing the pressure of film formation, or, if necessary, increasing the diamond surface area.

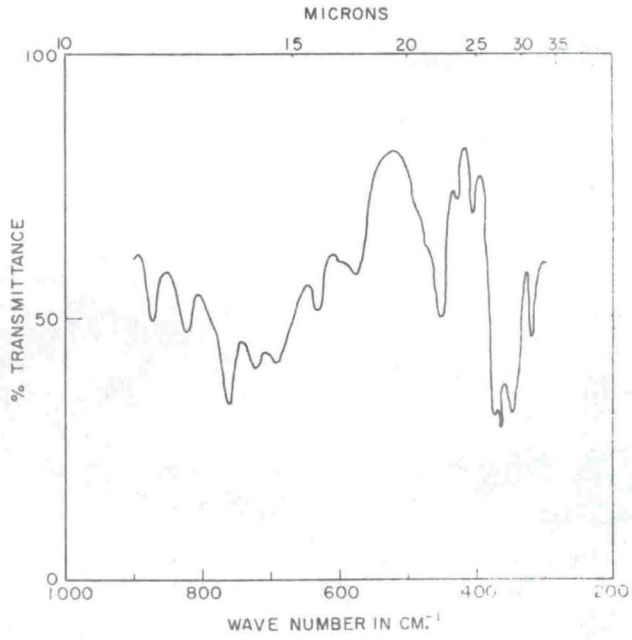


Figure 8. Infrared spectrum of l-ascorbic acid, 88 μg.

ACKNOWLEDGMENT

The authors thank F. J. Kasler, University of Maryland, microanalytical laboratory, for the use of the microbalance and for helpful discussions. Financial support from the National Science Foundation is gratefully acknowledged. They are indebted to the General Electric Co. for the specimen of cubic boron nitride.

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RECEIVED for review April 15, 1960. Accepted September 23, 1960. Division of Physical Chemistry, 138th Meeting, ACS, New York, N. Y., September 1960. A portion of a thesis submitted to the faculty of the Graduate School, University of Maryland, in partial fulfillment of the requirements for the degree of doctor of philosophy.