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THE LOW-KEY CRYSTALLOGRAPHY^{1,2}

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Over past years our Society has been honored by Presidential addresses delivered by proponents of best informed aspects of their various areas of interest. Later today we will enjoy a Roebling medal acceptance by an individual who will perform this function for my area. I will therefore try today to give recognition to some of the scattered collateral benefits that accrue to mineralogy and crystallography by virtue of the adaptation of information deduced by the good practitioners from adequate data to materials from which collectable data is not definitive. The remarkable successes that have accumulated in the 58 years of X-ray diffraction analyses have attracted an ever-growing number of scientists, providing an ever-increasing fund of facts on which to draw.

Currently, the availability of computer programs makes possible the solution of crystal structures from massive data collections with only limited time demands and assures a continuing proliferation of additional facts. The neglected area is that populated by the large number of crystalline solids too imperfectly constituted to provide the massive data collections. For their characterization recourse must be had to empirical-based principles.

Professor Linus Pauling was earliest to exploit extensively the recognition that complex stable structures were based on arrangements of relatively few coordinated polyhydral groupings and their articulations with each other. Any such polyhedron has a calculable transform that represents its potential to scatter radiation in any given direction and the same is equally true of any articulated assemblage of polyhedra. This potential amplitude then either is or is not delivered to observed intensities, depending on the disposition in space and dimensional correspondences with periodic repetition of such assemblages with respect to

¹ Presidential address to the Mineralogical Society of America, 12 November, 1970.

² Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support for several of the illustrations reviewed.

each other. Our present Roebling medalist is among those who have provided abundant examples of alternative arrangements with respect to each other of entire macro-areal layers of the various micaceous minerals.

As one who has habitually been faced with poorly organized mineral matter, and limited diffraction data, I have followed the course of seeking what advantages may be taken by borrowing from the better established principles. The few examples that I can cite here today can not possibly be comprehensive, nor can they include proper coverage of the many successes of other investigators who have faced similar situations.

Three little related sources from which borrowing is productive can be chosen as illustrative. They are: peculiar aspects of geometry, the utility of transforms of rigid bodies, and collateral information from specialized auxiliary instrumental methods.

GEOMETRY

It was originally observed by Hendricks (1939), among micas, and later by Bailey (1963), among the kaolinite minerals, that each group included one polymorph for which the monoclinic symmetry plane (or its near equivalent) was perpendicular to its orientation in the other members. The consequent redistribution of extinctions and relative positions of reflections in related row lines provides an automatic recognition of this geometry.

With discovery of agents able to intercalate between layers of the kaolin minerals it became a pertinent question whether the level of complete independence of adjacent layers of these minerals was achieved in the same sense that independence of adjacent layers of montmorillonite minerals is achieved in dilute suspensions.

The pattern of distribution of reflections in superposed 20 l and 11 l rows lines for the unique polymorph, nacrite, is plotted in a left hand column in Figure 1, together with scale-adjusted plots for observations taken from powder diffraction diagrams of reacted specimens in two magnitudes of swolleness (Deeds, van Olphen, and Bradley, 1967). For each it is seen that the pattern persists as the scale changes. This can be true only if no rotation about or translation across a normal to adjacent layers has occurred. Integrity of crystalline grains is maintained, and the same polymorph is recovered with lateral boundaries remaining congruent when the swelling agents are leached out. A hoped for, non-mechanical production of new layer surfaces is not fulfilled. The attack of swelling agents on these mineral grains must be looked upon as analogous with the optically-observed limited-degree swelling of vermiculite crystals (Walker, 1963), rather than as a dispersion.

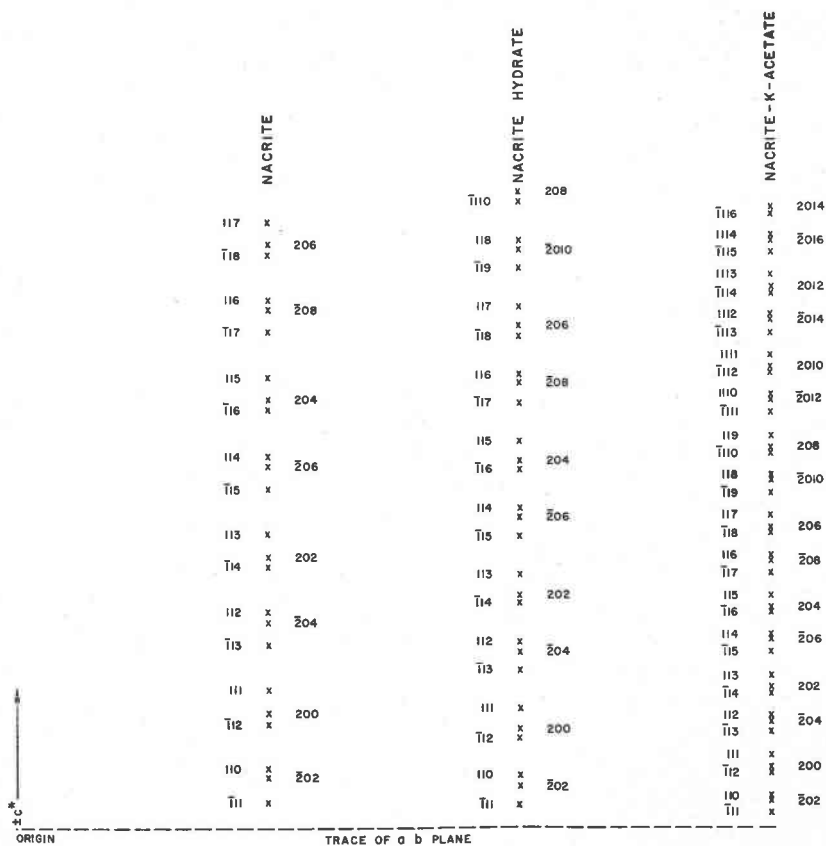


FIG. 1. A scaled plot of the patterns of distribution of $20l$ and $1l$ diffraction features for nacrite and for nacrite layers in two swollen states, each arranged as they would appear on a c^* rotation diagram. The small, intermediate, and large increments along c^* that remain proportional in each instance are distinguishable in powder diagrams and establish that the expansion was vertical.

RIGID BODY TRANSFORMS

The principle that points and patterns have defined reciprocal character is used in many ways. For those layered crystallizations that involve one remarkably long periodicity a maximum value accrues to the examination of a simple one-dimensional inversion normal to the long period. A first extension of the principle beyond application to actual structure analyses was the application to mixed layer assemblages by Hendricks and Teller (1942). One example can be cited for an alternation of compositions for nearly equally thick layers. A one dimensional trans-

form from a thin packet of vermiculite layers, smoothed by averaging sums of from 6 to 10 units, and a modulation function for amplitude contribution of Mg content equivalent to a chlorite present in alternate interlayer spaces, when added together, afford a calculation of relative scattering intensity that convincingly matches the observed record for a natural occurrence, as illustrated in Figure 2. More recent observations that layers of unequal thicknesses may coexist in regular or more nearly regular sequences have brought to attention the utility of treatment as pairs of complexes. The relations of the rectorite or allevardite minerals and their analogs provide an example. The rather small, but distinct difference between the transform of two layers fixed by sodium ion populations from those fixed by potassium ion populations permit distinction between the paragonite-related and the muscovite-related occurrences by simple inspection of observed relative diffraction intensities. Figure 3 (from Henderson and Bradley, 1970) compares observation of weaker and stronger adjacent intensities for several varied conditions for each ion. Figure 3A illustrates an improper match.

A somewhat less pertinent example for this Society is afforded by some paraffinic compounds. In Texas, oil is a mineral. The lateral packings of the straight chain hydrocarbons and their derivatives provide crystals with one remarkably long periodic repetition. For the orthorhombic paraffins themselves the common lateral packing is illustrated in Figure 4. Normal to this plane a one-dimensional transform reflects the number of carbons per chain in the undulant ranges as in Figure 5 and the increment of length per methylene unit by prominent large pulses. The prominent maximum fixed by methylene units appears, for example, for the even-numbered chains at positions that require the projected gap between chain ends to be five halves times the methylene increment. Equal amplitudes on each flank of the 0.7867 cm^{-1} position would fix the $5/2$ increment. Relative intensities of observed reflections on the flanks of these maxima provide a remarkably precise measure of the difference from $5/2$ for the projected gap, reducible in turn to van der Waals contact, from crystals of quality less than one would deliberately choose to analyze. The relative intensities of neighboring reflections on the flanks of one of these maxima was used by Smith (1953) for his measure of 1.274_5 \AA for the CH_2 increment in orthorhombic tricosane ($\text{C}_{23}\text{H}_{48}$). For an orthorhombic even numbered paraffin, triacontane ($\text{C}_{30}\text{H}_{62}$) a comparable estimate gives 1.272_0 \AA .

Recrystallization of the triacontane yielded a phase with chain axes inclined to the base at about 56° . In the perpendicular dispositions of chains, hydrogen atoms project to superposition on carbon positions, and do not alter the shape of the transform. With inclinations, this is no

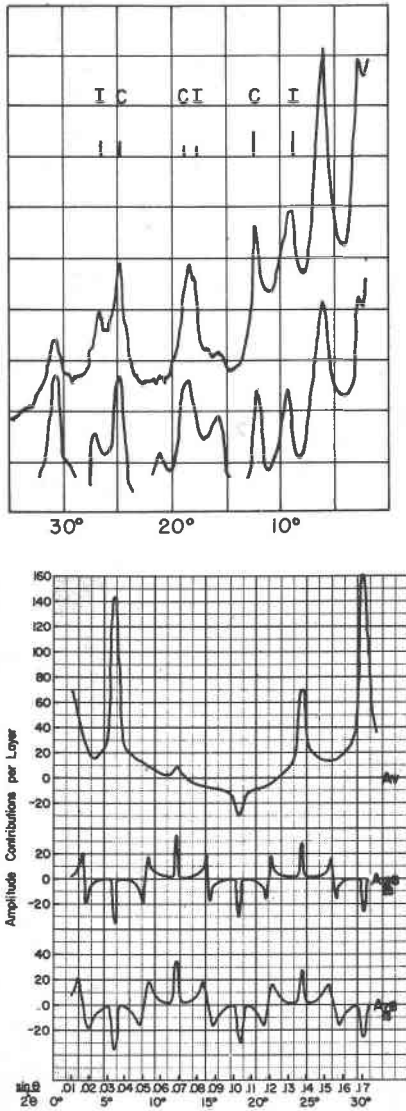


FIG. 2. (a) Observed (above) and calculated (below) log intensity distributions for a nearly regular corrensite-type clay mineral. The positions at which minor discrete accessories (i=illite, c=chlorite) contribute to the observed record are indicated by marks proportional to their contribution. (b) The vermiculite transform and two examples of amplitude modulations to be added to the vermiculite average (from Grim, Droste, and Bradley, 1960).

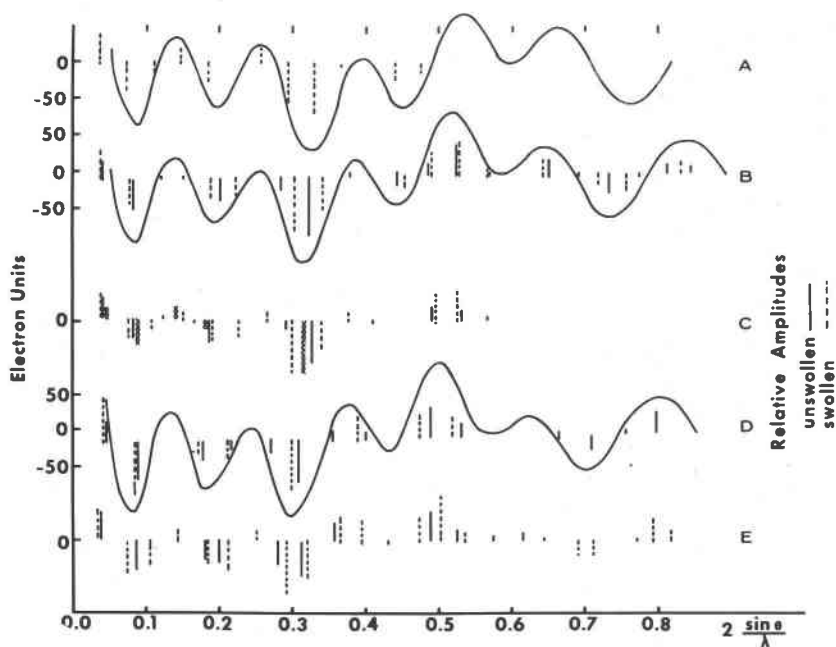


FIG. 3. A comparison of relative amplitudes reduced from diffraction data from various representative rectorite and rectorite-like clay minerals with pertinent one dimensional transforms for double layers.

A. A rectorite from the Fort Sandeman district, Baluchistan, Pakistan (Kodama, 1966) solvated with 2 layers of glycerol, and the transform for a pair of pyrophyllite layers.

B. Allevardite (Brindley, 1956) with two water layers and rectorite from Graland County, Arkansas solvated with 2 layers of ethylene glycol, and the transform for a pair of paragonite layers.

C. Typical records for the nearly regular rectorite-like mineral from north central Utah with one water layer, with two water layers, and with two layers of solvating ethylene glycol.

D. The one water layer and one ethylene glycol layer complexes for the interstratified material prepared from sericite (Tomita and Sudo, 1968) and the transform for a pair of muscovite layers.

E. Data from Cole (1966) for the two-water layer state, and from Hamilton (1967) for the two glycerol layer states for partially ordered potassium bearing clays from Tasmania and from New South Wales.

In each case the organic molecule solvated state is distinguished by the broken-line bars. All bars are normalized to approximately one-half of the scale for amplitude curves.

longer true, but by directing attention to sufficiently large diffraction angles hydrogen contributions become trivial and can be ignored.

For those crystals not orthorhombic or those including orthorhombic but based on inclined axes, maxima in the transform relate both to aver-

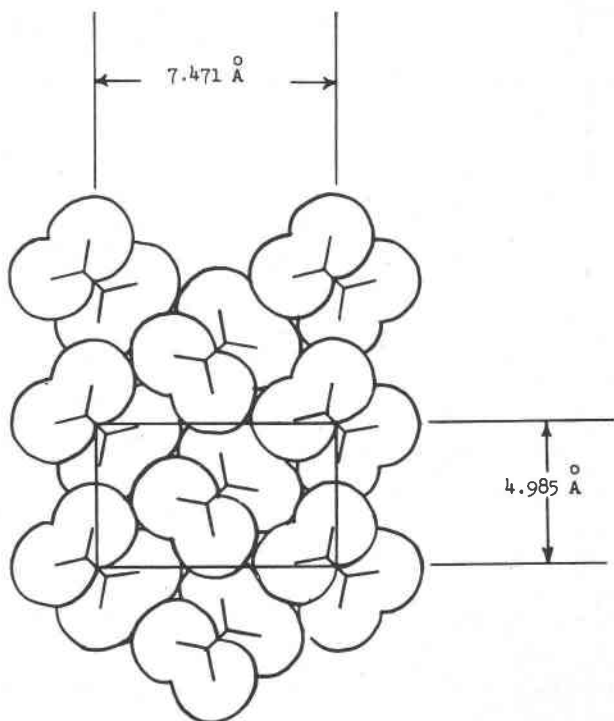


FIG. 4. The packing of hydrocarbon chains (after Segerman, 1965) to which this fatty amines and the γ -form of *n*-hexadecanoic alcohol may be referred. For the amines carbon atoms displaced by $\frac{1}{2}$ the 5 \AA axis and one methylene residue unit along c lie in planes parallel with 001 and in the alcohol carbon atoms displaced by $\frac{1}{2}$ the 7.5 \AA axis and one ethylene residue unit along c lie in planes parallel with 001. The monoclinic symmetry of the alcohol requires that b is the axis that relates with the conventionally chosen a -axis of orthorhombic forms.

age methylene increments and average ethylene increments. Periods normal to the basal planes are foreshortened and the relative importance of methylene indicators and ethylene indicators varies with the orientation of the molecular mirror plane to the vertical plane that includes the molecular axis. The calculated transform for 34 carbon atoms at 56° inclination shown in Figure 6 is substantially correlative with the observations of Abrahamsson, Larsson, and Von Sydow (1960) for *n*-hexadecanol.

Combined with space group criteria, an analysis of a structure can evolve from data utterly inadequate for conventional methods. This is illustrated for an even-numbered carbon fatty amine. Figure 7 displays the relative amplitude magnitudes for successive adjacent orders of diffraction from $n\text{-C}_{18}\text{H}_{37}\text{NH}_2$ for chain inclinations of 64.5° and molecular

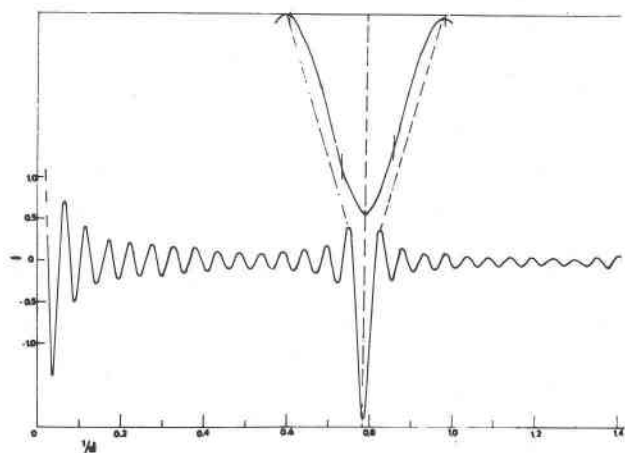


FIG. 5. A one dimensional transform for an even-numbered-carbon, orthorhombic paraffin, with the methylene subcell feature on a 5x expanded scale. The positions on the flanks for adjacent 31st and 32nd orders for the 30th and 33rd for $C_{30}H_{62}$ are indicated.

mirror planes 40° from the a - c plane of Figure 4. The chain orientations and space group criteria afford the structure analysis shown in Figure 8. The arrangement is a herring-bone pattern in two molecule repetitions

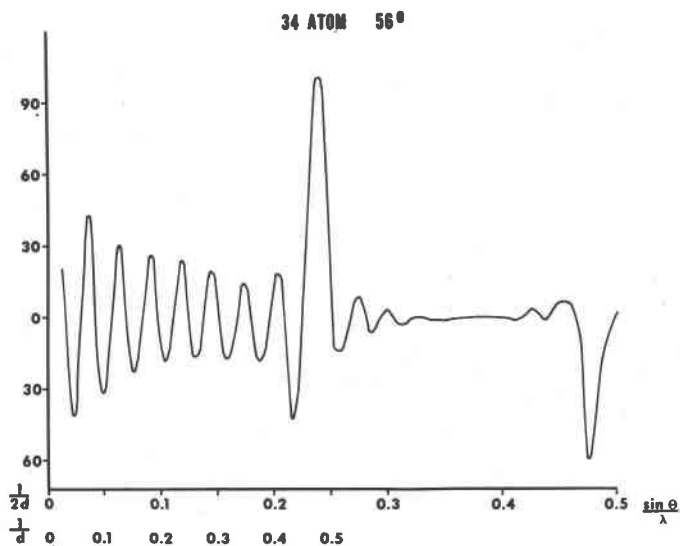


FIG. 6. A calculated one-dimensional transform for 34 carbon atoms in chains arranged as in the analyzed n -hexadecanol. (Abrahamsson, Larsson, and von Sydow, 1960).

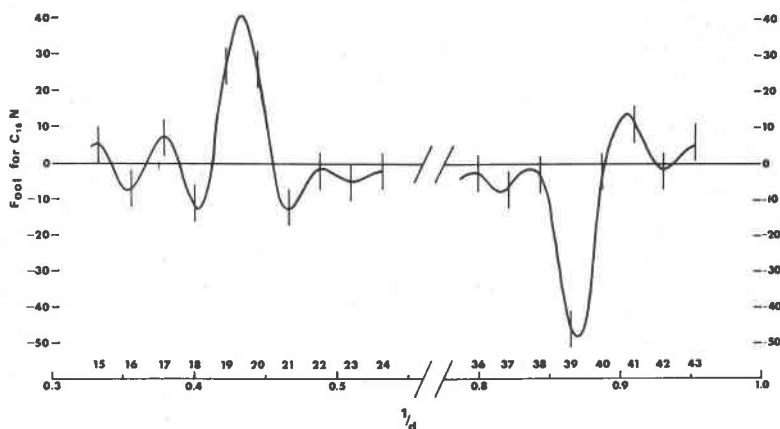


FIG. 7. The positions of reciprocal lattice nodes with respect to a transform along c^* in the ranges pertinent to establishment of molecular orientation of $C_{18}H_{37}NH_2$ in the orthorhombic structure.

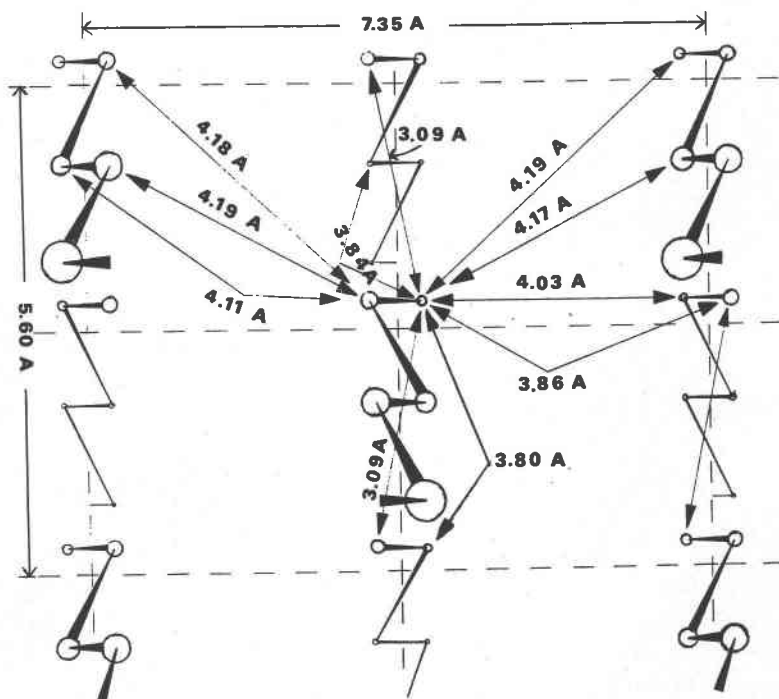


FIG. 8. The packings of amine nitrogens and of the methylene residues of contacting n -paraffinic chains. Presumed $N-H \cdots N$ hydrogen bonded associations nearly parallel the 2_1 axes thru the origins and $0, \frac{1}{2}, 0$.

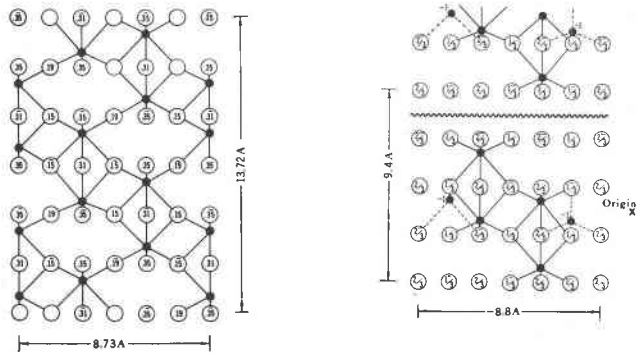


FIG. 9. Projections onto (1120) for hematite (left) and for the detail in the hydrated oxide (right) found reconcilable with its diffraction data. In the right hand idealization, two iron ions in a next (1120) level below the projection are located.

meeting the requirements of the space group $P2_1ab$. The comparable odd numbered fatty amines provide a four molecular double herring-bone aspect. This 4-molecule array in the space group $Pnab$ is also recently reported by MacGillavry and Wolthuis-Spuy (1970) for an orthorhombic methyl stearate.

Another utility of transform treatment is illustrated by a hydrolyzate of ferric nitrate (Towe and Bradley 1967). At the time of the analysis, I had no thought that it could be a mineral, but this year an observation was reported by Jackson and Keller (1970) for this phase collected from beneath the lichens in weathered crust of date-known flows from Moana Loa.

The architecture is borrowed from hematite, but only subcell diffraction effects are observed. The outstanding strong hematite diffraction lines due to rhombohedral order are missing. A reasonable reconciliation of observed diffraction data with the diffraction potential of four-octahedron details from hematite arranged as in Figure 9, plus molecular water to properly fill out the space available provides a probable valid structure.

COLLATERAL INFORMATION

It would not be proper for me to attempt an exhaustive catalogue of the sources from which valuable supplements to diffraction crystallography may be drawn. Perhaps the most popular is differential thermal analysis, and so is too familiar for comment here.

Less familiar is the utility of pleochroism in the absorption in the infrared. The ability to examine minerals in known orientation permits combination of the traditional criteria based on visible light with a com-

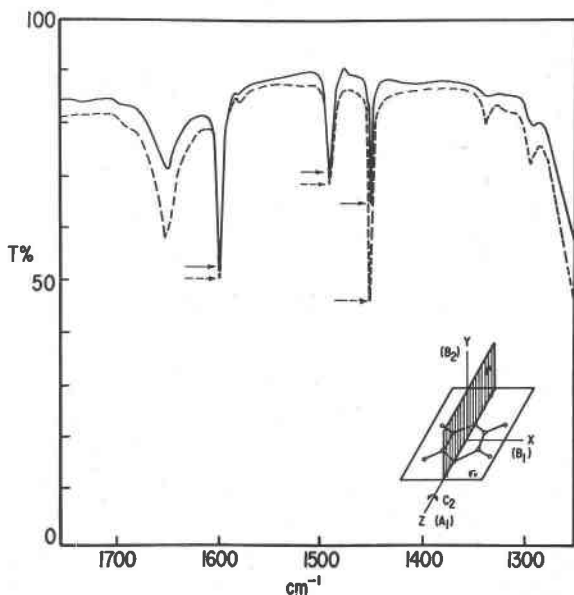


FIG. 10. Infrared absorption records for normal incidence (—) and for inclined incidence (---) of radiation on the basal plane for a C_{2v} molecule, benzonitrile absorbed on montmorillonite. The z and y axes are parallel with the base (from Serratos, 1968).

plement of specifiable absorption energies for vibrations of frequently encountered bonded radicals. An excellent example is the analysis of the benzonitrile complex with montmorillonite. Modes of vibrations along the C_{2v} axis, and those normal to it *in* the plane of the ring and *normal* to the plane of the ring differ in energies, and only those normal to the axis and in the plane of the ring become more active in absorption with inclined incidence. Figure 10 depicts the relationships. The fact that molecular water also has C_{2v} symmetry invites hope that more utility will be realized by additional applications.

CONCLUSION

In this rambling discourse it has been my hope to illustrate that opportunities still exist for the collection of useful information without the necessity to accumulate perfect data sets.

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