The Near InfraRed Absorption Spectra of Pentaerythritol and Diketopiperazine Obtained with Plane Polarized Light

Joseph W. Ellis and Jean Bath

Additional information on J. Chem. Phys.

from such a low frequency to the specific heat is very large; with the above choice of fundamentals we find C_p at 0°C to be 13.2 cal./mole. Thermal determinations give 10.39 cal. at 0°C[15] and again 10.13 cal. at 6°C.[16] Eucken and others reconcile the thermal and spectroscopic values by taking ω_4 as 732 cm^{-1}: a perpendicular band at this frequency would give satisfactory agreement. It will be remembered that careful purification of the cyanogen was found to be necessary; and the change in appearance of this band as hydrogen cyanide is eliminated may be seen in Fig. 1. E, (a) and (b). The band is of the parallel type and the separation of the P and R branches is 15.5 cm^{-1} corresponding to a moment of inertia of approximately 190×10^{-40} g cm^2: Recent electron diffraction measurements[17] give the interatomic distances as $C \equiv N = 1.16$ and $C - C = 1.37$ A, the corresponding moment of inertia being 180×10^{-40} g cm^2. It may be that the Q branch is very weak; but the analogous vibrations in CO_2 and C_2H_2 do not support this; the doublet structure also forbids its interpretation as $3\omega_4$.

[15] M. A. Masson, Ann. Chim. Phys. **53**, 257 (1858).
[16] A. Eucken and A. Bertram, Zeits. f. physik. Chemie **B31**, 361 (1935).
[17] L. Pauling and H. D. Springall, J. Am. Chem. Soc. **61**, 927 (1939).

Further reasons for not accepting 732 cm^{-1} as ω_4 are that anomalous values are obtained for the bending force constants and also that the combination bands B, D, E and F are more reasonably accounted for with $\omega_4 = 240$.

Unless the structure suggested is wrong it is difficult to see how any other allocation is possible, and hence the discrepancy in the specific heat values must await further experimental work before a final decision can be made. The final summary of the assignments is given in Table II.

With regard to the force constants it may be stated that the values $K_{CN} = 16.95$ and $K_{CC} = 5.17$ derived by Reitz and Sabathy[10] accord reasonably well with Pauling's work[17] since the Badger relationship gives 16.8 and 5.6×10^5 dynes/cm. If the electron diffraction results are true then the values obtained by Linnett and Thompson,[18] 17.51 and 6.69×10^5 are too high.

[18] J. W. Linnett and H. W. Thompson, J. Chem. Soc. 1399 (1937).

The Near Infra-Red Absorption Spectra of Pentaerythritol and Diketopiperazine Obtained with Plane Polarized Light

JOSEPH W. ELLIS AND JEAN BATH
University of California at Los Angeles, Los Angeles, California
(Received June 3, 1939)

Pentaerythritol, $C(CH_2OH)_4$, a crystalline alcohol, and diketopiperazine, $(CH_2NHCO)_2$, also crystalline, have been subjected to an infra-red absorption study with plane polarized waves in the region 1–2.5μ. Pronounced pleochroism is observed, and this dependence of absorption upon the plane of vibration of the electric vector, E_0, is used in identifying the bands associated with the normal vibrations of the methylene groups, CH_2, in each crystal. An interesting example of Fermi resonance arises.

In pentaerythritol the appearance of pronounced absorption by perturbed OH groups when E_0 oscillates along the c axis indicates that the feature of the crystalline structure, deduced from an x-ray diffraction study which orients all of the OH groups at right angles to this axis, must be modified.

The absence of the usual NH absorption near 1.50μ supports Corey's assumption of electron resonance in diketopiperazine.

PENTAERYTHRITOL and diketopiperazine are two dissimilar crystalline materials, which, because of the regularity of arrangements of their molecules with respect to the crystal axes, seemed to offer possibilities for obtaining

interesting spectroscopic and further structural information if their infra-red absorption were investigated with plane polarized light. The structures of these two crystals have been deduced by means of x-ray diffraction studies

by Llewellyn, Cox and Goodwin[1] and by Corey,[2] respectively. A study of the spectrum of pentaerythritol, $C(CH_2OH)_4$, was undertaken at the suggestion of Dr. E. G. Cox of the University of Birmingham, England, as a possible means of securing confirmatory evidence for the placements of the four hydroxyl groups per molecule. Spectra of diketopiperazine, $(CH_2NHCO)_2$, were originally recorded in connection with our investigation of substances containing NH groups. The study of this crystal was resumed subsequently to that of pentaerythritol because both crystals have methylene groups, CH_2.

The spectra were obtained with a recording quartz spectrograph and, as shown in reproductions of the original recordings in Fig. 2, were restricted to the range $1-2.6\mu$. Plane polarized radiation almost free from absorption bands in this region, except for the atmospheric water vapor bands W and a slight absorption caused by the quartz prisms, was obtained by sending the beam through a large Glan-Thompson prism. The 5-cm path of calcite in this prism introduces no appreciable bands because the extraordinary wave, which alone is transmitted, has the main component of its electric vector perpendicular to the planes of the CO_3 ions and thus is largely incapable of exciting the intensely absorbing planar oscillations within these ions.

We make no attempt to analyze the complete spectra of pentaerythritol and diketopiperazine nor to identify all of the bands of the restricted overtone region of Fig. 2. Rather, we pick certain features to discuss which we think are of interest. The nature of the specimens which we had to use was such that there was great loss of light. Consequently, the slit was opened so wide that it included at times a $\Delta\lambda$ as great as 0.01μ. It seemed that there was not sufficient justification for reducing the records to a percentage absorption basis, especially since it was difficult to get appropriate comparison curves.

1.5μ OH ABSORPTION OF PENTAERYTHRITOL

Pentaerythritol is an aliphatic alcohol which forms a tetragonal crystal having the symmetry

---

[1] Llewellyn, Cox and Goodwin, J. Chem. Soc., p. 883 (1937).
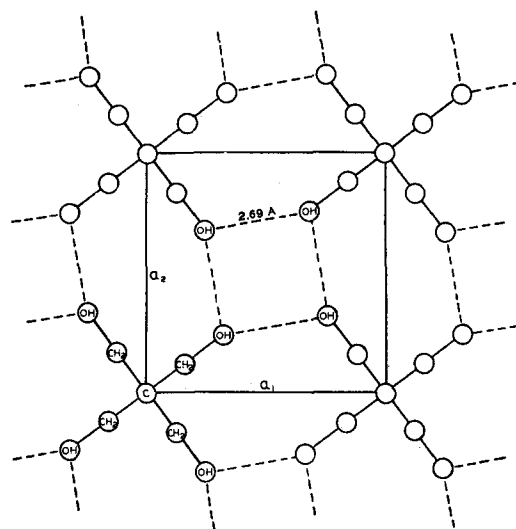[2] R. B. Corey, J. Am. Chem. Soc. **60**, 1598 (1938).

FIG. 1. Projection of four $C(CH_2OH)_4$ molecular units of pentaerythritol onto the (0 0 1) plane.

properties of the space group $I\bar{4}$. Although the $C(CH_2OH)_4$ molecular unit was originally supposed to have pyramidal structure, the work by Llewellyn, Cox and Goodwin[1] is now generally accepted as demonstrating a tetrahedral distribution of valencies around the central carbon atom. The body-centered cell of dimensions $a_0 = 6.10$ and $c_0 = 8.73$A contains two molecules of this type, each of which possesses a fourfold alternating axis of symmetry parallel to the c axis. The central carbon atom of one molecule is located at $(0, 0, 0)$ and that of the other is present at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

As shown in Fig. 1, which has been redrawn from the paper of Llewellyn and his co-workers, the molecular units are then arranged so as to place the oxygen atoms into planes parallel to the (0 0 1), i.e., perpendicular to the c axis. Oxygen atoms of four neighboring molecules form squares, shown by broken lines, whose sides are 2.69A long and inclined 10° to the a_1 and a_2 axes. The close approach, 2.69A, of two oxygen atoms to each other is regarded by Llewellyn, Cox and Goodwin as indicating the existence of hydrogen bonds, or "hydroxyl bonds" as they prefer to designate them. Moreover, they made the simplifying assumption that the H atoms all lie in the sides of the oxygen squares. From steric considerations alone there seems to be no clear-cut reason for con-
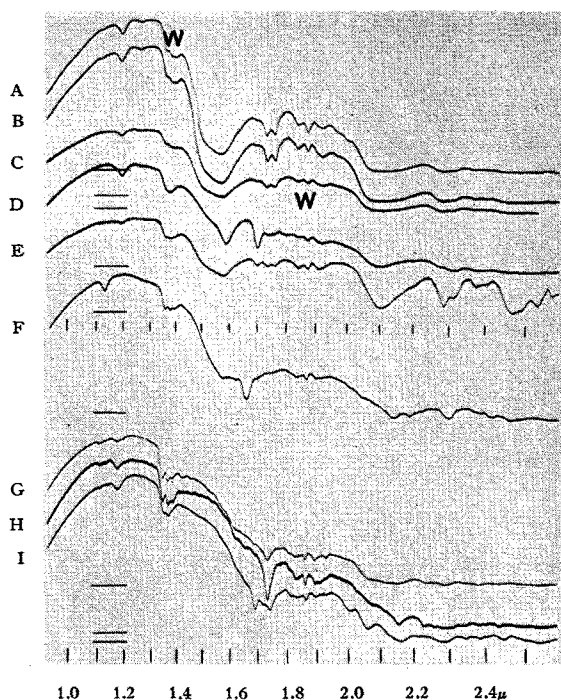
FIG. 2. Infra-red absorption spectra of pentaerythritol (*A–E*), resorcinol (*F*) and diketopiperazine (*G–I*). Bands *W* are caused by atmospheric water vapor.

sidering these atoms to be drawn into the oxygen planes.

X-ray diffraction is unable to locate the position of any H atoms. On the other hand it is just these light atoms whose oscillations give rise to absorption bands in the $1-3\mu$ region. Consequently, Dr. Cox, after reading our note[3] on the near infra-red absorption of sucrose crystals in polarized light, suggested that we investigate pentaerythritol in order to obtain if possible further information about the OH arrangements.

Five spectra of this material, taken under varying conditions, are reproduced in Fig. 2, A–E. The curves have different maximum displacements, as shown by the sections of base lines drawn in near 1.1μ. The absence in all of these of a sharp band near 1.44μ, such as is found in sucrose[3] and elsewhere, shows clearly the absence of unperturbed OH groups, in this respect supporting the assumed model. There appears the usual broad absorption region around 1.55μ characteristic of highly perturbed hydroxyl

groups. To obtain records *A* and *B* a single crystal was ground to yield a section 0.78 mm thick perpendicular to the *c* axis. In *A* and *B* the light was originally plane polarized with the electric vector making a 10° angle to a_2 and a_1, respectively, thus paralleling sides of the oxygen squares. The similarity of these records cannot be construed as indicating OH symmetry in the a_1a_2 plane, because the beam became partly depolarized owing to the "rings and brushes phenomenon" arising from the wide cone of light sent through the small crystal. In this instance, as in the other instances, we tested for the presence of depolarization by observing the visible radiation of the beam with a Polaroid plate inside of the spectrograph. Complications from rotatory dispersion need not be expected because of the absence of asymmetric carbon atoms.

The rings and brushes phenomenon will always limit the usefulness of polarized light in such studies whenever the beam travels along the optic axis. It should be recorded here that pentaerythritol is a slightly biaxial crystal, as shown by Ernst,[4] in spite of its tetragonal classification. Ernst points out that this probably results from strains associated with a tendency toward twinning. The angle between the optic axes varies from 8° to 0°, depending upon the specimen, but the bisector is always parallel to the *c* axis.

From the assumed OH arrangements a single OH band was anticipated in the region $1.6-1.7\mu$ rather than the twofold band observed with maxima at 1.51μ and 1.58μ. From the model, all OH groups should be perturbed equally, and the displacement from a "free" OH position near 1.44μ should be large because each OH group is perturbed by two others. In the language of hydrogen bonds, each OH group is the donor and the acceptor of H atoms. We believe that the concept of perturbation is in general more useful, however. We digress to enlarge upon this point.

That H atoms bonded to such electronegative atoms as O and N play a unique role in association processes has been realized for at least twenty years. That it also has a unique behavior

[3] Ellis and Bath, J. Chem. Phys. **6**, 221 (1938).

[4] E. Ernst, Zeits. f. Krist. **68**, 139 (1928).

when it exists as a part of two neighboring polar groups within a single molecule is also well known. The term "hydrogen bond" or "hydrogen bridge" has been used in connection with these various phenomena. The actual picture of what happens has varied from that of proton resonance between two states of pure valence to simple electrostatic perturbation. Bauer and Magat[5] have advanced arguments and carried out calculations supporting the latter point of view. In attempting to explain our spectroscopic phenomena we have found it advisable to adopt it also.

In our study of sucrose[3] we pointed out that not more than two OH groups can approach one another in that crystal. We have associated the broad doublet at 1.51, 1.58μ with the first overtone valence vibrations of OH groups in which the OH acts as the acceptor and the donor, respectively, in the hydrogen bonds. Or, from the perturbation viewpoint, following somewhat the ideas advanced by Cross, Burnham and Leighton[6] in their Raman analysis of liquid water and ice, we say that these two components originate, respectively, in OH groups perturbed by amounts Δ_1 and Δ_2. By measuring the displacements of 1.51μ and 1.58μ from the sharp 1.44μ band of unperturbed OH groups we obtain $\Delta_1 = 320$ cm^{-1} and $\Delta_2 = 620$ cm^{-1}. The Δ_2/Δ_1 ratio is approximately 2/1, in good agreement with the ratio of analogous perturbations found by Cross, Burnham and Leighton. Moreover, Δ_1 and Δ_2 are approximately 2.6 times as large as the values found by those investigators for fundamental OH oscillations in water and ice. This also is the magnitude of the ratio of first overtone to fundamental band perturbation obtained by substituting $v=2$ and $v=1$ into the wave mechanics perturbation expression:

$$\Delta \propto (2v^2 + 2v + 1).$$

Returning to pentaerythritol, the model of Llewellyn, Cox and Goodwin led us to expect a single band in the vicinity of 1.6μ, which represents a perturbation displacement of the order of magnitude of $(\Delta_1 + \Delta_2)$ from 1.44μ. The 1.44μ position given by sucrose can be assumed to be

reasonably near to the location of an unperturbed band in pentaerythritol, if such existed. The magnitudes Δ_1 and Δ_2 have been deduced from examples, ice[6] and sucrose,[3] in which tetrahedral directions have been satisfied by the perturbing OH groups. Such directions could not be involved in the assumed square arrangement of OH groups in pentaerythritol. Some strain would have to be assumed. Therefore, no exactness can be attached to the amount $(\Delta_1 + \Delta_2)$ in this instance.

The presence of two perturbed components, as in sucrose, indicates that there is a differentiation among the OH groups. This assumption is further supported by the appearance of absorption in this region when E_0 is parallel to c and the beam parallel to a_2, as in record D. The crystal for this spectrum was an 0.88-mm specimen cut at right angles from the section used in A and B. The 1.51μ component is greatly reduced and the 1.58μ component is shifted to 1.59μ. It is not safe to conclude that the OH groups whose directions deviate least from the oxygen planes and hence are predominantly excited by electrical oscillations perpendicular to c are the least highly perturbed ones; for owing to strains, there may be a large alteration in the frequency of an unperturbed OH group in which the H atom does not occupy one of the tetrahedral valence positions of the O atom. That is to say, it does not follow that greater perturbation is represented by the 1.59μ band than by the 1.51μ one.

Record C was taken under the conditions of record D with the exception that E_0 was parallel to a_1. That it should be similar to A and B is expected. Our tests with the Polaroid plate showed that the amount of depolarization of the light was small in all records except those of A and B. This slight amount arises from small rotations of the azimuths of vibration of the nonaxial rays of the cone.

In E the specimen was powdered pentaerythritol immersed in a mixture of CCl$_4$ and CS$_2$ designed to match refractive indices so far as possible. Unpolarized light was used. The distribution in the 1.51–1.58μ band is intermediate between those of $(A, B$ or $C)$ and D. This is reasonable. We return to the consideration of record E later.

[5] Bauer and Magat, J. de phys. et rad. 9, 319 (1938).
[6] Cross, Burnham and Leighton, J. Am. Chem. Soc. 59, 1134 (1937).

Resorcinol, $C_6H_4(OH)_2$, according to the x-ray analysis of Robertson,[7] seemed to be sufficiently similar to pentaerythritol in regard to the degree of perturbation of the OH groups as to make it desirable to investigate it. The only record taken, F, was with unpolarized light and powdered crystals in the CCl_4 and CS_2 mixture. Only a trace of the 1.51μ band occurs, and the longer wave maximum appears near 1.59μ. The strong aromatic CH band, 1.67μ, and its weaker companion, 1.63μ, characteristic of the benzene ring are not to be confused with the OH band. The x-ray model directs four oxygen atoms towards one another. But, unlike their arrangement in pentaerythritol, they exist at different levels along the c axis so as to form spirals rather than squares.

The OH absorption in resorcinol more nearly fulfills the expectation of a single type of perturbation than does that of pentaerythritol. We are inclined to associate this fact with the spiral arrangement of the hydrogen bonds, each OH group being more nearly aligned in conformity with steric requirements. All OH groups are thus equally perturbed and this perturbation should more nearly approach the value of $\Delta_1+\Delta_2$. Of all the materials which we have studied involving perturbed OH groups, the results of which we shall publish later, resorcinol shows the greatest displacement of the OH absorption band. The value $\Delta=760$ cm^{-1}, determined from the 1.42–1.59μ displacement, is however somewhat less than $\Delta_1+\Delta_2=940$ cm^{-1}. There is, however, no good reason for expecting exactly this amount, as we have already pointed out.

2.11μ AND 1.27μ OH ABSORPTION OF PENTAERYTHRITOL

Nayar[8] in a Raman study of pentaerythritol has identified the displacements 3252 and 3335 cm^{-1} with the fundamental OH absorption bands. His data also show two broad lines indicating molecular frequencies in the neighborhood of 1435 cm^{-1}. At least one of these doubtless arises from fundamental bending vibrations of the OH groups. Our broad intense band at 2.11μ (4750 cm^{-1}) is the combination of the 3300 and

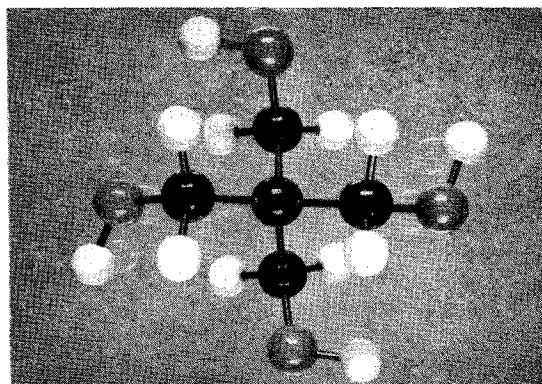[7] J. M. Robertson, Proc. Roy. Soc. **A157**, 79 (1936).
[8] P. G. N. Nayar, Proc. Ind. Acad. Sci. **7**, 251 (1938).

FIG. 3. Model of a pentaerythritol molecule, $C(CH_2OH)_4$.

1400 cm^{-1} bands. The weak band at 1.27μ (7880 cm^{-1}) is probably the combination of $[1.51, 1.58\mu]$ (6450 cm^{-1}) and 1435 cm^{-1}.

1.7μ CH$_2$ ABSORPTION OF PENTAERYTHRITOL

The pleochroism, that is, the dependence of absorption upon the azimuth of vibration of the electric vector, E_0, is more strikingly displayed near 1.7μ than near 1.55μ. 1.7μ is a region of hydrocarbon absorption, which in the present instances must be interpreted in terms of valence and deformation frequencies of methylene groups, CH_2. The study by Llewellyn, Cox and Goodwin[1] leaves little doubt that the four CH_2 groups per molecule in pentaerythritol are aligned, with the bisectors of the HCH angles all parallel to the c axis. Two of these groups point upward and two downward as shown in the molecular model of Fig. 3. Any absorption bands which appear near 1.7μ when E_0 vibrates parallel to c must be wholly or in part π-type bands, that is, have an electric moment change parallel to the bisector of the CH_2 group. The strong 1.703μ band of Fig. 2, D we identify as $2\nu_\pi$, the first overtone of the symmetrical CH_2 vibration. This interpretation is supported by the almost complete disappearance of this band in A, B and C, in which E_0 was perpendicular to the c axis. The small residual was probably introduced by the nonaxial rays in the light cone, whose vibrations had small components parallel to c.

The doublet 1.735, 1.763μ is excited by vibrations both perpendicular and parallel to the CH_2 bisector, but with the greater intensity

when these are perpendicular. The two components of the double band are about equal under all circumstances. Because of these facts the components must involve Fermi resonance between $2\nu_\sigma$ and $4\delta_\pi$, i.e., the first asymmetric valence overtone and the third deformation overtone. Equality of intensities indicates perfect superposition of $2\nu_\sigma$ and $4\delta_\pi$. Record F, taken with unpolarized light and randomly arranged small crystals, shows that the total absorption in B and C is greater than in A. This is reasonable because, although B and C were excited primarily through $2\nu_\sigma$-type vibration, the σ-type electric moment change should be greater than the valence π-type. Indeed, it is surprising that the 1.703μ $2\nu_\pi$ band should be as intense as it is. The corresponding water vapor band is not observable even in the fundamental, and its first overtone is ruled out by the selection rules deduced by Mecke.[9] According to these selection rules only $(\nu_\sigma+\nu_\pi)$ and $4\delta_\pi$ should be expected in this region. But it is impossible for us to correlate the bands at 1.7μ on the basis of the rules and so we conclude that they do not hold in such a CH_2 unit which forms part of a larger structure. Furthermore, the conclusion of Fox and Martin[10] that ν_σ is greater than ν_π, deduced from a consideration of ethylene, C_2H_4, as two coupled CH_2 oscillators, does not seem to hold in this instance. The one other assignment to the bands near 1.7μ which is consistent with the polarizations is: $1.703\mu=4\delta_\pi$; $[1.735, 1.763\mu]$ $=[2\nu_\sigma, 2\nu_\pi]$. This would still violate Mecke's selection rules but would not depart as much from the conclusions of Fox and Martin as our former assignment does. However, we shall see that only the former is consistent with the observations at 2.3μ.

1.7μ CH_2 ABSORPTION OF DIKETOPIPERAZINE

Diketopiperazine,[2] $(CH_2NHCO)_2$, forms a monoclinic crystal with the planes of the flat ring molecules as well as the symmetry axes of the two CH_2 groups per molecule parallel to the b axis and lying approximately in the $(1\,0\,1)$ plane. Fig. 2, I was obtained with the beam and E_0 parallel, respectively, to the c and b axes in a 0.60-mm specimen. H and G were secured

with the beam parallel to b and with E_0 vibrating, respectively, perpendicular and parallel to the $(1\,0\,1)$ plane in a 0.78-mm section. Since the planes of the two CH_2 groups are parallel to each other and perpendicular to the $(1\,0\,1)$ plane, greater σ-type excitation should occur in H than in G. In fact, it should be absent in G. We associate the residual 1.745μ band in G with imperfect alignment of the crystal and to the nonparallelism of rays in the beam.

Our interpretation of the 1.703, 1.745 and 1.754μ bands is similar to that for pentaerythritol. 1.703μ represents $2\nu_\pi$. 1.745μ and 1.754μ are essentially $2\nu_\sigma$ and $4\delta_\pi$. There is probably some Fermi resonance between these two states, since there seems to be evidence of 1.754μ absorption on the long wave side of 1.745μ in H. But the great intensity dependence upon polarization, as shown by G and H, indicates that this is slight. The small band between 1.703μ and 1.745μ, showing most plainly in I, we believe does not belong to the CH_2 groups. We shall discuss this band later.

THE ANHARMONICITY CONSTANTS OF THE CH_2 VIBRATORS

We can make use of the double absorption band at 2.3μ in pentaerythritol, long known[11] as an absorption region common to all hydrocarbons, to strengthen our identification of σ- and π-type vibrations in CH_2. This band shows particularly well in Fig. 2, E, obtained with unpolarized light and powdered crystals. To offset the great loss of transmitted intensity in the short wave region resulting from Rayleigh ν^4 scattering, the slit widths were greatly increased. Since unpolarized light was used there has been no distortion of relative intensities. Thus, the absorption in 2.285μ is greater than in 2.313μ. When E_0 vibrates along the CH_2 symmetry axis, as in 2, D, relative intensities are reversed. We thus identify 2.313μ with $3\delta_\pi$ and 2.285μ with $\nu_\sigma+\delta_\pi$. To account for the appearances of both components in 2, A–C, with E_0 perpendicular to the symmetry axis, it is necessary to assume a considerable amount of Fermi resonance, although not as much as in the 1.75μ bands.

[9] R. Mecke, Zeits. f. Physik **81**, 313 (1933).
[10] Fox and Martin, Proc. Roy. Soc. **167A**, 257 (1938).

[11] J. W. Ellis, Phys. Rev. **23**, 48 (1924).

By assuming that 5720 cm^{-1}, i.e., the average wave number of the 1.735 and 1.763μ bands, represents the first overtone of ν_σ as well as the third overtone of δ_π and that 4320 cm^{-1} (2.313μ) and 4375 cm^{-1} (2.285μ) represent the second overtone of δ_π and $\delta_\pi + \nu_\sigma$, respectively, it is possible to calculate approximately the fundamental values of ν_σ and δ_π as well as the magnitudes of the anharmonicity constants. The reasonableness of these latter values serves as a further check on our identifications. To make these calculations the wave mechanics energy expression is used:

$$E = (v+\tfrac{1}{2})\omega_0 - (v+\tfrac{1}{2})^2\omega_0 x = (v+\tfrac{1}{2})\omega_0 - (v+\tfrac{1}{2})^2\epsilon.$$

From this there is obtained for the wave numbers:

$$\nu = (v_2 - v_1)(\omega_0 - \epsilon) - (v_2{}^2 - v_1{}^2)\epsilon$$

or since v_1 equals 0 in each instance involved,

$$\nu = v(\omega_0 - \epsilon) - v^2\epsilon = v\omega' - v^2\epsilon.$$

By substitution of the appropriate data there are obtained:

$$\nu_\sigma = \omega_\sigma' - \epsilon_\sigma = 2915 \text{ cm}^{-1}$$
$$\delta_\pi = \omega_\delta' - \epsilon_\delta = 1460 \text{ cm}^{-1}$$
$$\epsilon_\sigma = 55 \text{ cm}^{-1}; \qquad \epsilon_\delta = 10 \text{ cm}^{-1}.$$

Assuming that $\epsilon = 55$ is also approximately correct for ν_π, we obtain:

$$\nu_\pi = 2985 \text{ cm}^{-1}.$$

To compare with δ_π, ν_σ and ν_π these are the values from Nayar's[8] Raman spectrum data: 1474, 2923 and 2961 cm^{-1}. The 2961 cm^{-1} line is stronger than the 2923 cm^{-1} one, as is expected for a ν_π vibration in the Raman spectrum. $\epsilon_\sigma = 55$ cm^{-1} may be compared with the value $\epsilon = 62$ found, for example, for cyclohexane and hexane.[12] $\epsilon_\delta = 10$ cm^{-1} may be compared with 17 cm^{-1} obtained from Mecke's[10] values for δ_π and $2\delta_\pi$ in the similar molecule, water vapor.

OTHER CH$_2$ BANDS OF PENTAERYTHRITOL

Bands at 1.19μ and 1.38μ are well-known hydrocarbon bands, but lack of resolution prevents them from revealing any information of value.

Two interesting doublets are found with centers at 4190 cm^{-1} (2.372, 2.397μ) and at 4030 cm^{-1} (2.467, 2.490μ). These have displacements of 1285 and 1125 cm^{-1}, respectively, from the center of ν_σ and $2\delta_\pi$. They are assumed to represent combinations of $(\nu_\sigma, 2\delta_\pi)$ with two active frequencies of the C(CH$_2$OH)$_4$ structure. In Nayar's data 1281 and 1130 cm^{-1} may be identified as these fundamental frequencies.

TWINNING IN PENTAERYTHRITOL CRYSTALS

It should be pointed out that two records, not shown in Fig. 2, obtained with a needle-like crystal of pentaerythritol, gave results apparently quite contradictory to all the others. Ernst[4] makes it quite clear that the crystals of this shape are far from single crystals. Twinning has resulted in a long skeleton pile of smaller crystals with their c axes perpendicular to the length of the needle. The deception is introduced by the fact that a final single crystal, with its c axis at right angles to all the others, caps the pile.

"NH" ABSORPTION OF DIKETOPIPERAZINE

The study of diketopiperazine originated in an examination of the spectra of proteins.[13] There is a remarkable display of pleochroism in the region 1.9–2.6μ, but we make no attempt to analyze this complex region. We do wish to point out, however, that the absence of a clear-cut strong NH absorption band at 1.5μ strongly supports Corey's[2] assumption that there is electron resonance among four different structures in the (CH$_2$NHCO)$_2$ molecule. So far as the NH groups are concerned there is resonance between a normal NH state and an ionized NH state. We associate the broad structured absorption running from 1.55μ into the 1.7μ CH$_2$ bands with this resonating NH condition. This great departure from normal NH absorption represents more than a hydrogen bond perturbation, as our study[13] of water bound to protein shows.

[12] J. W. Ellis, Phys. Rev. **33**, 27 (1929).

[13] Ellis and Bath, J. Chem. Phys. **6**, 723 (1938).