The Near InfraRed Absorption Spectrum of Sucrose Crystals in Polarized Light

Joseph W. Ellis and Jean Bath

LETTERS TO THE EDITOR

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A considerable amount of work has been done by different investigators upon the absorption of polarized infra-red waves in *inorganic* crystals. But little, if any, of this sort of work has been done with *organic* crystals. In the present study plane polarized waves in the region $0.8-2.5\mu$ were sent through two specimens of sucrose crystals, 2.26 and 0.92 mm thick, respectively. Sucrose belongs to the hemimorphic hemihedral class of the monoclinic system having three axes of unequal lengths, one perpendicular to the plane of the other two. The b axis, a twofold axis of symmetry, is perpendicular to the plane made by the a and c axes which make an angle β of $103°\ 30'$ with each other. The crystals were placed one at a time directly before and in contact with the slit of the recording spectrograph, with the b axis vertical and the c axis horizontal and with the rays traveling approximately along the a axis. Polarization was accomplished by using a Glan-Thompson prism. Because this prism transmits the extraordinary ray only, the absorption bands produced by the calcite of the prism are not strong in spite of the 5 cm length of the prism. Records were obtained with each specimen with the light polarized parallel to the b and the c axes. Complications arising from optical rotation are negligible. The following features of interest were revealed.

(a) Relatively sharp bands at 1.44μ and 0.98μ, regarded as first and second overtones, indicate that unperturbed OH groups exist in the crystal lattice. These bands have greater intensities when the electric vector of the wave oscillates along the b axis than when along the c axis. Assuming that the electric moment with which the light vector interacts is localized in the OH group and that the magnitude of the interaction depends upon the square of this moment, and taking into account the logarithmic law of absorption, one can estimate that there is a 50 percent greater alignment of unperturbed OH groups along the b axis than along the c axis.

(b) A broad doublet band with components of nearly equal intensities at 1.51μ and 1.58μ is regarded as the perturbed counterpart of the 1.44μ band. The 1.51μ and 1.58μ bands, separated respectively from the 1.44μ band by wave number intervals $\delta = 320$ cm^{-1} and $\Delta = 620$ cm^{-1}, are regarded as arising from OH oscillators perturbed through hydrogen bridges, the H of the bridge belonging to the OH oscillator in the latter instance and to another OH group in the former instance. This interpretation arises from the perturbation concepts put forth by Cross, Burnham and Leighton[1] in connection with their interpretation of the Raman spectrum of water. These authors regard the water vapor molecule as two coupled OH oscillators, and regard liquid water molecules as coupled OH oscillators perturbed in the δ and Δ manners indicated above. It is interesting to note that the ratio $\Delta : \delta$ has approximately the $2 : 1$ value assumed by Cross, Burnham and Leighton. The larger magnitudes of the perturbations found here are believed to arise, not because of any great difference in the nature of the H bridge, but rather because of the greater amplitudes involved in the *overtone* vibrations than in *fundamental* vibrations. This remark is based upon a comparison of the widths of fundamental and overtone absorption bands of water, and also upon a pronounced difference in the fundamental[2] and overtone[3] regions of the wave number separations between the bands characteristic of associated and unassociated alcohol molecules.

The 1.51μ component of the sucrose spectrum shows greater absorption when the light vector vibrates along the b axis, but the 1.58μ one remains about the same for both types of polarization. This difference in behavior indicates separate origins for the two broad components, an interpretation which is consistent with the explanation given above.

There is a striking similarity between the bands of (a) and (b) and the bands in the spectra of the alcohols,[3] and a corresponding perturbation explanation seems possible with liquid alcohols.

(c) The 1.7μ absorption band associated with CH groups in gaseous and liquid molecules also appears in these spectra of sucrose crystals. It has, in this instance, four main components and the ratios of intensities among the components alter with a change in the plane of polarization.

The spectroscopic evidence for the existence of both free and perturbed OH groups is in good agreement with the model for the arrangement of the sucrose molecules in the unit cell as suggested by x-ray crystal analysis.[4] The sucrose crystal has been found to have two molecules per unit cell, the dimensions of which are $a_0 = 11.06$A, $b_0 = 8.84$A and $c_0 = 7.76$A and $\beta = 103°\ 30'$. On the basis of the asymmetry of the molecule, the number of molecules in the unit cell and the halving of the 0 1 0 plane, sucrose is placed in the space group C_2^2, in which case there should be a molecule of sucrose located at one point in the lattice and another rotated through 180° at half the unit distance

from this along the b axis. Chemical evidence indicates that the most probable structure for sucrose is α-glucopyranose-β-fructofuranose. Using the three criteria of cell dimensions, space group symmetry and cleavage planes this molecule is found to fit into the unit cell best with its long axis parallel to the short diagonal of the unit cell, i.e., the $\bar{1}\,0\,1$, and the flat sides of the rings parallel to the $0\,1\,0$. In such an arrangement the hydroxyl groups between the flat rings of adjacent molecules along the b axis approach to within 2.5–3A of each other. This at once suggests the existence of hydrogen bridges along the b axis between adjacent molecules, a view which is substantiated by the fact that cleavage planes parallel to the $0\,1\,0$ do not occur. On this basis it is possible to compute that there are in the unit cell probably about four free OH groups and twelve OH groups perturbed by hydrogen bridges, six each in the Δ and δ manners. It is believed that, owing to spatial restrictions within the crystal lattice, only these two types of perturbation occur. Since the hydrogen bridging is assumed to be associated only with OH groups, the numbers perturbed in Δ and δ fashions must be equal. This equality is consistent with the approximate equality in the intensities of absorption in the 1.51μ and 1.58μ bands.

The results of this study indicate that infra-red absorption spectroscopy involving polarized light may be a useful adjunct to x-ray analysis of organic crystal structures. For, the most intense absorption bands, at least in the *near* infra-red, are associated with hydrogen atoms, which are just the ones whose locations x-ray analysis is unable to determine. Of course, infra-red analysis cannot locate single atoms in crystals, but the dependence of intensity of absorption upon plane of polarization should be able to give the relative number of alignments in different directions of specific groups, such as OH groups.

Joseph W. Ellis
Jean Bath

University of California,
Los Angeles, California,
March 14, 1938.

[1] Cross, Burnham and Leighton, J. Am. Chem. Soc. 59, 1134 (1937).
[2] Errera and Mollet, Nature 138, 882 (1936).
[3] Kinsey and Ellis, J. Chem. Phys. 5, 399 (1937).
[4] Unpublished work of J. D. Bath and O. L. Sponsler, University of California at Los Angeles.

The Liquid State

In the description of the liquid state which they are developing, Eyring and Hirschfelder[1] more than once stress the fact that in their theory the *total* free volume in a liquid, as in a gas, is shared by all the molecules; in the entropy of melting of a simple substance the most important term is the contribution R, arising from the fact that the entire free volume is jointly used by all the molecules.

It will be suggested below that we can perhaps obtain a clearer idea of the difference between the liquid and solid states, if we recognize that almost the whole of the additional entropy of a simple liquid arises from the local relationship between a molecule and its neighbors. About
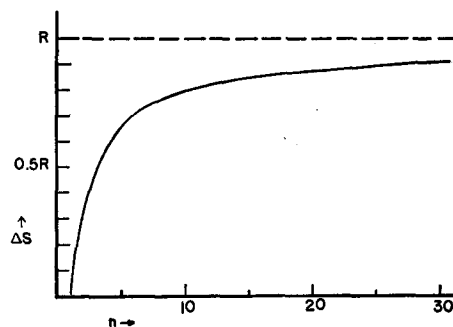

FIG. 1.

nine-tenths of the communal entropy R is due to a purely local sharing of free volume between a molecule and its immediate neighbors—a sharing of free volume which is intimately connected with those small fluctuations, which are impossible in a solid, but which in a liquid permit the viscous flow.

Consider first one mole of a gas contained in a fixed volume in which the partition function of a single molecule is f. Now suppose that by means of numerous partition walls the entire volume is divided into cells of equal size, each containing the same small number n of molecules (less than ten). The partition function for a molecule in any cell is now fn/N, and there are N/n cells. The entropy of the whole gas is

$$(N/n)(n \log (fn/N) - \log n!)k.$$

When there is one particle per cell $(n=1)$, the gas, as Hirschfelder and Eyring[2] have pointed out, is comparable with a solid, its entropy being $Nk \log f/N$. If, starting with $n=1$, we remove a few of the dividing walls, until in each cell n becomes equal to, say, 5, the increase in entropy is given by

$$\Delta S = R\left(\log \frac{fn}{N} - \frac{1}{n}\log n!\right) - R\log \frac{f}{N} = R\left(\log n - \frac{1}{n}\log n!\right).$$

For $n=5$ this already has the value $0.655R$, and Fig. 1 shows how rapidly the value of ΔS rises with increasing n. If the gas is degenerate, $n!$ in the above expressions must be replaced by a number smaller than $n!$, which makes the entropy increase still more rapidly.

These ideas are applicable to a liquid, if in place of the volume we introduce the free volume of the molecules. Inside any one cell the molecules will share their free volume in common. It appears that when each cell contains only 27 molecules the entropy of the liquid already amounts to 90 percent of its value for a liquid with unconstrained molecules.

R. W. Gurney
N. F. Mott

University of Bristol,
Bristol, England,
March 4, 1938.

[1] Eyring and Hirschfelder, J. Phys. Chem. 41, 249 (1937). Kincaid and Eyring, J. Chem. Phys. 5, 587 (1937).
[2] Hirschfelder, Stevenson and Eyring, J. Chem. Phys. 5, 896 (1937).