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tals at higher temperatures will clarify their structural nature and lattice dynamics.

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Tentative Assignment of the 1440-nm Absorption Band in the Near-Infrared Spectrum of Crystalline Sucrose

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The near-infrared spectra of complex molecules, especially those containing oxygen or nitrogen, are normally characterized by regions of broad absorption with

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no sharp features. This arises from the multitude of absorptions which will occur in a complex molecule and because of the peak-broadening effect of hydrogen bond formation. Sucrose is unusual in this respect, because the spectrum (Fig. 1) exhibits a narrow peak at 1440 nm. While the phenomenon has been known for some time,¹ its identity has been a mystery to near-infrared spectroscopists.

A Neotec 6350 Mark I NIR research composition analyzer (Pacific Scientific, Marlow, U.K.) was used to obtain spectra over the range of 1100–2500 nm at 2-nm intervals, which were averaged over 50 scans. The digitized spectra were transferred to a Data General DG10 computer, which operated the NCSTATE near-infrared software.² Sucrose samples ("Silver Spoon," British Sugar, Peterborough, U.K.) were ground with the use of a shatterbox grinder and blender (Glen Creston Ltd., Stanmore, U.K.).

The 1400–1500 nm region of the near-infrared spectrum is generally associated with absorptions due to the first overtone of OH stretch vibration.³ The longer wavelengths are associated with hydrogen bond formation. Sucrose contains eight OH bonds and no other bond which is likely to give rise to absorptions around 1440 nm. While it is generally assumed that the 1440-nm absorption must be due to an OH bond, it was difficult to explain why one (or more) bond should have such a different absorption. The 1440-nm peak only occurs in crystalline sucrose, as indicated (Fig. 1) by the spectrum of a powdered confectionery product (Needlers, glace fruit drops) in which sucrose is present in an amorphous state.¹ Sucrose solutions are similar, in not having any absorption at 1440 nm.

The near-infrared spectrum of methanol exhibits similar behavior.⁴ A 1% solution of methanol in deuteriochloroform (Fig. 2e) exhibits a narrow absorption band at 1398 nm, while the spectrum of pure methanol (Fig. 2d) has absorption bands between 1450 and 1550 nm but no evidence of a peak at 1400 nm. The interpretation of

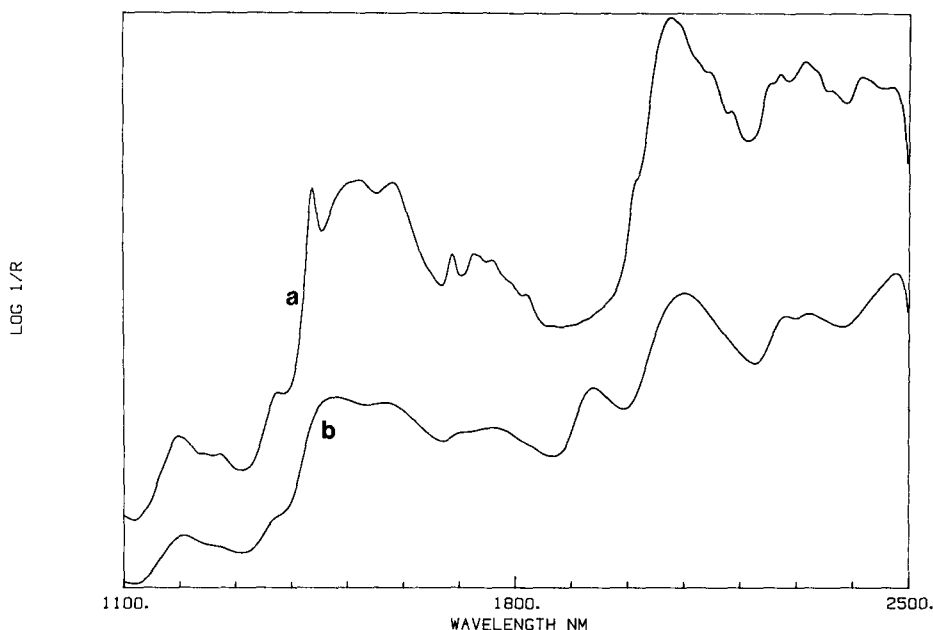


FIG. 1. Spectra of (a) crystalline and (b) amorphous sucrose.

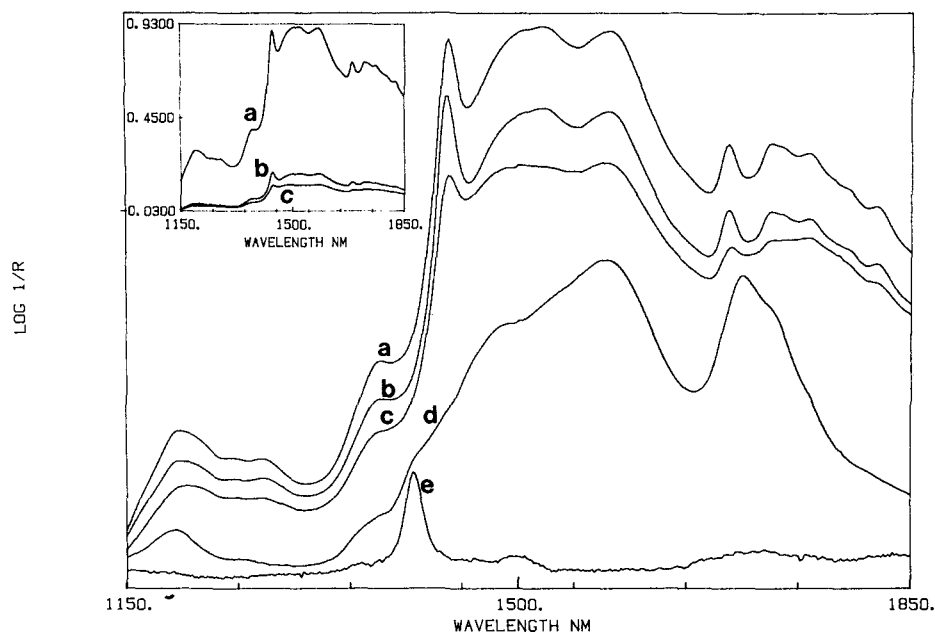


FIG. 2. Spectra of sucrose samples and methanol: (a) unground sucrose; (b) sucrose ground for 30 s; (c) sucrose ground for 10 min; (d) methanol (100%); (e) 1% methanol in deuteriochloroform. The insert shows the three sucrose spectra plotted on the same log 1/R scale. In the main plot the ordinate scale is arbitrary log 1/R units; each spectrum has been scaled to aid comprehension.

this behavior is that, in dilute solutions, in an oxygen-free solvent, hydrogen bond formation is prohibited. This is confirmed by the spectrum of a 1% solution of methanol in water, which also does not show absorption at 1440 nm.

From this evidence it can be suggested that the 1440-nm absorption in sucrose is due to an OH bond which is held in the crystal structure so that it cannot take part in inter- or intramolecular hydrogen bonds. The studies of Brown and Levy^{5,6} proved that the C₄OH bond does not take part in any hydrogen bond formation, and we conclude that this OH bond is the origin of the 1440-nm absorption. Figure 2 shows the effect of grinding on the NIR spectrum of crystalline sucrose. A short period of grinding in a "Shatterbox" considerably reduces the particle size of the crystals. This results in an enhanced reflection and a decreased absorption of NIR energy. The effect is seen as a sharpening of the spectral features, in comparison to those of the original coarse crystalline material; however, on prolonged grinding the 1440-nm band is much weaker than it was in the original spectrum. This effect can be interpreted as being due to hydrogen bond formation when the nonbonded OH is exposed by crystal fracture.

Verification of this hypothesis requires selective sub-

stitution of the C₄OH, and it is hoped that this note will prompt carbohydrate chemists to obtain NIR spectra of these compounds. Several other sugars [e.g., βD(+)-glucose, D(-)-arabinose, L(-)-fructose, and D(-)-mannose] exhibit similar absorption bands around 1440 nm. We would predict that these are also due to the presence of nonhydrogen bonded OH in the crystal structure.

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