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Note

Fourier-transform infrared spectroscopy of sugars. Structural changes in aqueous solutions

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Time-dependent, Fourier-transform infrared (F.-t.i.r.) spectra of glucose anomers in aqueous solution are here shown to provide new information on vibrational bands characteristic of α and β anomers. These results, and the superior quality of spectra obtained, demonstrate the advantages of F.-t.i.r. spectroscopy for identifying the vibrational bands of sugars.

The structural changes of sugars upon dissolution in water have been investigated[1] primarily by polarimetry and nuclear magnetic resonance techniques. These two methods are undoubtedly the most sensitive ones for monitoring the complex structural changes in aqueous solutions of sugars. Vibrational spectroscopy should in principle have equivalent sensitivity to structural changes, as any such changes should affect the molecular vibrations both in terms of vibrational band-positions and intensities. Some practical problems have, however, precluded the use of vibrational spectroscopy. As water, a natural medium for sugars, strongly absorbs i.r. radiation over a large frequency-range, the absorption peaks of sugars are buried in the solvent background. This single problem is the major hurdle in employing i.r. spectroscopy for studying structural dynamics in aqueous carbohydrate solutions. As a result, only such applications as measuring spectra of carbohydrates as pellets or mulls have been reported[2]. Nevertheless one attempt has been made[3] to monitor the mutarotation of glucose anomers in aqueous solution by using a dispersive i.r. instrument.

This article presents the structural changes in aqueous solutions of a sugar as revealed by F.-t.i.r. spectroscopy[4], and reports new i.r. bands characteristic of the α and β anomers of glucose.

Samples (1 g) of α- and β-D-glucose (Sigma Chemical Co.) in weighing bottles were stirred magnetically during addition of 5 mL of distilled water. The solutions were stirred for a few s and aliquots quickly drawn into syringes and transferred into cells having barium fluoride windows and a path length of 25 μm. The cells were placed in the sample compartment of a Nicolet 6000 C F.-t.i.r. spectrometer and data collection was started immediately. A TGS detector was employed and the spectral resolution was 2 cm^{-1}. The interferograms were averaged in blocks of

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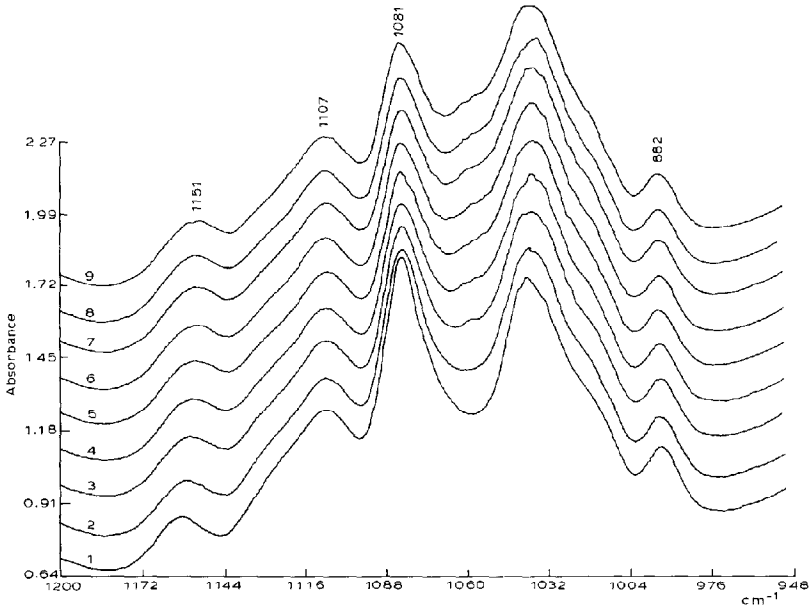

Fig. 1. Time-dependent i.r. spectra of β-D-glucose in aqueous solution. The first spectrum (labeled 1) was recorded 225 s after adding water to glucose. The subsequent spectra, labeled 2, 3, etc., were taken at 15-min intervals. All spectra are plotted on the same scale, except that each spectrum is shifted by one-half division upwards for clarity. The absorbance scale shown relates to the first spectrum.

32 and Fourier-transformed. The time interval between successive data collections was ~15 min.

The spectra in the 1200–950-cm^{-1} region for β-D-glucose in water are shown in Fig. 1. It may be noted that all bands change in intensity to some extent. Of particular significance are the bands at 1081 and 1055 cm^{-1}. The relative intensity of the band at 1080 cm^{-1} decrease, whereas that at 1055 cm^{-1} develops in time (for β-D-glucose). Reverse changes were found in the spectra for α-D-glucose. To give a better perspective, the difference between the last spectrum and the first spectrum is plotted in Fig. 2 for the anomers. The difference spectrum for β-D-glucose may be seen to be the mirror image of that for α-D-glucose.

The formation of a band at 1055 cm^{-1} and the decrease of intensity at 1081 cm^{-1} in solutions of β-D-glucose and the reverse changes for α-D-glucose suggest that these bands are associated with the α and β anomers, respectively. In addition, α-D-glucose in D_2O solution also showed a band centered at 1339 cm^{-1} that de-

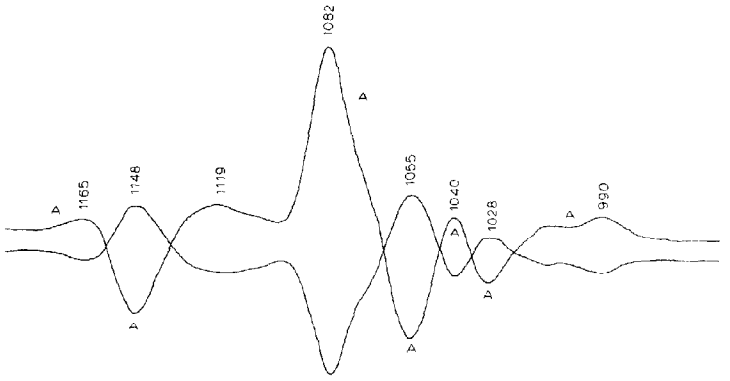

Fig. 2. Difference spectra for β- and α-D-glucose. The trace for β-D-glucose (B) depicts the difference between the last and first spectra shown in Fig. 1. The trace for α-D-glucose (labeled A) was obtained similarly.

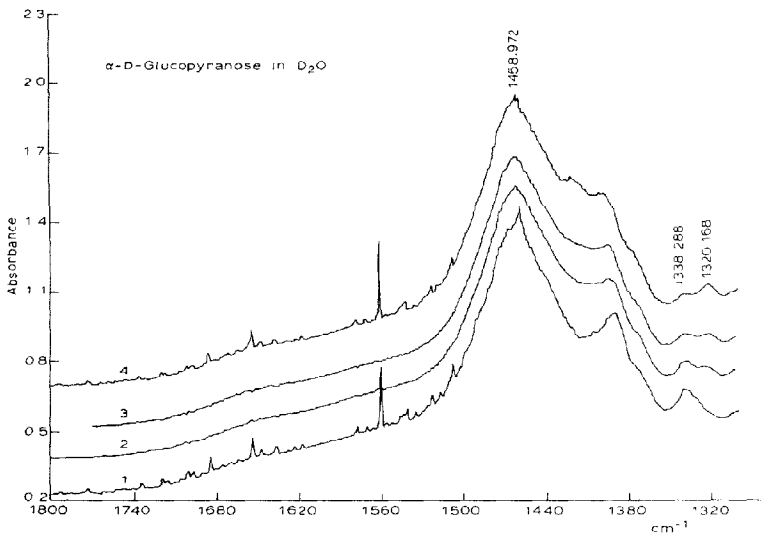

Fig. 3. Time-dependent, i.r. spectra for α-D-glucose in D_2O solution. The spectrum at the bottom was taken immediately after dissolution, and the subsequent spectra were taken after 1, 2, and 19 h, respectively.

creases in time and one at 1320 cm^{-1}, initially absent, that develops with time. These spectra are shown in Fig. 3. For β-D-glucose, the opposite behavior is observed. The bands at 1339 and 1320 cm^{-1} may clearly be considered characteristic of α- and β-D-glucose, respectively.

Earlier i.r. and Raman studies[2,5] showed the bands at 844 and 891 cm^{-1} to be characteristic of α and β anomers. Our F.-t.i.r. spectra in D_2O solution (not shown) indeed confirm this point, despite very weak i.r. absorption of these bands in solution. We have also evaluated the first-order rate constants for mutarotation of the glucose anomers and find them in agreement with those obtained polarimetrically[6]. More-detailed discussion of these results for glucose and also for lyxose will be reported.

These observations indicate that studies in aqueous solution are useful for assigning the vibrational bands of sugars. Reliable assignments are crucial for interpreting the circular dichroism[7] in vibrational transitions currently under investigation[8]. Although Raman spectroscopy has been widely employed and is informative, the new anomer-characteristic bands observed in this study could not be inferred from Raman studies. We conclude that F.-t.i.r. spectroscopy is a powerful technique for identifying the vibrational bands of sugars.

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