Carbohydrate Research, 133 (1984) 313–318
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

The vibrational spectrum and structure of D-fructose in solution

DEREK STEELE, JAGDISH LALL, AND JAGDISH PAMNANI

Department of Chemistry, Royal Holloway College (University of London), Egham, Surrey TW20 OEX (Great Britain)

(Received February 22nd, 1984; accepted for publication, April 5th, 1984)

D-Fructose exists as β-D-fructopyranose in the usual crystalline state[1,2]. However, in aqueous solution, an equilibrium exists between α- and β-pyranoses, α- and β-furanoses, and the open-chain form. U.v.[3], Raman[4], ^{1}H-n.m.r.[5], and ^{13}C-n.m.r.[6,7] spectroscopy have been used to study the equilibrium, as have g.l.c.–m.s.[8,9] and c.d.[10]. Using ^{13}C-n.m.r. spectroscopy, the distribution of the four cyclic forms has been determined at room temperature and the open-chain form detected at 80°, at which temperature its concentration is enhanced. An interpretation of the laser Raman spectra[4] of an aqueous solution of D-fructose was compatible with the n.m.r. data in suggesting ~60% of pyranose and ~40% of furanose forms. No features due to the open-chain form could be detected. However, this analysis does not withstand detailed scrutiny. In principle, vibrational spectroscopy has some merit over the n.m.r. method for studying the designated equilibria, in that the time-scale of separable events is orders of magnitude less. Thus, by Heisenberg's uncertainty principle, bands of interchangeable conformers some 10 cm^{-1} apart will be distinguishable provided the conformers have separate identities for $\tau \geqslant 1/4\pi.\Delta\nu = 2.6 \times 10^{-13}$s. For the n.m.r. method, a comparable time would be about 10^{-5} s.

The bands assigned[4] for aqueous solutions are nearly all present in the spectrum of the D-fructopyranose crystal. Only one band in the skeletal stretching region shows doubling compatible with a second conformer at ~20% concentration. The carbonyl stretch, $\nu_{c=o}$, being a highly polar vibration, gives rise to very weak Raman-scattering, but intense i.r. absorption. This absorbtion for an aqueous solution is compatible with the presence of ~0.9% of the open-chain form.

The Raman spectra of the solid are in good accord with those reported[4,11]. The most striking feature of our observations is the close similarity between the frequencies of the Raman bands for the crystal and an aqueous solution, and also between the frequencies measured in absorbtion and in Raman scattering (see Table I). This similarity is not obvious on a cursory inspection of the spectral traces

0008-6215/84/$ 03.00

TABLE I

VIBRATIONAL SPECTRA FOR D-FRUCTOSE IN THE CRYSTALLINE STATE AND IN AQUEOUS SOLUTION[a,b]

Raman		*I.r. KBr disc*
[ν/cm^{-1} *(int)pol ratio*]	[ν/cm^{-1} *(int)*]	(ν/cm^{-1})
	130	
	237(7)	
	250(12)	
	279(10)	
	289(14)	
	311(5)	
	343(9)	
	397(17)	
420(45)	420(44)	426 w
	427(42)	
458(18)	463(44)	
	469(42)	468 m
525(40)	525(55)	
		569 b,s
594(sh)	594(40)	596 w
629(105)0.11	626(120)	628 s
		684 vb,m
707(23)0.11		
743(3)dp		
781(8)0.5	780(13)	783 s
821(81)0.10	819(77)	819 m
879(125)0.16	874(78)	875 m
918(sh)dp	926(37)	924 m
964(9)0		
979(19)	978(41)	978 vs
1016(3)		
1048(35)0.6	1048(48)	1051 vs
1062(59)0	1060(36)	1062 sh
1083(62)0.42	1080(68)	1080 vs
	1085(sh)	1095 s
		1143 w
1147(9)dp	1143(35)	1150 s
1177(7) } 0.55 1185(10) }	1177(40)	1177 m
	1219(5)	1232 w
1244(sh)pol	1249(40)	1250 w
1267(45)0.59	1264(66)	1267 m
1310(1)dp	1325(8)	
1344(3)dp	1341(18)	1340 s
1376(9)	1372(5)	1362 w
1412(2)dp	1397(15)	1400 m
		1430 m
1459(80)0.53	1454(33)	1450 w
	1471(72)	1471 w

[a]Key: pol, polarised; dp, depolarised; b, broad; w, weak; m, moderate; s, strong; v, very; sh, shoulder.
[b]Intensities are on an arbitrary relative scale.

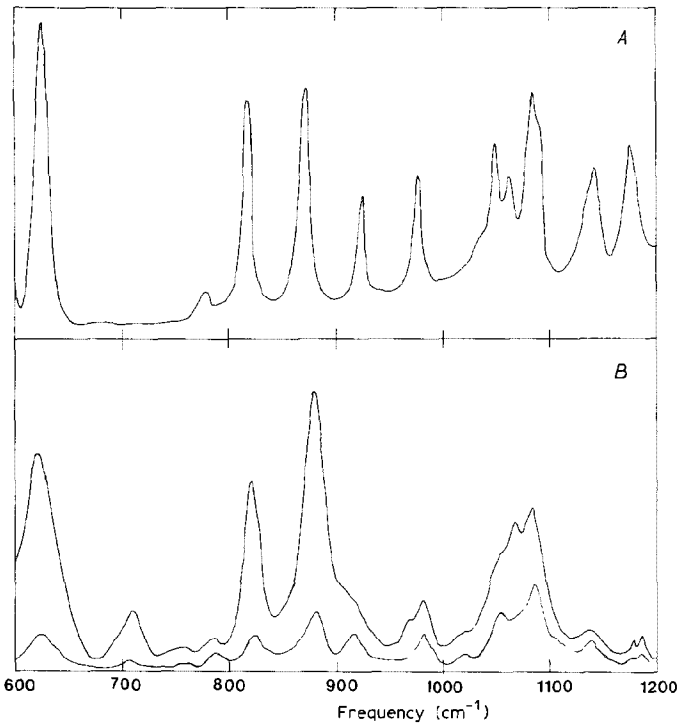

Fig. 1. Raman spectra (600–1200 cm^{-1}) of D-fructose: *A*, polycrystalline solid; *B*, aqueous solution and using polaroid analysers in the scattered beam to give I_{VV} and I_{VH} measurements.

(see Fig. 1). The band widths at half-maximum height are larger for the solution (>20 cm^{-1}) than for the solid (8–12 cm^{-1}). Even so, there is a surprising coalescence of the bands occurring in the solid at 1471 and 1454 cm^{-1}. Since the CH_2 scissoring vibration is involved, this effect must be ascribed to an increased restoring force arising from the crystal packing and change in bonding. In the crystal, the CH_2OH unit is only weakly hydrogen-bonded, giving rise to a ν_{OH} at 3525 cm^{-1}. This weak bonding is due primarily to an O-1–H-1 · · · O-3′ angle of 145°, and the frequency and angle are similar to those occurring in 1,3-diols[12].

The majority of bands (including those at 926, 874, and 460 cm^{-1}) assigned[4] to the fructofuranose form in solution occur for the crystal. The only new Raman-bands that are apparent are a moderately strong band at 707 cm^{-1} and a rather weak band at 1185 cm^{-1}. Thus, the analysis by Mathlouthi *et al.*[4] is in error and the fact that the relative intensities of the 2 bands selected as characteristic of pyranose and furanose forms were of the correct magnitude was entirely fortuitous. The band at 712 cm^{-1} was assigned to the intra-ring CCO vibration and the existence of a comparable band in sucrose was cited. There is a strong similarity[13] in the Raman spectra of aqueous solutions of D-glucose, maltose, cellobiose, and dextran, at least above 600 cm^{-1}. Many of these bands are also apparent in the spectrum of sucrose

(*cf.* Fig. 1 of ref. 11), and the frequencies of the monosaccharide units and their transition moments are not drastically modified on linking to form polysaccharides.

Many of the Raman bands for the crystal, including those at 1454, 1264, 1080, 874, 819, and 626 cm^{-1}, are also prominent for the solution and broadened by no more than a factor of two, but others in the ranges 1350–1300 and 1220–1100 cm^{-1} and near 1000 cm^{-1} are significantly weakened. Dissolution in D_2O further reduced these bands. In the glucose series[13], there were bands at about 1350, 1080, 1020, and 915 cm^{-1}, which were removed by deuteration of the hydroxyl groups. Thus, these bands are extra-ring modes involving significant O–H motion. The relatively low scattering power and the high absorbtion strength of these bands accords with the deformation of a highly polar bond such as C–O or O–H.

Since there is little difference between solution spectra of furanose and pyranose forms of a given carbohydrate, vibrational spectroscopy is of limited potential for studying equilibria of these forms in solution.

We have used the window in the i.r. at 2100–1250 cm^{-1} to estimate the amount of the open-chain form of D-fructose in solution. D-Fructose was deuterated by repeated exchange with D_2O, and a spectrum of a solution in D_2O between CaF_2 plates (using a 0.004-inch spacer) was then recorded. Subtraction of the spectrum for D_2O then gave the spectrum shown in Fig. 2. The band at 1725 cm^{-1} was absent from the spectrum of the solid obtained by deposition on KBr followed by

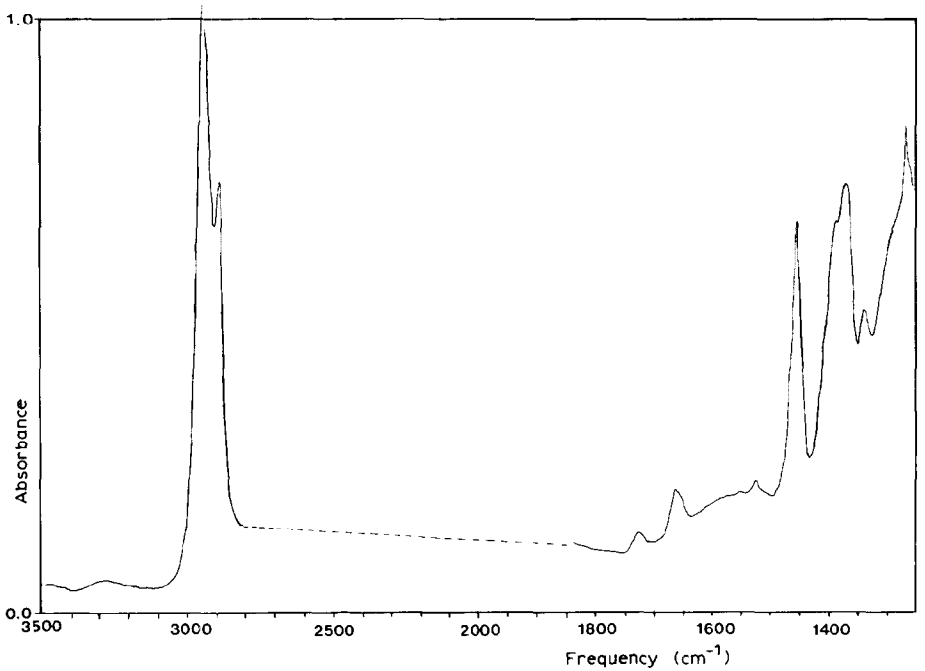

Fig. 2. A redrawn spectrum of a solution of *O*-deuterated D-fructose in D_2O; the section 2800–1900 cm^{-1} was obscured by the solvent.

vacuum removal of the D_2O and conversion into a disc. In order to estimate the percentage of open-chain form present, the relative areas of the CH-stretching and C=O-stretching regions were asumed to be proportional to the relative concentrations of these groupings in fructose and diethyl ketone. For diethyl ketone, the relative area under the absorbance curves for the ketone- and CH-stretching regions was 0.75, and for D-fructose it was 0.00845. Thus, it is deduced that there is ~0.9% of the open-chain form; u.v. measurements suggested[7] ~0.8% and n.m.r. data indicated <1%. Whereas the intensity of the C=O band in ketones is reasonably constant, the intensity of CH-stretching bands is very variable, being significantly less for CH adjacent to hydroxyl groups than for CH in hydrocarbons[14,15], and therefore 0.9% could be rather on the low side.

EXPERIMENTAL

D-Fructose was purified by slow recrystallisation from ethanol. Attempts to reduce a strong fluorescence background by repeated recrystallisation failed. As the quality of spectra obtained was good, despite a background of a similar magnitude to the strongest peak, this fluorescence was tolerated and subtracted in the computer processing. All Raman spectra were recorded using ~1 watt of 5146Å argon radiation. The spectrometer was a modified Coderg PHO with NPL holographic gratings and a cooled EMI photomultiplier. Spectrometer scan control and data processing was effected through a Tektronix 4052 computer. Pulse intervals of 1 s and resolution of 1 or 2 cm^{-1} were used throughout. Polarisations were made by using sheet polaroid analysers in the scattered beam.

I.r. spectra were recorded with a Perkin–Elmer 983 instrument with a PE data station. Aqueous solutions were contained in CaF_2 cells. Spectral data are given in Table I and a section of the Raman spectra is shown in Fig. 1.

ACKNOWLEDGMENT

We thank Mrs. Elizabeth Whitaker for assistance with some of the measurements.

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