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INFRARED AND RAMAN SPECTROSCOPY OF CARBOHYDRATES

PART IV. IDENTIFICATION OF CONFIGURATION- AND CONFORMATION-SENSITIVE MODES FOR D-GLUCOSE BY NORMAL COORDINATE ANALYSIS

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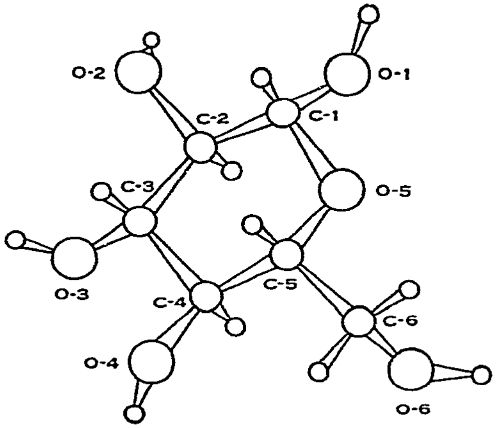
ABSTRACT

A theoretical study of the normal modes of vibration for D-glucose has been made by normal coordinate analysis. The calculated modes for β-D-glucose are shown to be in good agreement with the observed infrared and Raman frequencies, and the computed potential-energy distribution is compatible with previous experimental band-assignments. Lines at 840 cm^{-1} for α-D-glucose and at 898 cm^{-1} for the β-form, which are sensitive to the anomeric configuration, are predicted to occur at 845 and 901 cm^{-1}, respectively. These two modes have been found to be similar, consisting essentially of a C-1–H deformation coupled to a mixed CH_2 vibration. The band in the 1150 cm^{-1} region, which is characteristic of pyranose sugars, is predicted to be a complex ring-mode in each case. Also, the modes that are dependent upon the crystal structure for amylose and cellulose and occur at approximately 1432, 1334, and 1263 cm^{-1} are described as complex vibrations involving CH_2, C–O–H, and C–C–H motions.

INTRODUCTION

In a recent normal coordinate analysis of α-D-glucose, Vasko, Blackwell, and Koenig[1] obtained a reasonable agreement between the calculated frequencies and those observed in the i.r. and Raman spectra. Their results showed that, in the region below 1500 cm^{-1}, most of the normal modes were highly coupled vibrations rather than characteristic group-frequencies. The vibrational spectra of D-glucose, maltose, and cellobiose as well as cellulose, amylose, and dextran are very similar in the region below 1500 cm^{-1}, probably because of the fact that the individual D-glucose repeat-unit is so large that most vibrations arise within the isolated D-glucose residue, with only small contributions arising from inter-residue coupling. In this paper we report the normal coordinate analysis of β-D-glucose and use these results, along with the equivalent data for α-D-glucose, to describe several normal modes of vibration for these molecules. In particular, we are interested in the modes considered to be specific for the anomeric configuration of D-glucopyranose rings, and those modes that have been shown to be sensitive to the conformation of polysaccharide chains.



Formula: Structural formula for β-D-glucose showing the numbering of atoms.

The α- and β-anomers of D-glucose differ only in the configuration at C-1. In α-D-glucose the C-1–H bond is equatorial, whereas it is axial in β-D-glucose; the pyranoid rings are in the *C*1 conformation in each case. Based on i.r. studies of a number of D-glucopyranose derivatives, Barker *et al.*[2,3] assigned bands in the spectra that were considered to be sensitive to the anomeric configuration. They observed that pyranoid sugars show i.r. bands at approximately 844 or 891 cm^{-1}, depending on whether the C-1–H group is equatorial or axial, respectively. It was further suggested that these frequencies were the result of different vibrations of the C-1–H group, as the C-1–O-substituted derivatives likewise exhibited bands in the 844 and 891 cm^{-1} regions. Both glucose anomers and many other pyranose sugars show a band at ~1150 cm^{-1} that is considered to be characteristic of the ring structure[4]. Finally, conformation-sensitive modes involving motions of CH_2OH groups have been identified at 1430 cm^{-1} for cellulose[5] and at 1334 and 1263 cm^{-1} for amylose[6]. The vibrational analysis of the D-glucose monomers has been undertaken in order to determine the vibrational origin of these structure-sensitive modes, and ultimately to extend our knowledge of the structures of the glucan polysaccharides.

EXPERIMENTAL

β-D-Glucose was obtained from the Sigma Chemical Company. The i.r. spectrum was recorded on a Perkin–Elmer model 521 spectrophotometer, and the Raman spectrum was obtained with the instrument described previously[6].

The atomic coordinates for β-D-glucose used in this work were taken from the X-ray diffraction work of Chu and Jeffrey[7]; those for α-D-glucose were from the neutron-diffraction data of Brown and Levy[8]. The force constants used were those previously reported for α-D-glucose[1], (based on the work by Snyder and Zerbi[9] for aliphatic ethers, and Brooks *et al.*[10] for carboxylic acids), except that the following modifications to the force field were made: a force-constant value of 0.105 mdyn-Å was incorporated to describe the (bend–bend) interaction between the two HCC bends of the C-5–CH_2–OH group, instead of the value 0.012 mdyn-Å used previously. In addition, an assigned value of 0.011 mdyn-Å was made to describe the bend–bend interaction between <OCO and <COC for C-5–O-5–C-1–O-1, with C-5–O-5 and C-1–O-1 gauche (namely, in α-D-glucose). A value of −0.011 mdyn-Å was used when these same bonds were trans (namely, in β-D-glucose). These changes in the force constants produced small changes in the calculated frequencies, but should not have significantly affected the potential-energy distribution for α-D-glucose as reported by Vasko *et al.*[1]. Fuhrer *et al.*, in calculations for cyclohexanone[11], made much larger changes in their force field, which altered the calculated frequencies but had only a small effect on the potential-energy distribution, that is so say, on the coupling of the atomic vibrations. The calculations for α- and β-D-glucose were made for the isolated molecules without consideration of the intermolecular effects, except that the force constants for the stretching and deformations of the hydroxyl groups were taken from work involving hydrogen-bonded molecules[10].

The vibrational frequencies, potential-energy distribution, and the Cartesian displacement-coordinates were calculated by using the normal coordinate analysis program written by Boerio and Koenig[12]. All calculations were performed on a Univac 1108 computer.

Calculations were made on the following structures:

(*1*) α-D-glucose by using the modified force-field and atomic coordinates of Brown and Levy[8].

(*2*) β-D-glucose by using the atomic coordinates of Chu and Jeffrey[7].

Small but significant differences are detected in the puckering of the pyranoid rings of α- and β-D-glucose. Differences also occur in the orientations of the CH_2OH and OH groups in the two structures. In particular, in α-D-glucose the C-6–O-6 bond is gauche to C-5–O-5 and trans to C-4–C-5 (the *gt* conformation[13]). In β-D-glucose, however, the CH_2OH group is arranged with C-6–O-6 gauche to both C-4–C-5 and C-5–O-5 (the *gg* conformation). In the analysis it was not possible to separate effects due to different anomeric configurations from those due to different conformations for the ring and pendant side-groups. For these reasons, we calculated frequencies for the following additional structures:

(*3*) α-D-glucose modified only by changing the configuration at C-1 to that for β-D-glucose.

(*4*) α-D-glucose with the CH_2OH disposition changed from *gt* to *gg*.

(*5*) α-D-glucose with the CH_2OH disposition changed from *gt* to *gg* and the configuration at C-1 changed to the β-structure.

RESULTS AND DISCUSSION

The Raman spectrum of β-D-glucose in the regions 3000–2800 cm^{-1} and 1500–100 cm^{-1} is shown in Fig. 1. The frequencies observed in the i.r. and Raman spectra

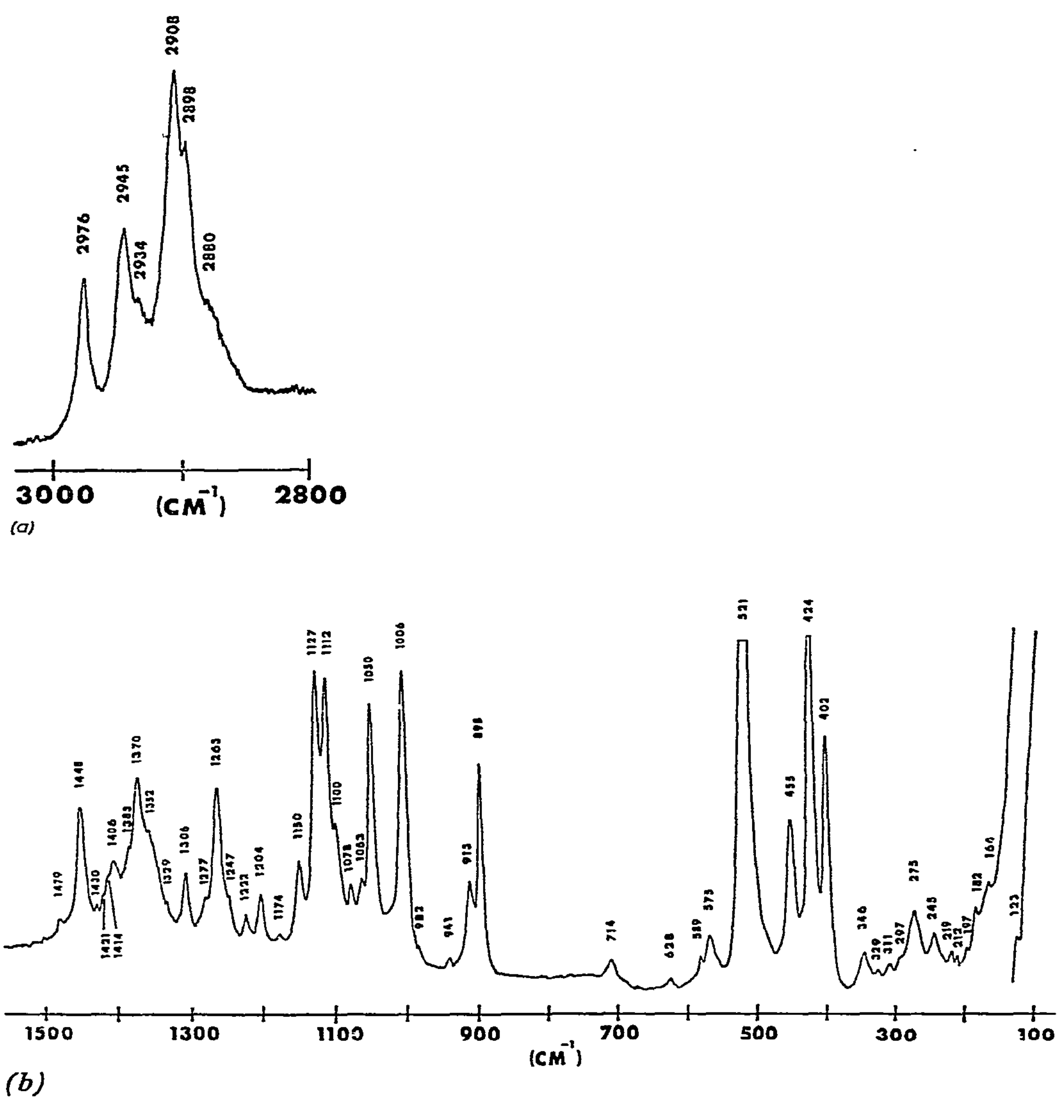


Fig. 1. Raman spectrum of crystalline β-D-glucose in the region 3000–2800 cm^{-1} (*a*) and 1500–100 cm^{-1} (*b*). The spectrum was recorded by using the 514.5-nm exciting line, with a time constant of 4 sec and slit widths of 50 μm.

for this material are listed in Table I, where they are compared to the frequencies calculated by using the coordinates of Chu and Jeffrey[7]. It can be seen that reasonably good agreement has been obtained between the observed and calculated frequencies. It should be emphasized that we are not suggesting at this time a rigorous one-to-one correspondence between the large number of observed and calculated fundamentals as shown in Table I. Verification of the agreement between theory and experiment will ultimately require the observed and calculated data for a more comprehensive range of deuterated analogues. The present analysis has utilized some deuteration results as a means for correlating a few of the observed frequencies with the calculated modes, and in these particular instances reasonable agreement was attained. In addition, no modes were calculated for β-D-glucose in the region 887 to 715 cm^{-1}; this result may afford a measure of the reliability of the calculations, as no frequencies are actually observed in this region in either the i.r. or the Raman spectra. Table II lists the calculated frequencies and potential-energy distribution for β-D-glucose as

TABLE I

COMPARISON OF OBSERVED AND CALCULATED FREQUENCIES FOR β-D-GLUCOSE

Observed frequencies (cm^{-1})		*Calculated frequencies (cm^{-1})*	*Observed frequencies (cm^{-1})*		*Calculated frequencies (cm^{-1})*
I.r.	*Raman*		*I.r.*	*Raman*	
		3399		1100 w, sh	1100
3550 m, br[a]		3398	1082 s	1078 w	1083
3400 m, br		3398		1063 w	
3350 s, br		3397	1050 w, sh	1050 vs	
3220 s, br		3397	1035 s, br		1038
2978 w, sh	2976 m	2979	1015 s, br	1006 vs	1017
2950 w, sh	2945 m	2945		982 w, sh	989
		2942		941 vw	973
2934 m	2934 w, sh	2937	915 m, sh	913 m	901
	2908 vs	2932	903 s	898 s	887
	2898 m	2930			
	2880 m, sh	2889			
	1479 vw	1492	710 m	714 w	715
1451 m	1448 m	1450	638 m	628 w	632
		1444	595 m	589 w	581
		1440	575 w, sh	575 m	571
1425	1430 vw	1429	523 w	521 vs	506
	1421 w, sh	1418	460 m	455 m	441
1411 w	1414 w, sh	1410	422 w	424 vs	416
	1406 m	1400	403 w	402 s	393
	1383 w, sh	1381	355 w	346 w	343
1372 s	1370 s	1364	323 m	329 vw	329
1350 w, sh	1352 m	1338	300 m	311 vw	307
	1329 w, sh	1325	292 w, sh	297 w, sh	293
1310 m	1306 m	1307	275 vw	275 m	281
1275 m	1277 w, sh	1280	262 vw		265
	1263 m	1254		245 w	244
1250 m, br	1247 w, sh	1250			233
1225 m, br	1222 w	1228		219 vw	220
1205 w, sh	1204 w	1209		212 vw	217
	1174 vw	1176		197 w, sh	210
		1156		182 w, sh	141
1150 s	1150 m	1150		164 w, sh	97
1130 w, sh	1127 vs	1125		123 w, sh	72
1112 m	1112 vs	1106			66

[a]Key: s, strong; m, medium; w, weak; vs, very strong; vw, very weak; sh, shoulder; br, broad.

TABLE II[a]

CALCULATED FREQUENCIES FOR α- AND β-D-GLUCOSE WITH POTENTIAL-ENERGY DISTRIBUTIONS

Calculated frequencies (cm^{-1})		*Approximate potential energy distribution[a] (β-D-glucose)*
α-D-glucose	*β-D-glucose*	
3398	3399	OH(100)
3398	3398	OH(100)
3398	3398	OH(100)
3398	3397	OH(100)
3397	3397	OH(100)
2985	2979	CH(98)
2944	2945	CH(98)
2940	2942	CH(99)
2937	2937	CH(99)
2934	2932	CH(99)
2930	2930	CH(100)
2884	2889	CH(100)
1473	1492	CCH(14), HCH(30), OCH(61)
1439	1450	CCH(49), OCH(55)
1404	1444	CCH(57), OCH(29)
1366	1440	CCH(50), OCH(38)
1360	1429	CCH(40), HCH(20), OCH(35)
1359	1418	CCH(61), OCH(34)
1347	1410	CCH(22), OCH(45), COH(36)
1335	1400	CCH(46), OCH(63)
1329	1381	CCH(48), OCH(38), COH(17)
1320	1364	CCH(44), OCH(54), COH(10)
1315	1338	CCH(23), OCH(58), COH(24)
1298	1325	CCH(26), OCH(58), COH(14)
1290	1307	CCH(48), OCH(17), COH(29)
1259	1280	CCH(47), OCH(30), COH(26)
1244	1254	CC(19), CCH(28), OCH(15), COH(37)
1228	1250	CC(11), CCH(30), OCH(12), COH(42)
1215	1228	CCH(14), OCH(20), COH(42)
1204	1209	CO(14), CC(18), CCH(12), OCH(16), COH(35)
1194	1176	CO(47), CC(21), COH(20)
1155	1156	CO(73), CC(10), COH(14)
1127	1150	CO(55); CC(30), CCC(11), CCO(10), COH(14)
1117	1125	CO(54), CC(53), CCO(10), COH(14)
1106	1106	CO(72), CC(17), COH(20)
1086	1100	CO(37), CC(40), CCO(11), COH(25),
1083	1083	CO(47), CC(29), CCO(11), COH(44)
1053	1038	CO(45), CC(19), CCO(20), COH(14)
1025	1017	CO(40), CC(47), CCO(11)
1000	989	CO(42), CC(31), CCO(17)
945	973	CO(42), CC(39), CCO(19), CCH(10)
901	901	CO(18), CC(20), CCO(10), CCH(44)
845	887	CO(44), CC(33), CCH(19)
732	715	CCO(48), CCH(19)
624	632	CCO(62), CCH(21)
613	581	CO(15), CCO(47), CCH(15)
535	571	CC(11), CCC(12), CCO(35), CCH(19), OCO(14)
529	506	CO(14), CC(22), CCO(39), CCH(15)
439	441	CC(12), CCC(23), CCO(30), CCH(14)
426	416	CO(11), CC(12), CCC(17), COC(13), CCO(20), CCH(10)
393	393	CCC(19), CCO(44), CCH(14)
358	343	CCO(70), CCH(11), CO(τ)[b](11)
316	329	CC(11), CCO(34), OCO(18), CO(τ)(14)

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[a] The percentage may be greater or less than 100 percent because of contributions of off-diagonal terms of the force-constant matrix. [b] Torsional vibration.

TABLE II (*continued*)

Calculated frequencies (cm^{-1})		*Approximate potential energy distribution*[a] (*β-D-glucose*)	*Calculated frequencies* (cm^{-1})		*Approximate potential energy distribution*[a] (*β-D-glucose*)
α-D-glucose	*β-D-glucose*		*α-D-glucose*	*β-D-glucose*	
308	307	CCO(63), CO(τ)(16)	219	217	CCO(13), CO(τ)(76)
294	293	CCO(19), CO(τ)(68)	200	210	CCO(17), CO(τ)(78)
252	281	CCO(52), CCH(33), CO(τ)(12)	127	141	CCC(17), COC(21), CCH(15), CCO(30)
249	265	CCC(19), COC(10), CCO(25), CO(τ)(21)	98	97	CCC(36), CCO(16), CC(τ)(40)
236	244	CCO(34), CO(τ)(43)	84	72	CCC(26), CCO(30), CC(τ)(32)
229	233	CCO(10), CO(τ)(77)			
221	220	CCO(15), CO(τ)(74)	62	66	CC(τ)(86)

well as the recalculated modes for α-D-glucose (column 1). Only those individual contributions exceeding 10 percent are listed in the potential-energy distribution.

Configuration-sensitive modes at 898 and 840 cm^{-1}. — The intense Raman line observed at 898 cm^{-1} in the spectrum of β-D-glucose (903 cm^{-1} in the i.r.) has previously been attributed to an axial C-1–H vibration[2,3]. From Table II it is seen that two frequencies were calculated at 887 and 901 cm^{-1} that could correspond to the observed Raman line at 898 cm^{-1}. The Cartesian displacement-coordinates for the two calculated modes are shown in Fig. 2 (the relative displacements are on the same scale, except where indicated). Our results indicated the virtually all of the atoms were displaced for each vibration; however, only the relatively large displacements are shown in these and subsequent figures.

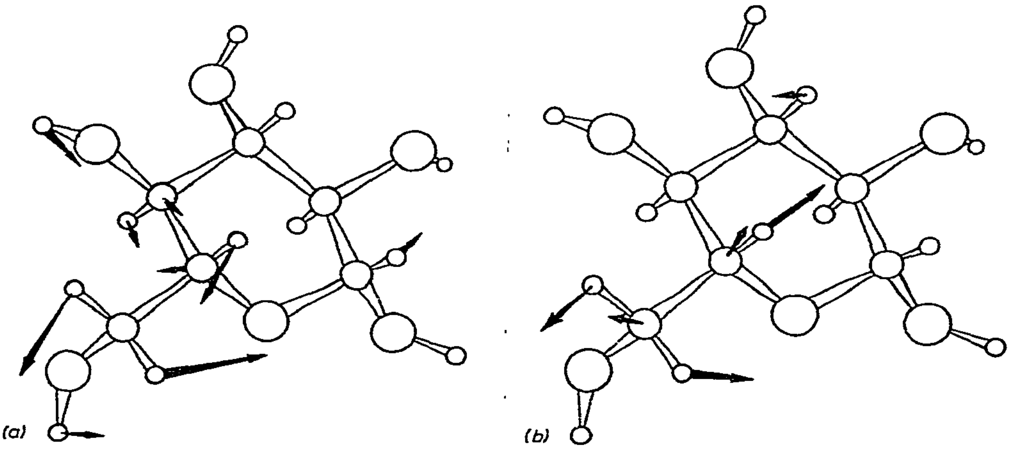

Fig. 2. Atomic displacements for the calculated frequencies of 901 cm^{-1} (*a*) and 887 cm^{-1} (*b*) for β-D-glucose.

The atomic displacements for the calculated frequency of 901 cm^{-1} are shown in Fig. 2*a*; it can be seen that this mode contains coupling of CH_2 and C-1–H motions. Although the C–O–H bending contribution to the potential-energy distribution is less than 10 percent, a noticeable degree of C–O–H bending is revealed at C-4 and C-6. The calculated frequency of 887 cm^{-1} in Fig. 2*b* exhibits coupling of the CH_2 and C-5–H groups with no observed contributions from C-1–H or C–O–H bending. In the deuteration studies of carbohydrates, Vasko *et al.*[14] showed that the Raman line at 890 cm^{-1} for cellobiose in aqueous solution decreases in intensity on changing the solvent from H_2O to D_2O, which indicates a C–O–H bending component for this mode. A similar effect was detected in the i.r. for C-D deuterated cellulose specimens in which the hydrogen atoms of the CH_2 and C-1–H groups had been replaced by deuterium[15]. Furthermore, this same band for cellulose decreases in intensity when the hydroxyl hydrogen atoms are exchanged by deuterium[4]. These observations are consistent with the assignment of the molecular vibration calculated at 901 cm^{-1}, rather than that at 887 cm^{-1}, to the configuration-sensitive line observed at 898 cm^{-1}.

Similar arguments lead to assignment of the characteristic line for α-D-glucose at 840 cm^{-1} in the Raman spectrum (836 cm^{-1} in the i.r.). Vasko *et al.*[1] calculated two frequencies for α-D-glucose in this region, at 836 and 902 cm^{-1}. In the present analysis (Table II, column 1) the same modes occur at 845 and 901 cm^{-1}; fortuitous change of the force constants has achieved a better match for the 840 cm^{-1} mode. The molecular displacements for these two modes are shown in Fig. 3. The mode at

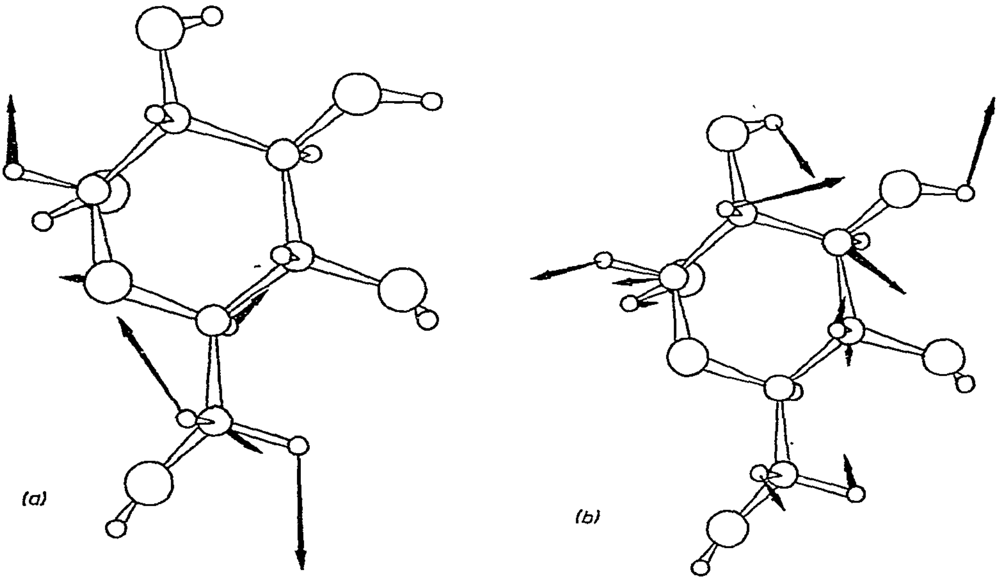

Fig. 3. Atomic displacements for the calculated frequencies of 845 cm^{-1} (*a*) and 901 cm^{-1} (*b*) for α-D-glucose. The displacements are scaled ×2 in (*b*).

845 cm^{-1} (figure 3*a*) shows coupling of CH$_2$, C-1–H, and C-5–H motions, whereas that at 901 cm^{-1} (Fig. 3*b*) contains CH$_2$, C-1–H, as well as several C–C–H bending motions. Also, a considerable C–O–H bending component is present for the 901-cm^{-1} mode, which does not occur for that at 845 cm^{-1}. The Raman lines in the 913-cm^{-1} region of D-glucose, maltose, dextran[14], and amylose[6] have been found to disappear on deuteration of the OH groups. The same band in the i.r. spectrum of α-D-glucose decreased in intensity on deuteration of C-1–H (D-glucose-*1-d*$_1$) and the CH$_2$ group (D-glucose-*6,6-d*$_2$)[14]. Thus the 913-cm^{-1} line contains contributions from C-1–H, CH$_2$, and C–O–H bending motions and can be assigned to the 901-cm^{-1} calculated mode. Only slight intensity-changes for the Raman line in the 840-cm^{-1} region were detected for the glucans in D$_2$O solution; however, the i.r. spectra of D-glucose-*1-d*$_1$ and D-glucose-*6,6-d*$_2$ revealed a decrease in band intensity. Thus the configuration-sensitive mode at 840 cm^{-1} has contributions from C-1–H and CH$_2$ motions but no C–O–H component, and is assigned to the calculated frequency at 845 cm^{-1}.

The molecular vibrations assigned to the Raman lines at 840 and 898 cm^{-1} in α- and β-D-glucose, respectively, appear to be reasonably consistent with previous deuteration assignments[14]. It is seen that the vibrations responsible for these frequencies contain motions of the C-1–H group, thus confirming the original suggestion of Barker *et al.*[2,3]. Also, a considerable degree of CH$_2$ coupling is revealed for both modes, each showing mixing of CH$_2$ twisting and rocking motions. Allowing for the difference in configuration, the two modes can be seen to be very similar, particularly so considering the differences between these modes and those calculated at nearby frequencies. This similarity is further confirmation of the assignments.

On rotation of the CH$_2$OH group from *gt* to *gg* in α-D-glucose, the mode at 845 cm^{-1} shifts to 866 cm^{-1}. However, the molecular vibration at this new frequency is very similar to that for the *gt* form. When the α-D-glucose structure is modified to the β-form but retains the *gt* side-chain disposition, the configuration-sensitive mode is at 903 cm^{-1}, compared to 901 cm^{-1} for Chu and Jeffrey's structure where the CH$_2$OH group is in the *gg* disposition. When the α-coordinates are converted into β with the *gg* side-chain, the mode at 903 cm^{-1} shifts to 880 cm^{-1}. The molecular vibrations, which include CH$_2$ motions, are very similar, despite the change in orientation for this group. Only small frequency-changes are predicted and the configuration-sensitive modes are relatively intensitive to the ring and side-chain conformations.

The 1150-cm^{-1} *mode.* — Fig. 4 shows the molecular vibrations of the calculated frequencies 1155 and 1150 cm^{-1} for α- and β-D-glucose, respectively. This band, which is strong in the i.r. and medium to weak in the Raman spectrum, has been found common to most saccharides; however, its assignment to any particular vibration has been a matter of controversy[4]. In i.r. studies of methyl α-D-glucoside, cycloamyloses, and amylose, this band has been found to be affected by O–H deuteration[16], and similar effects have been detected for cellulose, lactose, and cellobiose[4]. This band has been tentatively assigned by Segal *et al.*[17] as a coupled vibration involving C–O stretching and C–O–H bending modes. As shown in Fig. 4*a*, the mode at

1155 cm^{-1} calculated for α-D-glucose exhibits complex coupling of C–O and C–C stretching with C–O–H and C–C–H bending. The mode at 1150 cm^{-1} calculated for β-D-glucose is shown in Fig. 4*b*, and can be seen to consist of similar coupled motions. The similarity of these two modes and their differences from the modes at adjacent frequencies further confirms their assignment. For example, for β-D-glucose, another mode in this region is calculated at 1156 cm^{-1}; however, this molecular vibration is very different from that calculated for α-D-glucose, and it cannot be described as a true ring-vibration. Thus the 1150-cm^{-1} frequency observed for most saccharide structures is assigned as predominantly a ring-vibrational mode, with some C–O–H and C–C–H bending components.

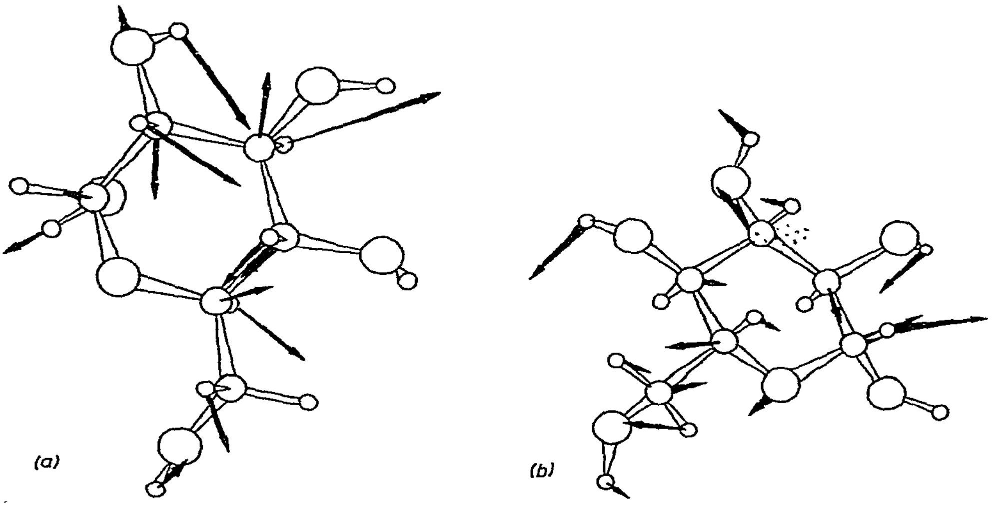

Fig. 4. Atomic displacements for the calculated frequencies of 1155 cm^{-1} for α-D-glucose (*a*) and 1150 cm^{-1} for β-D-glucose (*b*). The displacements are scaled ×2.

Conformation-sensitive modes (for polysaccharides). — In our previous paper on amylose[6], we used the band assignments for α-D-glucose to interpret the spectral changes as V-amylose was converted into the B-form. In the region below 1500 cm^{-1}, a line observed at 1334 cm^{-1} for V-amylose was observed to decrease in intensity, whereas a line at 1263 cm^{-1} was found to shift to 1254 cm^{-1} on conversion of V- into B-amylose. The observed changes were found to be consistent with the proposed mechanism for V→B conversion[18], which involves extension of the amylose 6_1 helix and changes in the intramolecular hydrogen-bonding. The observed lines at 1334 and 1263 cm^{-1} were assigned as complex modes of the CH_2OH group. In the Raman spectrum of deuterated V-amylose[6], a decrease in intensity is observed for the line at 1334 cm^{-1}, indicating a COH contribution to this mode. Similarly, the i.r. band at 1335 cm^{-1} in the spectrum of α-D-glucose is absent from the spectrum of CH_2-deuterated D-glucose[14]. This mode for amylose and α-D-glucose is thus assigned as a complex vibration involving C–O–H bending and CH_2 twisting motions[6]. Figure 5*a* shows the atomatic displacements for the calculated mode at 1335 cm^{-1} for α-D-glucose. This mode is extremely complex, and consists of CH_2 twisting, several C–O–H bendings, and a high degree of C–C–H bending. Assignment of the observed frequency to this mode is certainly consistent with the deuteration data.

In the Raman spectra of D-glucose, maltose, and cellobiose, the Raman line in the 1260–1270-cm^{-1} region was found to decrease during deuterium exchange, whereas that at 1270 cm^{-1} in dextran, an α-D-linked (1 → 6) polysaccharide, showed no effect[14]. It was therefore suggested that this line could be assigned to a C–O–H bending mode of the CH_2OH group. Figure 5*b* shows the atomic displacements for the calculated mode of 1259 cm^{-1} in α-D-glucose. It is seen that this mode contains a far greater degree of coupling than previously observed experimentally; not only does bending of the C-6–O–H group occur, but also all C–O–H groups contribute as well as several C–C–H modes.

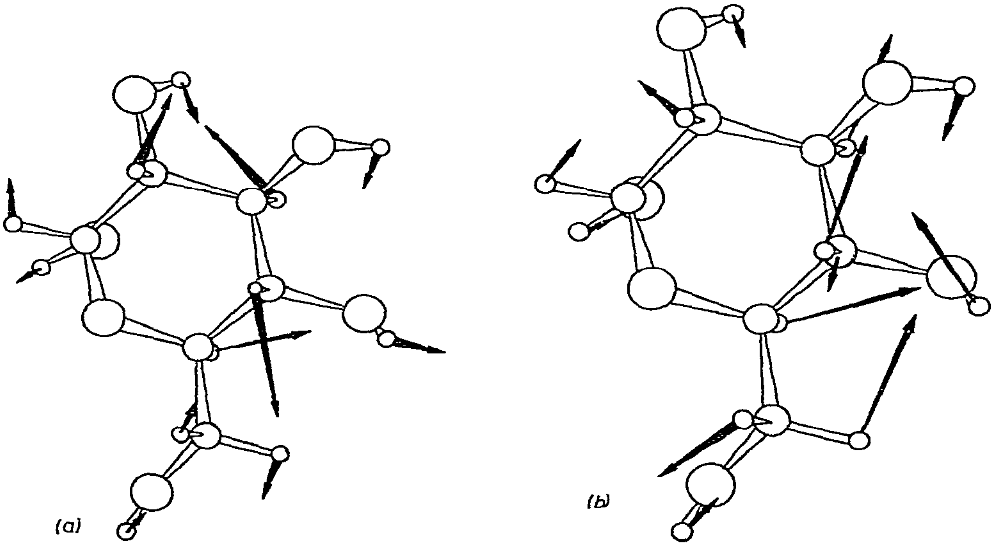

Fig. 5. Atomic displacements for the calculated frequencies of 1335 cm^{-1} (*a*) and 1259 cm^{-1} (*b*) for α-D-glucose.

Studies of polysaccharide spectra have frequently included discussion of bands assigned to CH_2-deformation modes in the frequency region above 1430 cm^{-1}. For example, the band at 1430 cm^{-1} for cellulose has been considered to be due to the symmetric deformation mode of the CH_2 groups[15,19,21,22]. Our present calculations for α-D-glucose show a single mode at 1473 cm^{-1}, which contains a high degree of CH_2 deformation as well as an O–C–H deformation. The atomic displacements are shown in Fig. 6*a*, and this mode is assigned[1] to the observed frequency at 1462 cm^{-1}. Interestingly, for β-D-glucose, two frequencies are calculated at 1492 and 1429 cm^{-1}, which have appreciable CH_2 bending contributions. These two modes are shown in Figs. *6b* and *c*. The observed frequencies are at 1448 cm^{-1} and 1479 cm^{-1} (weak). Furthermore, Michell has observed that the 1440 cm^{-1} band in the i.r. spectrum of cellobiose is split on cooling the sample to liquid nitrogen temperatures, resulting[20] in two bands, at 1495 and 1430 cm^{-1}. Our calculations show that none of these CH_2 modes for the α and β-forms can be considered to be pure CH_2 vibrations.

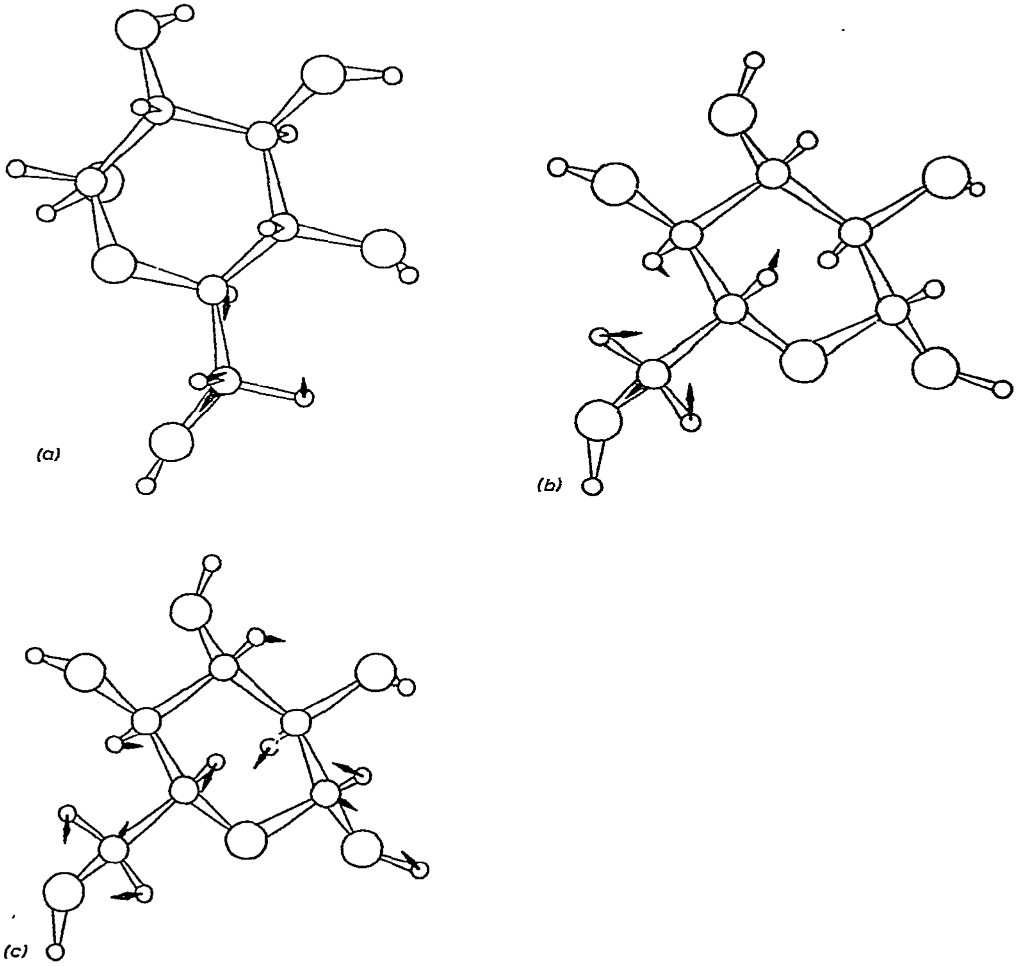

Fig. 6. The atomic displacements for the calculated frequencies of 1473 cm^{-1} for α-D-glucose (*a*), and 1492 cm^{-1} (*b*) and 1429 cm^{-1} (*c*) for β-D-glucose. The displacements are scaled ×0.2.

CONCLUSION

Our results show that, in the region below 1500 cm^{-1}, the degree of coupling present is far greater than previously assumed, and none of the modes arise from a single type of molecular vibration. Similar results have been found by Fuhrer *et al.*, for the chair conformation of cyclohexanone[11]. In their normal coordinate analysis, they considered a mode to be a characteristic group-frequency if, from the potential-energy distribution, there were a component greater than 66%. Of their 45 calculated normal modes, only 8 satisfied this requirement in the region below 1500 cm^{-1}. For α and β-D-glucose, none of the calculated modes in this region can be so classified. This observation necessitates caution in the interpretation of the dichroic behavior of such polysaccharides as cellulose and chitin, where characteristic group-frequencies have been used in the region below 1500 cm^{-1} to determine chain packing, hydrogen-bonding schemes, and the like. We are now using Cartesian displacement-coordinates to determine the direction of the transition moments for the fundamental vibrational modes of glucose. These results will be applied to dichroism data for cellulose, amylose, and other polysaccharides, and should allow for more detailed structural analysis.

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