INFRARED AND RAMAN SPECTROSCOPY OF CARBOHYDRATES.

PART II: NORMAL COORDINATE ANALYSIS OF α-D-GLUCOSE.

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ABSTRACT

A theoretical study of the vibrational spectra of α-D-glucose has been made by normal coordinate analysis. The predicted vibrational frequencies are compared with those observed in the infrared and Raman spectra of α-D-glucose, both as a crystalline solid and in aqueous solution. The computed potential-energy distribution shows that most of the modes are highly coupled vibrations. In most cases, this distribution is compatible with the experimental band-assignments, based on deuterium exchange methods, and the like. Overall, the agreement between the observed and calculated data is considered reasonably satisfactory for a molecule as large as α-D-glucose.

INTRODUCTION

In this series of papers, the infrared and Raman spectra of carbohydrates are examined, in order to obtain information on the chain conformation and crystal structure of several glucans. In paper I, assignments for some of the C–H and O–H modes were made by means of deuterium substitution of model monomers and dimers[1]; this information has been used in interpreting the spectra of polysaccharides, details of which will be published shortly.

It has become increasingly clear that, in the spectra of carbohydrates, many of the lines in the region below 1500 cm^{-1} are due to complex vibrational modes, and that group-frequency assignments are highly suspect. For example, disappearance of a mode when the O–H groups are deuterated, simply means that the mode is due to an O–H *related* vibration. The vibration could be a pure O–H mode, or a complex mode including an O–H contribution, in which case the coupling would be expected to break down on deuteration. In addition, deuteration of the O–H groups may affect the coupling for other modes, with a result that a few bands, which have no apparent O–H contribution, may shift or disappear.

In view of these difficulties, we have made a theoretical study of the α-D-glucopyranose molecule using the methods of normal coordinate analysis. To the best of our knowledge, this is as yet the largest molecule for which such an approach has been used. Only recently has it become possible, with the aid of high-speed computers, to solve a problem of this magnitude. Because of this magnitude, we could not expect to obtain an exact fit between the calculated and observed frequencies. Nevertheless, the results obtained should be valuable for the interpretation of carbohydrate spectra.

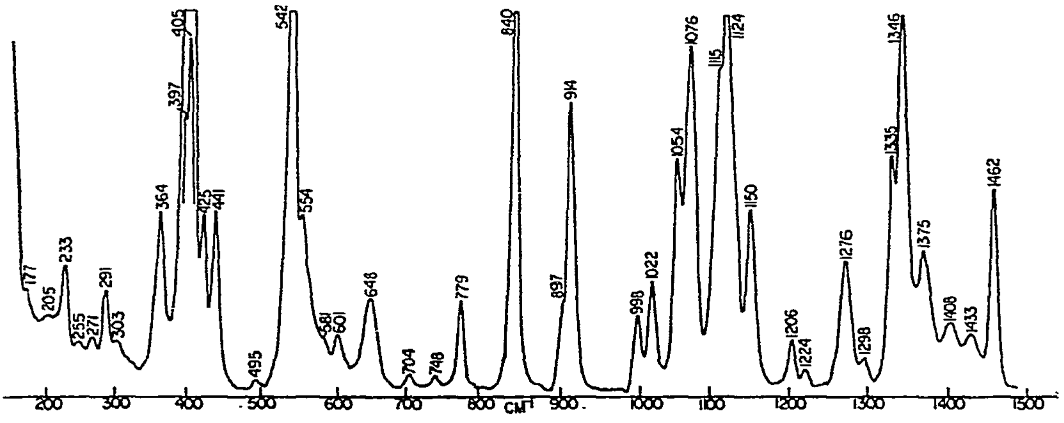


Fig. 1. Raman spectrum for crystalline α-D-glucopyranose.

EXPERIMENTAL

Details of the preparation of specimens of α-D-glucopyranose, in the crystalline state and in solution, and of the apparatus used to record the infrared and Raman spectra, have already been given[1]. The Raman spectrum of crystalline α-D-glucose is shown in Fig. 1. The observed frequencies for the Raman and infrared spectra of crystalline α-D-glucose, and the Raman data for the aqueous solution are collected in Table I.

Computations were made by use of a Univac 1108 computer.

TABLE I

VIBRATIONAL ASSIGNMENTS FOR α-D-GLUCOPYRANOSE

α-D-Glucose (crystalline)		*D-Glucose in solution*	*Deuteration assignment*	*Band assignment*
Raman (cm⁻¹)	*I.r. (cm⁻¹)*	*Raman (cm⁻¹)*		
1462	1457	1461	CH_2	CH_2 (bending)
	1442			
1433	1427			
1408	1402	1405	C-2-H	C–H bending with some O–H bending contribution
1375	1378	1373		
	1369			
	1360		C-1-H	
1346		1349	C–O–H	C–O–H bending
1335	1337	1335	CH_2	CH_2
	1328	1328		
1298	1293	1298		

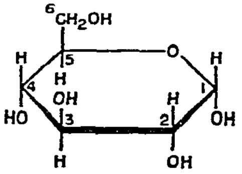
TABLE I (continued)

α-D-Glucose (crystalline)		*D-Glucose in solution*	*Deuteration assignment*	*Band assignment*
Raman (cm^{-1})	*I.r. (cm^{-1})*	*Raman (cm^{-1})*		
1272	1270	1278	C-6–O–H or C-1–O–H	C-6–O–H and/or C-1–O–H related vibration
	1250		C-1–H	C-1–H deformation
1224	1219	1222	CH_2	CH_2
1206	1197	1206		
	1189			C–O and C–C stretchings with C–H, C–O–H deformations
1153		1152		
	1142			
1124		1130		
1115	1116			
	1164			
1076	1076	1071	C-1–H and C–O–H	C-1–H and C–O–H deformation
1054	1047	1041	C-1–H	C-1–H deformation
1022	1026	1020	C–O–H	C–O–H deformation
998	1011		CH_2	CH_2
	988			
914	911	913	C-1–H and C–O–H	C-1–H and C–O–H deformation
897	890	898		C–H vibration for β-form (?)
		859		
840	836	847	C-1–H	C-1–H deformation
779	768	771		
748		747		
	721			C–C, C–O stretchings
704		705		
648	645	633		
	622			
601	603			
581				
554	555			
542		541		
	522	514		Mainly skeletal modes
495		498		
441		443		
425		425		
405		409		
397				
		381		
364				
		342		
303				Torsional modes
294		291		
271				
255				
233				
205				
177				

VIBRATIONAL ASSIGNMENTS FOR α-D-GLUCOSE

The Raman spectrum of crystalline α-D-glucose is very similar to that for D-glucose in aqueous solution; this suggests that there is little or no intermolecular coupling between the vibrational modes of the four molecules in the unit cell of the crystal. In an equilibrated solution in water, the ratio of the α- to the β-anomer is ~1:2, and the presence of the β-form was detected by the increased intensity of the band at 898 cm^{-1}. This line is only a weak shoulder in the Raman spectrum of crystalline α-D-glucose. It is possible that a small proportion of β-D-glucose was present in the specimen of the crystalline α-form that we used. However, for amylose, where all the D-glucopyranose residues have the α-configuration, a line with weak intensity as detected at 895 cm^{-1}. The few differences observed between the solid and solution spectra are thought to be due to the presence of the β-anomer in the solution, and effects due to the different environments of the D-glucose molecules in the crystal and in aqueous solution. For most of the observed lines, the differences in frequency (between solution and the solid state) were less than the experimental error (±4 cm^{-1}).

The differences in the relative intensities between equivalent bands in infrared and Raman spectra arise due to the different phenomenological basis of the two effects. Since the glucose molecule has no symmetry, all 66 (=3N−6) vibrational modes are active in both infrared and Raman. Thus the two spectra contain lines at the same frequency, but, in general, these have different relative intensities. All 66 modes are not observed in the spectrum of α-D-glucose due to the inherent breadth of the lines and the consequent overlap. In both the infrared and Raman spectra we can detect only the most intense lines, or non-overlapped weaker lines, and these are not necessarily due to the same modes in each case.



Study of the Raman spectra of D-glucose, cellobiose, maltose, and dextran in H_2O and D_2O solution[1] revealed that lines at 1349, 1071, 1020, and 913 cm^{-1} are due to C–O–H related vibrations. On deuteration, frequency shifts occurred in the line at 1278 cm^{-1} in the spectra of all of these carbohydrates except dextran, so this line is presumably related to vibration of the C-1–O–H and/or the C-6–O–H groups. Comparison of the infrared spectra of crystalline α-D-glucose and three *C*-deuterated D-glucoses facilitated assignment of some of the C–H and CH_2 related modes. The bands due to CH_2 vibrations are at 1457, 1337, 1219, and 1011 cm^{-1}, and these probably involve the bending, wagging, twisting, and rocking modes, respectively. Six bands assigned to modes involving deformation vibrations of the X–C-1–H group (X = C-2, O-1, or O-5) are at 1360, 1250, 1076, 1047, 913, and

836 cm^{-1}. The last-mentioned band has generally been considered typical of anomeric configurations having C-1–H equatorial. A further band at 1402 cm^{-1} is assigned to a Y–C-2–H related mode (Y = C-3, C-1 or O-2).

For the remaining bands, it is not possible to be quite so definite. The unassigned bands in the region 1500–1300 cm^{-1} are probably due to Z–C–H deformations (Z = O or C), although some contribution of C–O–H deformation is also expected since cellulose, for example, shows four bands in this range that are sensitive to deuteration[2]. In the frequency range below ~1300 cm^{-1}, additional contributions due to C–O and C–C stretching modes are expected. The modes below 800 cm^{-1} are probably due to skeletal modes, low-frequency vibrations of the ring, and so on.

VIBRATIONAL ANALYSIS OF α-D-GLUCOSE

For any molecule, a vibrational analysis requires accurate knowledge of the atomic coordinates and a defined set of force constants. The coordinates for α-D-glucose used in this work were those obtained by Brown and Levy[3]. This structure was determined by neutron diffraction, which gives accurate positioning of the hydrogen atoms as well as of the carbon and oxygen atoms.

The force constants for this work are listed in Table II. These potential constants are compiled from the results of Schachtschneider and Snyder[4,5] for paraffins, Snyder and Zerbi[6] for aliphatic ethers, and the work by Brooks and Haas[7] and by Mikawa *et al.*[8] on carboxylic acids. The values designated as "assigned" in Table II are our own values based on the work just cited.

TABLE II

VALENCE FORCE-CONSTANTS FOR α-D-GLUCOSE

Force constant type	*Coordinates involved*	*Force constant*[a]	*Atoms common to interacting coordinates*
	Stretch		
1	CO	5.090	
2	CC	4.261	
3	CH	4.688	
4	OH	6.440[b]	
	Bend		
5	CCC	1.071	
6	COC	1.313	
7	CCO	1.182	
8	CCH	0.718	
9	HCH	0.471	
10	O-5–CH	1.200[b]	
11	O-5–CH	0.961	
12	OCH	0.961[b]	
13	COH	0.760[b]	

TABLE II (continued)

Force constant type	*Coordinates involved*	*Force constant*[a]	*Atoms common to interacting coordinates*
	Torsion		
14	CC	0.024	
15	CO	0.026	
	Stretch–stretch		
16	CC, CC	0.101	C
	CC, CO		C
17	CO, CO	0.101^b	C
18	CO, CO	0.288	O
19	CH, CH	−0.046	C
	Stretch–bend		
20	CO, HCO	0.387	C–O
21	CC, HCC	0.478	C–C
22	CO, HCC	0.0	C
	CC, HCO		C
23	CO, COC	0.483	C–O
24	CO, CCO	0.618	C–O
25	CC, CCO	0.403	C–C
26	CC, CCC	0.417	C–C
27	CO, COH	0.387^b	C–O
	Bend–bend		
28	CCO, COH	−0.031^b	C–O
29	OCO, COH	0.004^b	C–O
30	HCO, HCO	−0.005	C–O
31	HCO, HCC	0.155	C–H
32	HCC, HCC	0.012	C–H
33	OCH, OCH	0.130^b	C–H
34	H_aCC, H_bCC	0.004	H_aC–CH_b (gauche)
35	H_aCC, H_bCC	0.121	H_aC–CH_b (trans)
36	HCO, CCO	−0.031	C–O
	HCC, CCO		C–C
	HCC, CCC		C–C
37	HCO, COC	0.004	HC–OC (gauche)
38	HCO, COC	−0.112	HC–OC (trans)
39	HCC, CCO	−0.113	HC–CO (gauche)
40	HCC, CCO	0.028	HC–CO (trans)
41	HCC, CCC	−0.052	HC–CC (gauche)
	HCC, CCC	0.049	HC–CC (trans)
42	CCO, CCO	−0.041	C–O
	CCO, CCC		C–C
43	COC, OCC	0.011	CO–CC (gauche)
	OCC, CCO		OC–CO (gauche)
	CCC, CCC		CC–CC (gauche)
44	COC, CCC	−0.011	CO–CC (trans)
	OCC, CCO		OC–CO (trans)
	CCC, CCC		CC–CC (trans)

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[a] Units: Stretch force-constants are mdyn. $Å^{-1}$; Bending force-constants are mdyn. Å.rad^{-2}; Torsional force-constants are mdyn. Å.rad^{-2}; Stretch–bend force-constants are mdyn.rad^{-1}. [b] Assigned values.

The vibrational frequencies and potential-energy distributions were calculated by using the normal-coordinate analysis program written by Boerio and Koenig[9]. The results are compared with the observed frequencies and assignments in Table III.

TABLE III

CALCULATED AND OBSERVED FREQUENCIES AND POTENTIAL-ENERGY DISTRIBUTION FOR α-D-GLUCOSE

Observed frequencies (cm^{-1})		*Calculated frequencies (cm^{-1})*	*Approximate potential-energy distribution (%)*
I.r.	*Raman*		
		3397	OH(99)
		3397	OH(93)
	3550	3397	OH(97)
	broad	3397	OH(98)
		3397	OH(94)
	2961	2985	CH(96)
	2947	2944	CH(94)
		2939	CH(90)
		2937	CH(98)
	2911	2933	CH(97)
	2891	2929	CH(89)
	2877		
	2850	2883	CH(95)
1460	1462	1469	OCH(50), CH_2(43)
1442			
1427	1433	1434	OCH(85), OCH(85), CCH(14)
1405	1408	1375	CCH(28), OCH(27), COH(24)
1378	1375	1360	CCH(50), OCH(29), COH(13)
		1358	CCH(50), OCH(25), COH(13)
		1356	CCH(44), OCH(18), COH(17)
	1346	1347	CCH(48), OCH(24), COH(14)
1337	1335	1337	CCH(59), CO(15), OCH(12)
1328		1335	CCH(47), COH(25)
		1320	CCH(59), OCH(37)
1293	1298	1295	OCH(61), CCH(37)
		1290	COH(43), CCH(30)
		1284	OCH(30), COH(29), CCH(22)
	1272	1256	OCH(59), CCH(36)
	1224	1226	COH(44), OCH(24), CCH(18)
1219		1216	CCH(28), OCH(21), COH(21), CO(20)
1197	1206	1201	CO(39), CCH(19), COH(16)
		1194	OCH(33), COH(26), CCH(18)
		1185	CO(29), COH(24), CCH(22), OCH(20)
1152	1153	1149	CO(50), CC(27), COH(18)
		1123	CO(50), CCH(14), COH(13)
	1124	1120	CO(47), CC(47)
	1115		
1104		1108	CC(45), CO(34), COH(17)
	1022	1083	CO(55), COH(24), CC(17)
1076	1076	1075	CO(57), CC(25), COH(23)
1047	1054	1051	CO(79), CC(19)
1026			

TABLE III (continued)

Observed frequencies (cm^{-1})		*Calculated frequencies* (cm^{-1})	*Approximate potential energy distribution (%)*
I.r.	*Raman*		
1011		1014	CC(45), OCH(15), CCH(13), CCO(13)
998	998	996	CC(43), CO(30), CCH(15)
937		946	CC(42), CO(39), CCH(19)
911	914		
890	897	902	CC(35), CO(25), CCO(20)
836	840	863	CO(43), CCH(26), CC(18)
768	779		
	748	736	CO(16), CCO(15), CC(14), CCH(14)
721			
	704		
645	648	625	CCO(57), CCH(20)
622		616	CCO(41), CCH(20), CO(11), CC(11)
603	601		
	581		
555	554	537	CCO(32), CC(18), CCH(16), CO(14)
	542	531	OCC(35), OCO(18), CO(17)
	495		
	441	443	OCC(38), CCC(15)
	425	428	CCO(34), CCC(30), CCH(26)
	405		
	397	390	CCO(46), OCO(16), CCC(11)
	364	359	CCO(41), CCH(16), CC(16)
		316	CCO(59), CC(13)
	303	307	CCO(59), CC(11)
	291	294	CCO(63), CCH(17)
	271		
	255	252	CO(τ)(49), CCO(20), CCH(16)
		249	CO(τ)(59), CCO(14)
	233	235	CO(τ)(92)
		229	CO(τ)(85)
		221	CO(τ)(86)
		219	CO(τ)(55), CCO(24)
	205	200	CCO(35), CO(τ)(31)
	177		
		127	CCC(25), COC(21), CC(τ)(10)

DISCUSSION

It may be seen from Table III that there is a good agreement between the calculated and observed data, and, for a molecule as complex as α-D-glucose, this agreement is considered very satisfactory. Certainly the frequency match cannot be expected to be exact, but, for those frequencies which *are* observed, the agreement is in most cases within 10 cm^{-1}. The potential-energy distribution shows that most of the modes are highly coupled vibrations, as expected for such a system, although in a few cases, the modes can be considered to arise from only one type of motion.

The calculated frequency at 1469 cm^{-1} has a major portion of CH_2 motion and matches the observed CH_2 mode at 1462 cm^{-1}. The other observed frequencies at 1335, 1224, and 998 cm^{-1}, which were also identified as CH_2-related modes by deuteration, come close to the calculated frequencies of 1337 (and 1335), 1226 (and 1216), and 996 cm^{-1}, respectively, all of which contain significant C–C–H contributions. These modes probably involve the CH_2 group, but also have contributions from other structures.

The calculated frequencies in the range of 1450 to 1350 cm^{-1} do not match the observed frequencies quite so well as in other frequency ranges, but there are enough (five) to explain the four observed. All of the calculated modes contain a high proportion of C–C–H and O–C–H contribution, which justifies the assignment of the observed bands to Z–C–H deformations. In addition, the potential distribution indicates a small contribution to each mode of C–O–H deformation to each mode. This contribution has been detected for cellulose[3], but not for D-glucose. The calculated frequencies at 1320, 1295, and 1290 cm^{-1} probably correspond to the observed modes at 1328 and 1298 cm^{-1}, which were assigned as Z–C–H deformation modes. These calculated modes all contain sizeable C–C–H contributions, although the frequency at 1290 cm^{-1} also contains 43% of C–O–H, which was *not* demonstrated by deuteration.

Of the other infrared bands assigned, by deuteration, to Z–C–H related modes, those modes observed at 1250 and 840 cm^{-1} match calculated modes at 1256 and 863 cm^{-1} that contain C–C–H contributions. These calculations are in agreement with the original assignment of the band at 840 cm^{-1} to a mode related to vibration of the anomeric C–H. The band at 914 cm^{-1} comes nearest to the calculated mode at 902 cm^{-1}, but the latter contains no Z–C–H motions. However, if this observed band is assigned to the calculated mode at 946 cm^{-1}, which contains 19% of C–C–H contribution, the calculated mode at 902 cm^{-1} could correspond to the observed band at 897 cm^{-1}. Although we have allowed for contamination by the β-anomer of the band at 897 cm^{-1}, a band at this frequency is observed for amylose. The bands observed at 1076 and 1054 cm^{-1} are assigned to Z–C–H modes, and match the calculated frequencies of 1075 and 1051 cm^{-1}. These calculated modes contain no C–H-related components, and the results observed are only compatible if the coupling of these modes breaks down on deuteration.

The Raman lines observed at 1346, 1272, 1076, 1022, and 914 cm^{-1} are assigned as C–O–H related modes[1]. Of these, the first three appear to correspond to the calculated modes at 1347, 1284, and 1075 cm^{-1}, which have C–O–H contributions in their potential-energy distribution. The other two probably match at 1014 and 902 cm^{-1} (as already discussed), although neither of these calculated modes has any calculated C–O–H contribution; in these cases we suggest that the coupling breaks down on deuteration. The frequency correspondence in this region is not good, as additional bands may be observed because of contamination by the β-anomer, and possible hydrate formation.

The general assignment of the bands in the regions of the spectrum involving

C–O and C–C stretching, skeletal, and torsional modes is essentially justified by the calculations. The complex nature of these vibrations is indicated by the potential-energy distributions.

The agreement between the observed and calculated frequencies is quite good, and in most cases the potential-energy distribution is compatible with previous band-assignments. The fit could certainly be improved by variation of the atomic coordinates and force constants, and the effect of deuteration could be simulated for more direct comparison. Such work would involve a considerable amount of computer time and it is not clear that very much more information would be gained by this procedure. The work described here gives further insight into the complex problem of interpretation of the vibrational spectra of carbohydrates, and provides an additional basis from which the data for the glucan polysaccharides can be examined.

ACKNOWLEDGMENTS

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REFERENCES

1 P. D. Vasko, J. Blackwell, and J. L. Koenig, *Carbohyd. Res.*, 19 (1971) 297.
2 J. Blackwell, P. D. Vasko, and J. L. Koenig, *J. Appl. Phys.*, 41 (1970) 4375.
3 G. M. Brown and H. A. Levy, *Science*, 147 (1965) 1038.
4 J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, 19 (1963) 117.
5 R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, 21 (1965) 169.
6 R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, 23A (1976) 391.
7 W. V. F. Brooks and C. M. Haas, *J. Phys. Chem.*, 71 (1967) 3; *J. Phys. Chem.*, 71 (1967) 656.
8 Y. Mikawa, J. W. Basch, and R. J. Jakobsen, *J. Mol. Spectroscopy*, 24 (1967) 314.
9 F. J. Boerio and J. L. Koenig, *J. Polym. Sci. A-2*, 9 (1971) 1517.