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INFRARED SPECTRA AND NORMAL VIBRATIONS OF β-D-GLUCOPYRANOSE

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ABSTRACT

Infrared spectra of β-D-glucopyranose have been measured in the 4000–50 cm^{-1} region and normal vibrations of β-D-glucopyranose have been investigated. The normal coordinates are treated by using the Urey–Bradley force-field, and vibrational assignments of the observed bands are made on the basis of the potential-energy distributions. The calculated vibrational-frequencies agree well with the observed frequencies in the region above 250 cm^{-1}.

INTRODUCTION

Infrared spectra of sugars have been measured in the mid-i.r. region of 4000–400 cm^{-1} by Kuhn[1] and by Barker *et al.*[2]. However, the resolution of these spectra was not high enough to allow discussion of normal vibrations. Vibrational assignments for β-D-glucopyranose have not been established. Absorption bands due to bending, torsional, and ring-deformation vibrations are expected to appear in the far-i.r. region. In our previous studies[3], far-i.r. spectra of D-glucose, L-sorbose, sucrose, and cellobiose were measured at room and at liquid-helium temperatures in the region of 500–50 cm^{-1}. β-D-Glucopyranose is one of the most common sugars, and the β-D-glucopyranose residue is a component of many carbohydrates.

In the present study, i.r. spectra of β-D-glucopyranose have been recorded at room temperature for measurements in the region of 4000–400 cm^{-1} and at liquid-helium temperature in the 500–50 cm^{-1} region. The normal coordinates are treated by using the Urey–Bradley force-field and the vibrational assignments of the observed bands are made on the basis of the potential-energy distributions.

EXPERIMENTAL

I.r. absorption spectra of β-D-glucopyranose were recorded in the 4000–400 cm^{-1} region with a Hitachi EPI-G3 grating i.r. spectrophotometer. The instrument was calibrated with polystyrene in the region above 900 cm^{-1} and by water vapor in the 900–400 cm^{-1} region. The sample was suspended in Nujol for measurements in the 1300–750 and 690–400 cm^{-1} regions or in hexachlcrobutadiene in the 4000–2200, 1500–1300, and 750–690 cm^{-1} regions, and the sample was contained between KRS-5 plates at room temperature. The observed spectra are shown in Fig. 1(a)–(e). Calibration marks are indicated in the spectra. The far-i.r. spectrum of β-D-glucopyranose was recorded in the 500–50 cm^{-1} region at liquid-helium temperature with a far-i.r. grating spectrometer constructed in our laboratory[4]. The instrument was calibrated with water vapor. The spectrum is shown in Fig.2.

NORMAL-COORDINATE TREATMENT

The normal coordinates of a β-D-glucopyranose molecule were treated by Wilson's *GF* matrix-method[5]. The molecular geometry used was taken from the X-ray diffraction data of Chu and Jeffrey[6] for crystalline β-D-glucopyranose. The indices assigned for the carbon, oxygen, and hydrogen atoms are shown in Fig. 3. The bond-stretching (Δr), bond-angle bending ($\Delta\phi$), and internal-rotation coordinates (Δt) were used as the internal coordinates. The bond lengths, bond angles, and internal rotation angles calculated from the results of the X-ray diffraction analysis[6] are listed in Table I. The atomic masses of 12.000000 for carbon, 15.994914 for oxygen, and 1.007825 for hydrogen were used for calculating the *G* matrix. In deriving the *F* matrix, the Urey–Bradley force-field[7, 8] was used, and the initial set of force constants were transferred from such related molecules as dimethyl ether, methyl alcohol[9], and cyclohexane[10]. The values of κ about the angles around each carbon atom were assumed to be zero in the calculation. As the wavenumbers calculated by using the initially transferred force-constants agreed fairly well with the observed wavenumbers, I proceeded to least-squares refinement of the force constants. Of the twenty-four force constants used in the calculation, *K*(CC), *K*(CO), *K*(CH), *K*(OH), *H*(CCC), *H*(CCO), *H*(CCH), *H*(OCH), *H*(HCH), and *H*(COH) were determined within their dispersions by the least-squares adjustment. However, *H*(COC), *H*(OCO), *Y*, and *F* could not be determined definitely, and were constrained to the initial values or to the values estimated by reference to the observed wavenumbers. The final set of force constants thus obtained is listed in Table II, where values reported for related molecules are also included for comparison. In Table III, the observed and calculated wavenumbers are listed, together with the potential-energy distributions[11]. The L_x matrix[12] was also calculated from the eigenvectors of the *GF* matrix, and the atomic displacements for each normal vibration were obtained. The results for the low-wavenumber modes are illustrated in Fig. 4(a)–(d).

RESULTS AND DISCUSSION

Vibrational assignments of the observed i.r. bands are made on the basis of results of the normal-coordinate treatment. Twenty-four atoms in a β-D-glucopyranose molecule results in $3 \times 24 - 6 = 66$ degrees of vibrational freedom. The 66 bands are listed in Table III. According to the calculations, O–H and C–H stretching

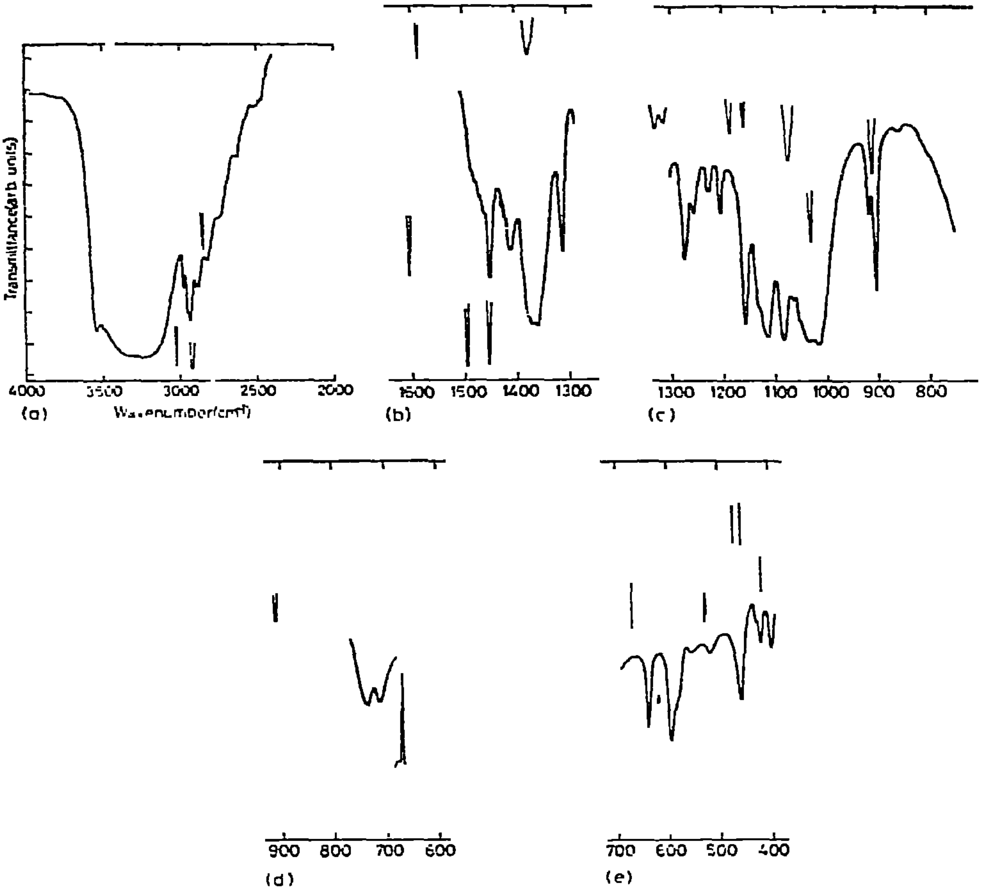

Fig. 1. Infrared spectra of β-D-glucopyranose in the regions of (a) 4000–2200, (b) 1500–1300, (c) 1300–750, (d) 750–690, and (e) 690–400 cm^{-1}.

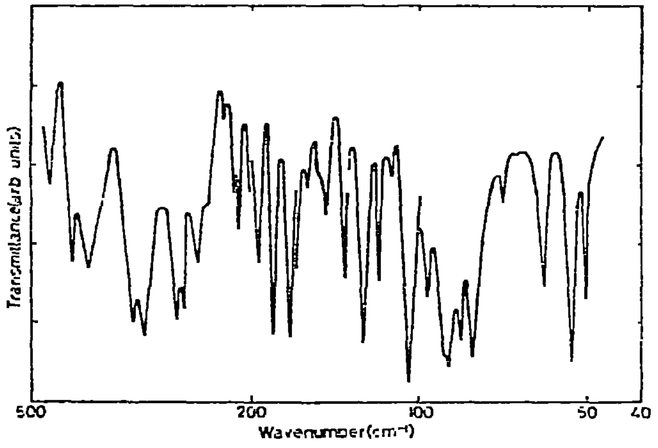

Fig. 2. Far-i.r. spectrum of β-D-glucopyranose in the region of 500–50 cm^{-1} at liquid-helium temperature.

TABLE I

MOLECULAR PARAMETERS OF β-D-GLUCOPYRANOSE

i	j	k	l	r_{kl} (A)	ϕ_{jkl} (°)	t_{ijkl} (°)
		C-1	H-13	1.075		
		C-1	C-2	1.525		
H-13	C-1	C-2	C-3	1.519	112.050	67.750
C-1	C-2	C-3	C-4	1.512	110.500	50.767
C-2	C-3	C-4	C-5	1.529	109.817	−53.383
C-3	C-4	C-5	C-6	1.513	114.933	179.017
C-3	C-2	C-1	O-11	1.433	108.533	−53.667
H-13	C-1	C-2	O-8	1.4285	108.483	−53.583
C-1	C-2	C-3	O-9	1.433	108.700	170.483
C-2	C-3	C-4	O-10	1.419	111.050	−173.067
C-4	C-5	C-6	O-12	1.419	111.933	−59.083
C-3	C-2	C-1	O-7	1.384	108.200	−169.467
H-13	C-1	C-2	H-14	1.039	108.683	−171.033
C-1	C-2	C-3	H-15	1.076	106.067	−68.033
C-2	C-3	C-4	H-16	1.017	105.617	68.633
C-3	C-4	C-5	H-17	1.055	109.417	−61.883
C-4	C-5	C-6	H-18	1.108	110.267	174.217
C-4	C-5	C-6	H-19	1.051	108.683	59.667
C-2	C-1	O-7	H-20	0.953	101.883	−147.317
C-1	C-2	O-8	H-21	1.0285	114.433	−99.767
C-2	C-3	O-9	H-22	0.894	103 050	109.983
C-3	C-4	O-10	H-23	0.981	109.617	−96.000
C-5	C-6	O-12	H-24	0.978	128.417	−124.183

TABLE II

FORCE CONSTANTS (mdyn/A) OF β-D-GLUCOPYRANOSE AND RELATED MOLECULES

Force constant	*β-D-Gluco-pyranose*	*Related molecule*[a]		*Force constant*	*β-D-Gluco-pyranose*	*Related molecule*
K(CC)	2.424*	2.304		Y(CC)*ring*	0.090** (mdyn.A)	0.107
K(CO)	3.090*	2.899	3.366	Y(CC)*side*	0.090** (mdyn.A)	0.107
K(CH)	3.831*	4.050		Y(CO)*ring*	0.100** (mdyn.A)	0.099
K(OH)	5.534*	7.265		Y(CO)*side*	0.350** (mdyn.A)	
H(CCC)	0.305*	0.320		F(CCC)	0.200	0.200
H(CCO)	0.305*	0.350		F(CCO)	0.600	0.600
H(COC)	0.390**	0.445		F(COC)	0.200	0.200
H(OCO)	0.380**	0.400		F(OCO)	0.700**	0.700
H(CCH)	0.221*	0.217		F(CCH)	0.482	0.482
H(OCH)	0.279*	0.282		F(OCH)	0.850**	0.756
H(HCH)	0.405*	0.435		F(HCH)	0.069	0.069
H(COH)	0.413*	0.380		F(COH)	0.750**	0.719

[a] See text for identity. *Indicates the force constants determined by the least-squares adjustment. **Indicates the force constants constrained to the values estimated by reference to the observed wavenumbers.

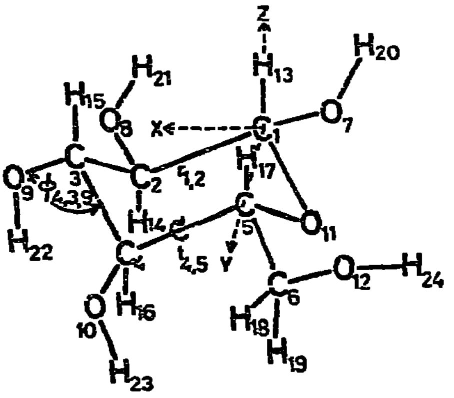

Fig. 3. Indices assigned for the carbon, oxygen, and hydrogen atoms, and internal coordinates.

vibrations are expected to appear in the 3300–2850 cm^{-1} region. I.r. bands observed at 3250 and 2980–2820 cm^{-1} are due to O–H and C–H stretching modes, respectively. The band observed at 1465 cm^{-1}, which is calculated to occur at 1474 cm^{-1}, is assigned to the CH_2 scissoring vibrations. The bands appearing in the region of 1474–1199 cm^{-1} are due to O–C–H, C–C–H, and C–O–H bending vibrations. The bands observed in the 1153–904 cm^{-1} region are assigned to C–O and C–C stretching modes, because they are calculated to lie in the region of 1147–907 cm^{-1}. In the region below 800 cm^{-1}, bands due to skeletal deformation and internal-rotation modes are expected. The observed bands between 800 and 519 cm^{-1} are due to the internal-rotation modes about C–OH (side) bonds. The bands appearing in the region 463–250 cm^{-1} are due mainly to C–C–O bending vibrations.

The band observed at 127 cm^{-1} is assigned to C–C–O, C–C–C, and C–O–C bending modes, coupled with C–O ring internal-rotation modes, and is calculated to lie at 143 cm^{-1}. The coupling with internal-rotation modes about C–O ring bonds causes the wavenumber of this vibration to be much lower than those of general bending-vibrations. The bands observed at 104, 88.6, and 60.1 cm^{-1} are due to C–C internal-rotation modes and possibly lattice vibrations.

β-D-Glucopyranose crystallizes into a orthorhombic lattice of space group $P2_12_12_1$. The crystallographic unit-cell contains four β-D-glucopyranose molecules. Four molecules results in $3 \times 4 - 6 = 6$ degrees of vibrational freedom represented[13] by $A_u + 2B_{1u} + B_{2u} + 2B_{3u}$. Six i.r.-active bands are expected to appear. They are ungerade species. Besides the bands shown in Table III, fourteen absorption bands are observed, at 265, 215, 212, 195, 183, 171, 148, 137, 118, 96.9, 84.3, 79.9, 53.6, and 50.3 cm^{-1}. Six of them are caused by intermolecular vibrations in the unit cell, and others are caused by intermolecular vibrations outside the unit cell.

The force constants determined for β-D-glucopyranose may be compared with the corresponding force constants of related molecules. The value of $K(CC) =$ 2.424 mdyn/A agrees well with that[10] of cyclohexane (2.304 mdyn/A). The value of

$K(\mathrm{CO}) = 3.090$ mdyn/A is close to the corresponding value[9] for methyl alcohol (2.899 mdyn/A) or the value[9] for dimethyl ether (3.366 mdyn/A). The value of $K(\mathrm{CH}) = 3.831$ mdyn/A is close to that[10] of cyclohexane (4.050 mdyn/A). The values of $H(\mathrm{CCC}) = 0.305$ mdyn/A, $H(\mathrm{CCO}) = 0.305$ mdyn/A, $H(\mathrm{CCH}) = 0.221$ mdyn/A, $H(\mathrm{OCH}) = 0.279$ mdyn/A and $H(\mathrm{HCH}) = 0.405$ mdyn/A agree well with those of related molecules[9,10,14]. As β-D-glucopyranose molecules in the crystal are bound by intermolecular hydrogen-bonds, the wavenumbers of torsional vibrations occur as high as 600–700 cm^{-1}. Accordingly, the value of $Y(\mathrm{CO})_{side}$ is estimated to be 0.350 mdyn.A, which is much larger than the value of $Y(\mathrm{CO})_{ring}$.

TABLE III

OBSERVED AND CALCULATED FREQUENCIES AND POTENTIAL-ENERGY DISTRIBUTIONS (P.E.D.) OF β-D-GLUCOPYRANOSE

ν_{obs} (cm^{-1})	$\nu_{calc.}$ (cm^{-1})	P.E.D. (%)	ν_{obs} (cm^{-1})	$\nu_{calc.}$ (cm^{-1})	P.E.D. (%)
3250	3286	$r_{\mathrm{OH}}(100)$	1111	1104	$r_{\mathrm{CO}}(57)$, $r_{\mathrm{CC}}(23)$, $\phi_{\mathrm{CCO}}(22)$
3250	3260	$r_{\mathrm{OH}}(100)$	1080	1096	$r_{\mathrm{CO}}(63)$, $r_{\mathrm{CC}}(42)$
3250	3247	$r_{\mathrm{OH}}(100)$	1060	1085	$r_{\mathrm{CC}}(56)$, $r_{\mathrm{CO}}(42)$
3250	3228	$r_{\mathrm{OH}}(100)$	1049	1070	$r_{\mathrm{CO}}(79)$
3250	3223	$r_{\mathrm{OH}}(100)$	1036	1065	$r_{\mathrm{CO}}(72)$, $r_{\mathrm{CC}}(18)$
2977	2983	$r_{\mathrm{CH}}(102)$	1028	1030	$r_{\mathrm{CO}}(69)$, $r_{\mathrm{CC}}(23)$
2948	2928	$r_{\mathrm{CH}}(101)$	1014	1014	$r_{\mathrm{CO}}(52)$, $r_{\mathrm{CC}}(30)$, $\phi_{\mathrm{CCO}}(15)$
2934	2919	$r_{\mathrm{CH}}(102)$	—	987	$r_{\mathrm{CC}}(47)$, $\phi_{\mathrm{CCO}}(27)$
2923	2906	$r_{\mathrm{CH}}(102)$	913	945	$r_{\mathrm{CO}}(35)$, $\phi_{\mathrm{CCH}}(22)$
2900	2901	$r_{\mathrm{CH}}(103)$	904	907	$r_{\mathrm{CC}}(31)$, $\phi_{\mathrm{CCH}}(21)$, $r_{\mathrm{CO}}(17)$
2880	2884	$r_{\mathrm{CH}}(102)$	738	703	$t_{\mathrm{CO}side}(31)$, $\phi_{\mathrm{CCO}}(30)$, $\phi_{\mathrm{CCH}}(16)$
2822	2855	$r_{\mathrm{CH}}(100)$	713	662	$\phi_{\mathrm{CCO}}(30)$, $t_{\mathrm{CO}side}(24)$, $\phi_{\mathrm{OCO}}(16)$
1474	1478	$\phi_{\mathrm{OCH}}(73)$, $\phi_{\mathrm{CCH}}(26)$	638	631	$\phi_{\mathrm{CCO}}(61)$, $t_{\mathrm{CO}side}(15)$
1465	1474	$\phi_{\mathrm{HCH}}(63)$, $\phi_{\mathrm{OCH}}(37)$	—	610	$t_{\mathrm{CO}side}(88)$
1458	1462	$\phi_{\mathrm{OCH}}(72)$, $\phi_{\mathrm{CCH}}(25)$	595	594	$t_{\mathrm{CO}side}(47)$, $\phi_{\mathrm{CCO}}(22)$
1449	1451	$\phi_{\mathrm{OCH}}(63)$, $\phi_{\mathrm{CCH}}(25)$	579	576	$t_{\mathrm{CO}side}(85)$
1438	1445	$\phi_{\mathrm{OCH}}(52)$, $\phi_{\mathrm{CCH}}(40)$	—	574	$t_{\mathrm{CO}side}(27)$, $\phi_{\mathrm{CCO}}(27)$
1424	1444	$\phi_{\mathrm{OCH}}(79)$, $\phi_{\mathrm{CCH}}(18)$	556	559	$t_{\mathrm{CO}side}(70)$, $\phi_{\mathrm{CCO}}(17)$
1421	1429	$\phi_{\mathrm{OCH}}(67)$, $\phi_{\mathrm{CCH}}(26)$	519	537	$t_{\mathrm{CO}side}(45)$, $\phi_{\mathrm{CCO}}(24)$
1410	1423	$\phi_{\mathrm{OCH}}(31)$, $\phi_{\mathrm{HCH}}(30)$, $\phi_{\mathrm{CCH}}(23)$	463	489	$\phi_{\mathrm{CCO}}(36)$, $r_{\mathrm{CO}}(16)$
1400	1388	$\phi_{\mathrm{OCH}}(40)$, $\phi_{\mathrm{COH}}(37)$, $\phi_{\mathrm{CCH}}(28)$	421	419	$\phi_{\mathrm{CCO}}(39)$, $\phi_{\mathrm{CCH}}(13)$
1377	1374	$\phi_{\mathrm{OCH}}(38)$, $\phi_{\mathrm{CCH}}(34)$, $\phi_{\mathrm{HCH}}(22)$	399	384	$\phi_{\mathrm{CCC}}(32)$, $\phi_{\mathrm{CCO}}(24)$
1370	1370	$\phi_{\mathrm{COH}}(40)$, $\phi_{\mathrm{CCH}}(38)$, $\phi_{\mathrm{OCH}}(20)$	—	368	$\phi_{\mathrm{CCO}}(38)$, $\phi_{\mathrm{CCC}}(21)$
1358	1352	$\phi_{\mathrm{CCH}}(62)$, $\phi_{\mathrm{COH}}(25)$	327	326	$\phi_{\mathrm{CCO}}(66)$, $\phi_{\mathrm{CCH}}(12)$
1342	1349	$\phi_{\mathrm{CCH}}(74)$, $\phi_{\mathrm{COH}}(15)$	313	313	$\phi_{\mathrm{CCO}}(43)$, $\phi_{\mathrm{OCO}}(21)$
1308	1345	$\phi_{\mathrm{CCH}}(48)$, $\phi_{\mathrm{COH}}(30)$, $\phi_{\mathrm{OCH}}(23)$	277	283	$\phi_{\mathrm{CCO}}(86)$
1269	1245	$\phi_{\mathrm{CCH}}(43)$, $\phi_{\mathrm{COH}}(29)$	272	273	$\phi_{\mathrm{CCO}}(58)$, $\phi_{\mathrm{CCH}}(11)$
1251	1230	$\phi_{\mathrm{CCH}}(48)$, $\phi_{\mathrm{COH}}(33)$	250	248	$\phi_{\mathrm{CCO}}(51)$, $\phi_{\mathrm{CCC}}(19)$
1222	1224	$\phi_{\mathrm{COH}}(64)$, $\phi_{\mathrm{CCH}}(15)$	—	241	$\phi_{\mathrm{CCO}}(33)$, $\phi_{\mathrm{COC}}(18)$
1199	1221	$\phi_{\mathrm{COH}}(65)$, $\phi_{\mathrm{CCH}}(16)$	127	143	$\phi_{\mathrm{CCO}}(22)$, $\phi_{\mathrm{CCC}}(19)$, $\phi_{\mathrm{COC}}(15)$, $t_{\mathrm{CO}ring}(13)$
1153	1147	$r_{\mathrm{CO}}(53)$, $r_{\mathrm{CC}}(18)$, $\phi_{\mathrm{CCC}}(17)$	104	96.1	$t_{\mathrm{C}ring}(43)$, $\phi_{\mathrm{CC}ring}(31)$, $\phi_{\mathrm{CCO}}(14)$
1127	1121	$r_{\mathrm{CO}}(58)$, $\phi_{\mathrm{COH}}(26)$	88.6	72.9	$t_{\mathrm{CC}side}(32)$, $t_{\mathrm{CC}ring}(22)$, $\phi_{\mathrm{CCO}}(20)$, $\phi_{\mathrm{CCC}}(12)$
1118	1112	$r_{\mathrm{CC}}(64)$, $\phi_{\mathrm{CCO}}(16)$	60.1	71.8	$t_{\mathrm{CC}side}(48)$, $\phi_{\mathrm{CCC}}(18)$, $t_{\mathrm{CC}ring}(14)$

r, stretching mode; ϕ, bending mode; and r, internal-rotation mode.

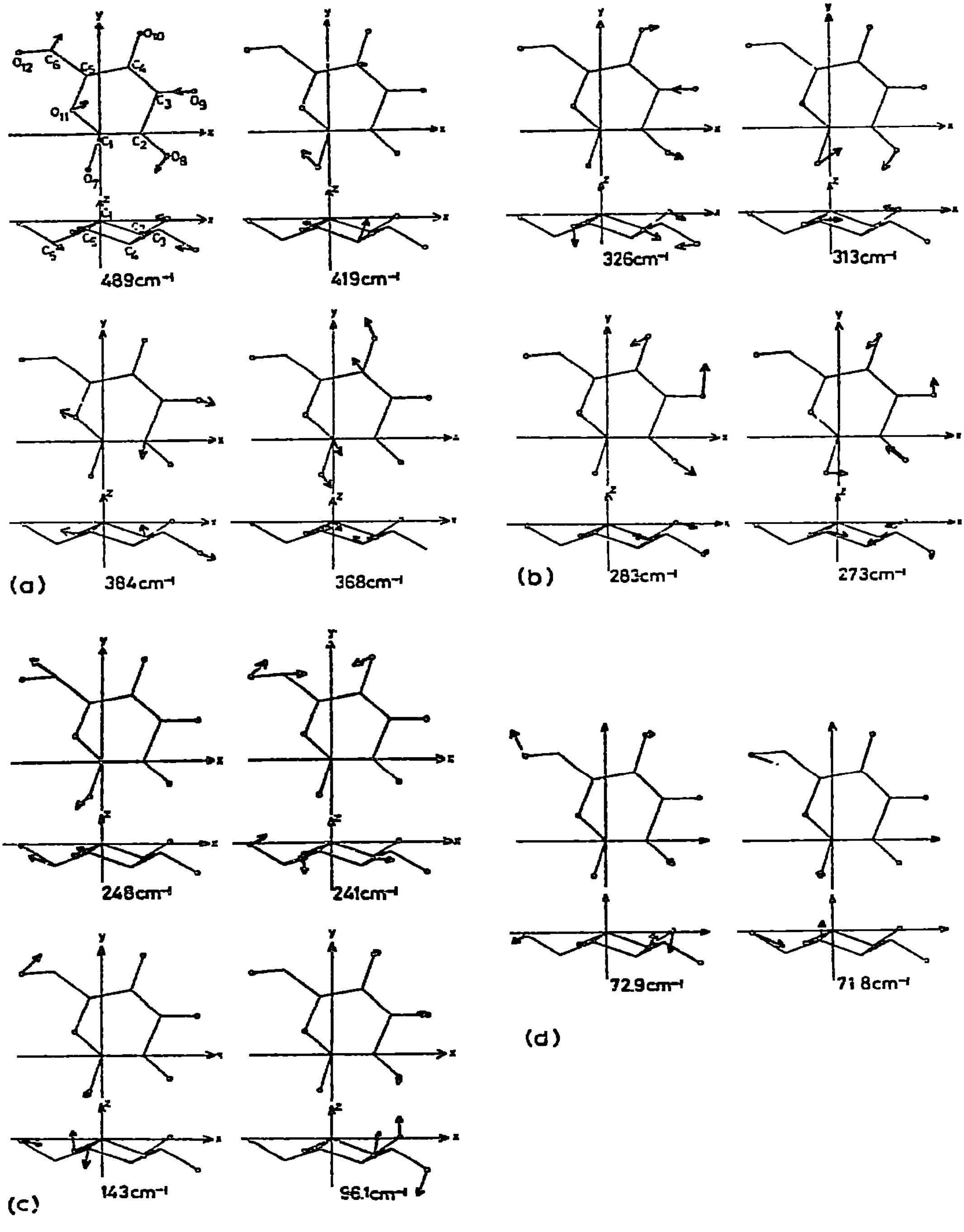

Fig. 4. Atomic displacements for normal vibrations in the regions of (a) 489-368, (b) 326-273, (c) 248-96.1, and (d) 72.9-71.8 cm^{-1}.

The values of the repulsive force-constants are constrained to the values for related molecules in the least-squares calculation.

The calculated wavenumbers agree well with the observed ones in the region higher than 250 cm^{-1}; thus the difference between observed and calculated wavenumbers is within 1.5% on average. However the difference is about 4.1% in the whole region.

CONCLUSIONS

The mid- and far-i.r. spectra of β-D-glucopyranose have been recorded in the 4000–50 cm^{-1} region. The normal-coordinate treatment has been made by use of the Urey–Bradley force field, and the vibrational assignments of the observed i.r. bands are made on the basis of the potential-energy distributions.

Many earlier investigators have conducted experimental interpretations. However, it is important to perform the primary calculation of normal vibrations of sugars. It is clear that the assumptions and approximations used here hold good in the primary calculation, so that the results as a whole are satisfactory.

In the region above 250 cm^{-1}, the observed spectra may generally be interpreted by the one-molecular model. In fact, in this study the agreement between observed and calculated wavenumbers is good. However, in the region below 250 cm^{-1}, results of the calculation based on the one-molecular model do not always explain the observed spectra because of the effects of intermolecular interactions. In order to explain the spectra below 250 cm^{-1}, the crystal vibrations, including intermolecular interactions, should be treated.

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