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CONFORMATIONAL DEPENDENCE OF CH(CD)-STRETCHINGS IN D-GLUCOSE AND SOME DEUTERATED DERIVATIVES AS REVEALED BY INFRARED AND RAMAN SPECTROSCOPY

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ABSTRACT

The Raman and i.r. spectra in the C–H- and C–D-stretching region of D-glucose and five selectively deuterated derivatives in the solid state have been recorded. The C–H (C–D) bonds have different force constants depending on their position and conformation in the pyranose ring and on the dihedral angle HCOH (DCOH). Calculations of the intensities of the i.r. bands confirm these conclusions. Modifications of the force field are proposed that account for the changes in the spectra for solutions in D_2O, which are useful for the interpretation of vibrational c.d. spectra.

INTRODUCTION

Previous i.r. studies of sugars[1,2] have not considered explicitly the CH-stretching region, and in general this region has for long been assumed to be "conformationally uninteresting"

Koenig *et al.*[3,4] proposed a force field for D-glucose in which all the CH bonds have the same force constant. However, McKean[5] has shown that CH-stretching modes are sensitive to conformation and, for ethers and alcohols, there is a striking correlation between the CH-stretching frequencies of isolated CH oscillators and the fine electronic properties of the CH bond. The CH-stretching frequencies, as well as the bond length and the dissociation energy, are related to the orientation of the CH bond with respect to vicinal electronegative atoms (such as oxygen) or to the adjacent CH bonds. In accord with this trend is the magnitude of localised charge on the hydrogen atom[6] and, through it, the intensity of the i.r. CH-

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stretching band. Also, local mode spectroscopy in the near i.r. (n.i.r.) region has allowed uncoupled CH-stretching overtones to be measured[7] and gives further support to McKean's findings.

We now report on the application of these criteria to calculations of normal co-ordinates and i.r. intensities through which a reasonable assignment of the i.r. and Raman spectra of α- and β-D-glucose and five deuterated derivatives could be made. Furthermore, a rationale is provided for the differences in the vibrational spectra of D-glucose in solution and in the solid state, which could be useful in the interpretation of vibrational c.d. (v.c.d.) spectra[8,9] of aldohexoses in solution in D_2O.

EXPERIMENTAL

α- (**1**) and β-D-glucopyranose (**2**) (Sigma) and D-glucopyranose-*1-d*$_1$ (**3**) and -*6,6-d*$_2$ (**4**) (Merck) were commercial materials. D-Glucopyranose-*5,6,6-d*$_3$ (**5**), -*2-d*$_1$ (**6**), and -*3-d*$_1$ (**7**) were gifts from Professor A. S. Perlin (McGill University).

The $\alpha\beta$-ratios of **3**–**5** and **7** were checked[10] by ^{1}H-n.m.r. spectroscopy (performed by Drs. G. Torri and G. Zoppetti, Istituto "G. Ronzoni", Milano) on fresh solutions in $(CD_3)_2SO$, using Perkin–Elmer R36 and Bruker CXP-300 spectrometers and the signals for HO-1. Thus, the $\alpha\beta$-ratio of **1** was 9:1[11], whereas **5** and **7** were exclusively α. There were impurities in **5** and **7** probably arising from the intermediate steps of the deuteration reaction[12]. The $\alpha\beta$-ratio of **6** could not be determined due to the limited amount of the sample.

I.r. spectra were recorded for KBr pellets, using FTIR Nicolet 7000 instruments for **1**–**4** (Dipartimento di Chimica Industriale del Politecnico, Milano) and **5**–**7** (Syracuse); 512 scans were taken with a resolution of 2 cm^{-1}. Raman spectra were recorded for powders contained in capillary tubes. For **1**, **2**, and **4**, a Spex Ramalog 400 instrument (University of Trieste) was used with a 3-cm^{-1} resolution, 300-mW laser power at the laser tube exit, 5-s time constant, 60 cm^{-1}/min monochromator velocity, and 3×10^3 counts/s; for **6**, a Jarrel Ash instrument (Istituto di Chimica delle Macromolecole, Milano) was used with 6-cm^{-1} resolution, 300-mW laser power, 10-s time constant, 10 cm^{-1}/min monochromator velocity, and 10^3 counts/s (for both instruments, the exciting line was the 488.0-nm line of an Ar^+ Spectra Physics laser); for **3**, **5**, and **7**, a Dilor multichannel spectrometer OMARS-89 equipped with an array of 512 diodes was employed, using an Ar^+ Spectra Physics laser with the exciting line at 514.6 nm and a resolution of ~4 cm^{-1}.

RESULTS

Fig. 1 shows the i.r. spectra of **1**–**7** in the CH-stretching region, and the corresponding Raman spectra in the C–H and C–D stretching region are shown in Figs. 2 and 3. The observed frequencies in the C–H and C–D stretching regions, respectively, are summarised in Tables I and II.

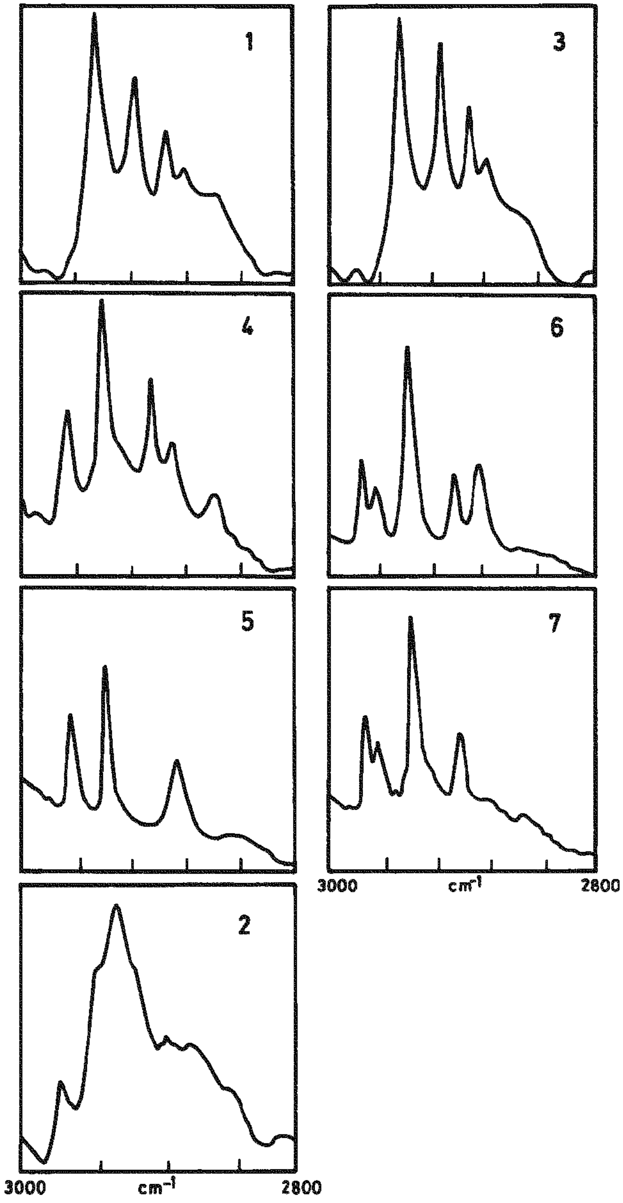

Fig. 1. I.r. spectra in the CH-stretching region of α-D-glucose (**1**), α-D-glucose-*1*-d_1 (**3**), α-D-glucose-*6,6*-d_2 (**4**), α-D-glucose-*5,6,6*-d_3 (**5**), D-glucose-*2*-d_1 (**6**), α-D-glucose-*3*-d_1 (**7**), and β-D-glucose (**2**) (see Experimental).

The i.r. and Raman spectra of **1–4** accord with those previously reported[1–4,13], except that[13] for **4**, since the α form did not show the Raman feature at 2990 cm^{-1} observed also for **5** and **7**.

Vibrational assignments. — (a) C–H stretching region (2800–3000 cm^{-1}). Figs. 1 and 2 show that the α and β forms have quite different i.r. and Raman spectra.

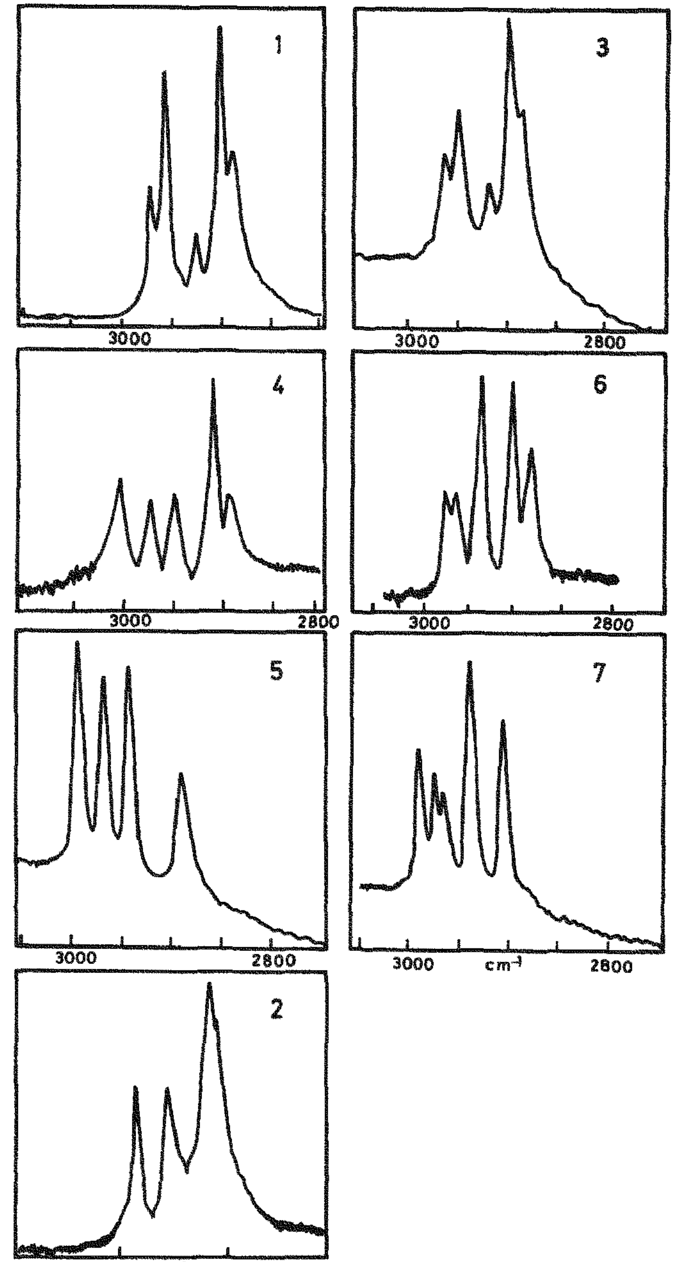

Fig. 2. Raman spectra in the CH-stretching region of α-D-glucose (**1**), α-D-glucose-*1*-d_1 (**3**), α-D-glucose-*6,6*-d_2 (**4**), α-D-glucose-*5,6,6*-d_3 (**5**), D-glucose-*2*-d_1 (**6**), α-D-glucose-*3*-d_1 (**7**), and β-D-glucose (**2**) (see Experimental).

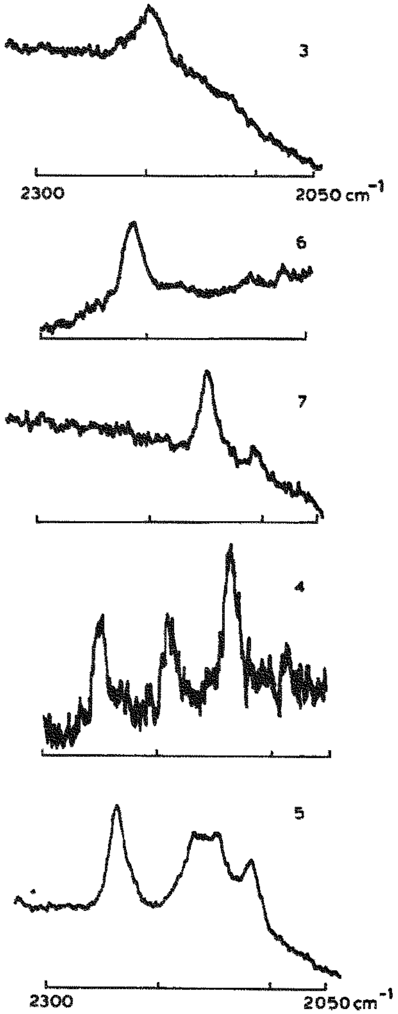

Fig. 3. Raman spectra in the CD-stretching region of α-D-glucose-*1*-d_1 (**3**), α-D-glucose-*6,6*-d_2 (**4**), α-D-glucose-*5,6,6*-d_3 (**5**), D-glucose-*2*-d_1 (**6**), α-D-glucose-*3*-d_1 (**7**) (see Experimental).

Thus, in the i.r., β-D-glucose (**2**) has five features in a unique band at 2880–2948 cm^{-1} and a characteristic single band at 2978 cm^{-1}, whereas α-D-glucose (**1**) shows five well resolved peaks.

The i.r. and Raman spectra of α-D-glucose-*1*-d_1 (**3**) are almost identical to those of **1** except for the bands at 2946 (i.r.) or 2948 cm^{-1} (Raman), which have decreased intensities, suggesting that C-1–H contributes at ~2945 cm^{-1} in the α form.

The i.r. spectrum of α-D-glucose-*6,6*-d_2 (**4**) differs from that of **1** at high frequencies, in the presence of a band at 2963 cm^{-1} and in a slight change in frequency and intensity of the band at 2944 cm^{-1}; these bands are also different in the Raman spectrum. Thus, there could be some contribution of CH$_2$-stretching in

TABLE I

OBSERVED I.R. AND RAMAN FREQUENCIES (cm^{-1}) IN THE CH-STRETCHING REGION FOR D-GLUCOPYRANOSES

α-D-*Glucose*	*α*-D-*Glucose*-1-d$_1$	*α*-D-*Glucose*-6,6-d$_2$	*α*-D-*Glucose*-5,6,6-d$_3$	D-*Glucose*-2-d$_1$	*α*-D-*Glucose*-3-d$_1$	*β*-D-*Glucose*
I.r.						
				2974	2973	2978
2960 sh	2958 sh	2963	2964	2964	2964	2947
2944	2946	2938	2937	2938	2936	2933
2914	2914	2920 sh			2924	2920
2892	2891	2901		2903	2902	2898
2877	2876	2884	2884	2883		2880
2855	2855	2855				(2855)
Raman						
		2993	2994	2982	2993	
2966	2964	2968	2968	2973	2978	2978
2948	2948	2941	2941	2947	2968 2939	2948
2919	2916			2912		2934
2895	2892	2905	2891	2892	2905	2910
2883	2880	2887				2901
						2883

TABLE II

OBSERVED RAMAN FREQUENCIES (cm^{-1}) IN THE C–D STRETCHING REGION FOR DEUTERATED D-GLUCOPYRANOSES

α-D-Glucose-*1*-d_1	2196.2
α-D-Glucose-*6,6*-d_2	2240.0 2181.0 2123.0
α-D-Glucose-*5,6,6*-d_3	2232.3 2163.8–2143.6 2113.5
D-Glucose-*2*-d_1	2214
α-D-Glucose-*3*-d_1	2144.3

the band at 2944 cm^{-1} in conjunction with other motions. 6,6-Dideuteration should drastically modify the highly coupled motions. Furthermore, in the range 2920–2850 cm^{-1}, one band has disappeared in both the Raman and the i.r. spectra, suggesting a significant contribution of the CH_2 group also in this region. The Raman band at 2993 cm^{-1} observed for **4**, with no i.r. counterpart and not reported in ref. 13, is difficult to explain.

All bands which appeared in the i.r. and Raman spectra of α-D-glucose-*5,6,6*-d_3 (**5**) are found also in those of **4**, at the same frequencies, except for the two i.r. bands at 2901 and 2855 cm^{-1} and the Raman band at 2905 cm^{-1}, suggesting that these are the frequencies of two delocalised normal modes both containing contributions from C-5–H.

The i.r. and Raman spectra of D-glucose-*2*-d_1 (**6**) and D-glucose-*3*-d_1 (**7**) are difficult to interpret. In all the spectra, there is a band at 2975 cm^{-1}, characteristic of the β form. The other i.r. and Raman bands are found also in the spectra of **4**(α), with different intensities, thus suggesting that **6** and **7** are α as confirmed by the n.m.r. data for **7**. For **6**, the Raman band at 2993 cm^{-1} and the i.r. band at 2855 cm^{-1} are not observed. On comparing the spectra of **7** and **6**, it is seen that the band at 2883 cm^{-1} (i.r. and Raman) is absent from the former, while the unusual band at 2990 cm^{-1} is present and there are differences in the relative intensities of bands in the Raman spectra. The only certain assignment is that for the signal at 2883 cm^{-1} which is characteristic of C-3–H.

Thus, for α-D-glucopyranose (**1**), C-1–H gives an isolated band at 2945 cm^{-1}, the CH_2 group is associated with a band at 2945 cm^{-1} and possibly at 2963 cm^{-1}, another stretching of this group is present at frequencies lower than 2920 cm^{-1}, C-5–H contributes to the band at 2901 and/or 2855 cm^{-1}, and the band for C-3–H is at 2890 cm^{-1}.

The CH-stretching normal modes of these molecules are delocalised over several CH bonds; hence, deuteration at a single position does not allow precise determination of the force constant of the corresponding bond.

(b) C–D-Stretching region (2300–2000 cm^{-1}). Here it is possible to observe the frequencies of either isolated or less delocalised modes. Only Raman spectra were obtained (see Fig. 3 and Table II).

D-Glucose-*2-d*$_1$ (**6**) gave a single band, which means that the frequency of C-2–D is high when the mode is isolated. α-D-Glucose-*3-d*$_1$ (**7**) showed one main feature at the low value of 2144 cm^{-1}, which seems to parallel the situation in the C–H–stretching region. α-D-Glucose-*1-d*$_1$ (**3**) showed a band at 2196 cm^{-1}, higher than ν(C-3–D) and slightly lower than ν(C-2–D), in agreement with the assignment made in the C–H-stretching region. α-D-Glucose-*6,6-d*$_2$ (**4**) showed three bands (Table II), suggesting the existence of two fundamental vibrations and a combination (or overtone) in Fermi resonance with some CD$_2$-stretching motions. It is not known whether the two fundamentals are the symmetric and antisymmetric motions of two equivalent CD bonds or correspond to two different isolated CD-stretchings. The spectrum of α-D-glucose-*5,6,6-d*$_3$ (**5**) contains three bands (Table II), with frequencies approximately the same as those of α-D-glucose-*6,6-d*$_2$. The band of highest frequency did not change in intensity and shape. The intermediate band was broader, suggesting that it was due to C-5–D plus the Fermi resonant overtone. The lowest band had decreased in intensity, suggesting some contribution of C-5–D (in conjunction with some C-6–D).

(c) Normal co-ordinate calculations. From the foregoing considerations, it is apparent that specific deuteration is not sufficient to allow a complete assignment of C–H stretchings. The removal of a hydrogen atom does not result simply in the disappearance of a single band, which makes the fitting of force constants to experimental frequencies impossible. Hence, a "theoretical" force field is proposed which is derived from the known behaviour of CH bonds of model molecules in analogous environments. Based on the results of our normal co-ordinate calculations, the data of our spectra will be re-interpreted.

Early studies of the vibrational dynamics of D-glucose[3,13] involved calculations based on previous force fields for alkanes[14], ethers[15], and carboxylic acids[16], and were intended to characterise deformation motions. For CH-stretching motions, the same force constant was kept for all positions in the pyranose ring and gave approximately the same calculated frequency; the methylene CH's gave two frequencies corresponding to the symmetric and antisymmetric modes. This simple scheme does not correspond to the complexity of the observed spectra; furthermore, it predicts that the α and β forms should have approximately the same CH-stretching frequencies[3,4,13].

The differences between the spectra of the α and β forms may simply reflect the absolute configuration at C-1. The CH-stretching frequencies in ethers[5,17,18] are quite different and depend on the orientation of the CH bonds with respect to the lone pairs of the adjacent oxygen. This conclusion was reached on the basis of i.r. spectra of partially deuterated species and intensity studies[6,19], and has been confirmed through local mode spectroscopy[7,20]. These studies suggest that the influence of the oxygen does not go much beyond the first neighbour and, indeed, the characteristic frequencies of the CH_3 group are similar in alkanes[21], ethyl ether[7], and ethanol[22]. Furthermore, a comparison of the spectra of cyclohexane and 1,4-dioxane[17] shows that the influence on frequencies of the relative orientation of neighbouring CH bonds is considerably less than the effect of the oxygen. If, as a first approximation, only first-neighbour effects due to oxygen are considered, the differences in the spectra of α- and β-D-glucopyranose cannot be explained by reference only to O-5. The orientation of CH with respect to the OH at each chiral centre must be considered in the solid. These orientations are determined by the mutual arrangement of the molecules, which is known for α-D-glucose from neutron diffraction studies[23] and for β-D-glucose from X-ray studies[24]. From these structures, the corresponding Newman projection of each CH bond through the CO bond, as viewed from the vicinal hydroxyl group, was calculated (Fig. 4). The CH bonds in the β form are more closely spaced than in the α form, suggesting that they should have similar characteristic frequencies, as observed experimentally.

Various values for the diagonal CH-stretching force constants in *trans* or *gauche* conformations with respect to lone pairs of a vicinal oxygen have been reported[5,17,18,25]. Table III contains the frequency values for ethanol and 1,4-dioxane and the diagonal force constants calculated therefrom according to ref. 5; little is known for either the *cis* or intermediate conformations. For the *trans* conformation, application of quantum mechanics[18] indicates that there is considerable interaction of the oxygen lone-pair and the CH, depicted as a back-donation of charge from the lone-pair orbital into an antibonding σ^* orbital of the CH bond, which is then weakened. In turn, this causes a decrease in the Mulliken population of the oxygen as shown theoretically by Pople[26] for methanol and fluoromethanol and confirmed experimentally by the i.r. intensities for formaldehyde[27]. In fluoromethanol[26], the value of the oxygen population is the same as in methanol, both when the two CH's are *trans* or *cis* to lone pairs. Hence, the same low diagonal force-constant for a CH bond in either a *trans* or *cis* conformation with respect to a lone pair[†] has been assumed.

For the CH's outside the plane defined by CO and the lone-pair axis, higher force constants have been used. In order to complete this force field, the interaction of the CH's was examined. It has been proposed[29] that, in *n*-paraffins, there are first- and second-neighbour CH-stretching/CH-stretching interactions. This conclusion was reached on the basis of the observed dependence of CH-stretching frequencies on chain length and conformation. Alternatively, the diagonal CH-stretching force constants could vary along the *n*-paraffin chain[5]. For D-glucose, the CH-stretching frequencies are determined mainly by the interaction of CH's with

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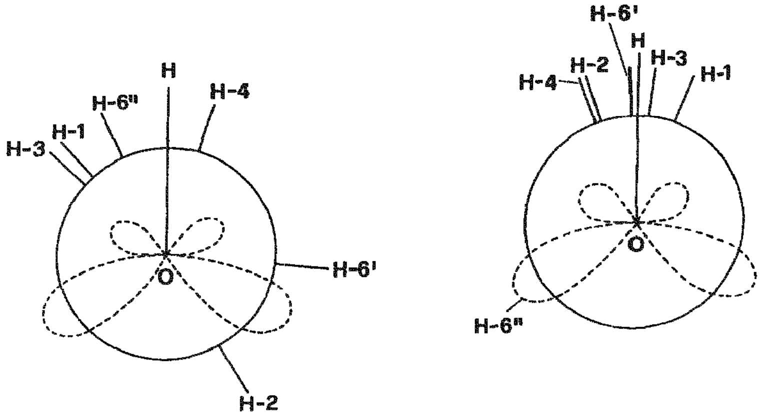
[†] For methanol, Sage[28] has proposed such a dependence of the CH-stretching force constant on the dihedral angle HCOH so as to imply a value for the *cis* conformation higher than those for *trans* and *gauche*. When applied to D-glucose, his rule would predict most of the CH stretchings for the β form to be at frequencies lower than those for the α form, which is contrary to observation.



α-D-Glucose β-D-Glucose

Fig. 4. Newman projections of HCOH groups in α- and β-D-glucopyranose, as viewed from O to C, in the crystalline state.

the neighbouring oxygens, and the effect was modelled by changing the diagonal force constants. The CH–CH interactions in the α and β forms should be similar and not of primary importance in explaining the marked differences in the spectra. Finally, reported[29] values of the CH–CH interaction force-constants were applied to CH–CH–CH and CH–O–CH. For the hydroxymethyl group, the mutual orientation of C-6–H′,H″ and C-5–H in the α and β forms, determined by the crystal structure, is presented in Fig. 5.

Normal co-ordinate calculations were then performed. The force field of Vasko *et al.*[3] was modified only in the part relative to the CH-stretching force constants. Table III contains the values most appropriate to the CH's in the extreme *trans* (=*cis*) and *gauche* conformations; the values for ethanol were used

TABLE III

EXPERIMENTAL FREQUENCIES FOR ISOLATED C–H-STRETCHINGS AND CORRESPONDING DIAGONAL FORCE CONSTANTS[a]

	Ref.	*CH* trans *to lone pair*		*CH* gauche *to lone pair*	
		ω_{CH} *(cm^{-1})*	f_t^{CH} *(mdyne/Å)*	ω_{CH} *(cm^{-1})*	f_g^{CH} *(mdyne/Å)*
Ethanol	25[b]	2898	4.594	2957	4.789
Dioxane	17[b]	2876	4.530	2962	4.805
	20[c]	2860	4.481	2950	4.768
Tetrahydropyran	20[c]	2831	4.390	2911	4.642

[a]Calculated according to ref. 5. [b]Deduced from the i.r. spectra of selectively deuterated molecules. [c]Deduced from n.i.r. spectroscopy.

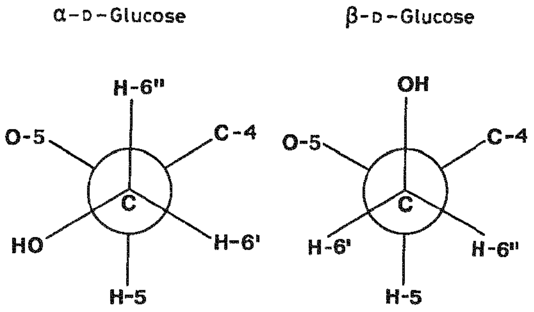


Fig. 5. Newman projections of CH_2OH group in α- and β-D-glucopyranose, as viewed from C-6 to C-5, in the crystalline state.

for all CH's, except for C-1–H and C-5–H. For C-5–H, the force constant of CH_{ax} in 1,4-dioxane was used, whereas, for C-1–H, averages from 1,4-dioxane and ethanol were used. With Fig. 4 in mind, the values reported in Table IV were obtained ultimately. Slight changes in the extremes were suggested by comparison with the experimental data, provided that the "theoretical" rule for defining force constants was not contravened. In particular for β-D-glucose, the values of the force constants for C-2–H and C-4–H were less than those obtained by a rigorous application of the results of Table III, thereby explaining the intense feature observed at 2935 cm^{-1}. The force constants for α-D-glucose relative to C-2–H and C-3–H near the *cis* and *trans* conformation relative to a lone pair, respectively, were reduced. The i.r. band at 2884 cm^{-1} for α-D-glucose-*5,6,6-d*$_3$ and the triplet of bands in the same frequency range for α-D-glucose-*6,6-d*$_2$ could then be interpreted as strongly coupled motions involving C-2–H and C-3–H (and C-5–H in **4**) (see below).

Tables V and VI contain the values of the frequencies thus calculated for CH- and CD-stretchings and the description of the corresponding normal modes in terms of internal eigenvectors. Calculations for the α and β forms of **6** are reported, since no n.m.r. data were obtained.

(d) Calculation of i.r. intensities. Such calculations can nowadays describe the qualitative behaviour of the bonds[6,19] and, for simple molecules, there is a correlation between force constants and intensity parameters[19].

TABLE IV

VALUES OF THE DIAGONAL FORCE CONSTANTS (mdyne/Å) FOR THE CH-STRETCHINGS OF D-GLUCOSES

α-D-Glucose		*β-D-Glucose*	
C-5–H	4.530	C-5–H	4.530
C-3–H	4.540	C-6–H"	4.530
C-2–H	4.550	C-1–H	4.640
C-6–H'	4.550	C-4–H	4.730
C-1–H	4.702	C-2–H	4.730
C-6–H"	4.730	C-3–H	4.799
C-4–H	4.750	C-6–H'	4.799

TABLE V

CALCULATED FREQUENCIES (cm^{-1}) AND EIGENVECTORS (a.m.u.)$^{-1/2}$ FOR α-D-GLUCOPYRANOSES

α-D-Glucose-5,6,6-d$_3$		*α-D-Glucose*-6,6-d$_2$	
2958	1.02C-4–H − 0.16C-2–H	2959	1.02C-4–H − 0.16C-2–H
2943	1.03C-1–H + 0.10C-2–H	2943	1.03C-1–H + 0.10C-2–H
2894	0.76C-2–H − 0.69C-3–H	2900	0.79C-3–H − 0.22C-2–H − 0.64C-5–H
2889	0.67C-2–H + 0.77C-3–H + 0.12C-4–H	2892	0.98C-2–H − 0.11C-1–H + 0.14C-4–H − 0.25C-5–H
2199	0.68C-6–D″ − 0.37C-6–D′	2879	0.78C-5–H + 0.67C-3–H + 0.14C-2–H
2147	0.73C-5–D + 0.21C-6–D′	2199	0.68C-6–D″ − 0.37C-6–D′
2120	0.63C-6–D′ + 0.34C-6–D″ − 0.21C-5–D	2122	0.66C-6–D′ + 0.34C-6–D″
α-D-Glucose		*α-D-Glucose*-1-d$_1$	
2965	0.86C-4–H − 0.12C-2–H − 0.56C-6–H′	2965	0.86C-4–H − 0.56C-6–H′ − 0.12C-2–H
2944	0.35C-1–H + 0.14C-2–H − 0.50C-4–H + 0.19C-6–H′ − 0.80C-6–H″	2944	0.85C-6–H″ − 0.20C-6–H′ + 0.55C-4–H − 0.11C-2–H
2943	0.97C-1–H + 0.23C-4–H + 0.27C-6–H″	2901	0.72C-3–H − 0.65C-5–H − 0.28C-6–H′ − 0.12C-6–H″ − 0.17C-2–H
2901	0.72C-3–H − 0.66C-5–H − 0.16C-2–H − 0.26C-6–H′ − 0.12C-6–H″	2893	0.94C-2–H − 0.12C-3–H + 0.13C-4–H − 0.22C-5–H − 0.33C-6–H′
2892	0.92C-2–H − 0.11C-1–H − 0.14C-3–H + 0.12C-4–H − 0.20C-5–H − 0.36C-6–H′	2889	0.82C-6–H′ + 0.17C-6–H″ + 0.48C-3–H + 0.35C-2–H
2888	0.39C-2–H + 0.47C-3–H + 0.81C-6–H′ + 0.17C-6–H″	2877	0.77C-5–H − 0.40C-6–H′ + 0.56C-3–H + 0.10C-2–H
2877	0.56C-3–H + 0.77C-5–H − 0.40C-6–H′	2185	0.76C-1–D
α-D-Glucose-2-d$_1$		*α-D-Glucose*-3-d$_1$	
2964	0.85C-4–H − 0.59C-6–H″ + 0.10C-6–H′	2964	0.86C-4–H − 0.56C-6–H″ + 0.10C-6–H′ − 0.12C-2–H
2943	0.83C-6–H″ − 0.20C-6–H′ + 0.59C-4–H	2944	0.51C-4–H + 0.80C-6–H″ − 0.19C-6–H′ − 0.36C-1–H − 0.14C-2–H
2942	1.04C-1–H	2943	0.97C-1–H + 0.23C-4–H + 0.28C-6–H″
2901	0.71C-3–H − 0.68C-5–H − 0.31C-6–H′ − 0.12C-6–H″	2894	0.71C-6–H′ + 0.69C-5–H + 0.19C-6–H″
2889	0.87C-6–H′ − 0.18C-6–H″ + 0.51C-3–H + 0.10C-5–H	2892	1.0C-2–H − 0.11C-1–H + 0.16C-4–H + 0.13C-5–H + 0.14C-6–H′
2877	0.77C-5–H + 0.56C-3–H − 0.41C-6–H′	2882	0.76C-5–H − 0.70C-6–H′
2150	0.76C-2–D	2149	0.76C-3–D

TABLE VI

CALCULATED FREQUENCIES (cm^{-1}) AND EIGENVECTORS $(a.m.u.)^{-1/2}$ FOR β-D-GLUCOSES

β-D-Glucose-2-d$_1$		*β-D-Glucose*	
2975	1.02C-3–H − 0.17C-1–H − 0.10C-5–H	2975	1.020C-3–H − 0.17C-1–H
2970	1.03C-6–H′	2970	1.03C-6–H′
2951	1.03C-4–H	2961	0.73C-2–H − 0.74C-4–H
2925	0.98C-1–H + 0.14C-3–H − 0.30C-5–H	2941	0.73C-2–H + 0.72C-4–H − 0.11C-1–H
2890	0.75C-6–H″ + 0.67C-5–H + 0.11C-3–H + 0.22C-1–H	2925	0.97C-1–H + 0.15C-3–H − 0.30C-5–H
2877	0.71C-6–H″ − 0.72C-5–H − 0.17C-1–H	2890	0.75C-6–H″ + 0.67C-5–H + 0.11C-3–H + 0.22C-1–H
2192	0.76C-2–D	2877	0.72C-5–H − 0.71C-6–H″ + 0.17C-1–H

TABLE VII

CALCULATED FREQUENCIES (cm^{-1}) AND ABSOLUTE INTENSITIES ($esu^2.cm^2 \times 10^{39}$), WITH THE SETS OF CHARGES FOR α-D-GLUCOSES

ν	*A*	*B*
α-D-*Glucose*		
2964.6	0.259	0.440
2944.2	4.213	7.581
2942.5	9.907	11.083
2901.1	0.628	0.718
2892.5	9.739	8.748
2888.4	3.069	3.076
2877.0	9.423	5.544
α-D-*Glucose*-1-d_1		
2964.6	0.240	0.420
2944.0	7.576	12.240
2901.1	0.662	0.750
2893.0	10.724	9.800
2888.5	2.975	2.910
2877.0	9.418	5.540
2184.8	5.429	5.250
α-D-*Glucose*-2-d_1		
2963.7	0.399	0.610
2943.5	9.330	14.490
2942.2	5.637	5.470
2900.8	0.284	0.330
2889.0	5.519	4.380
2877.1	10.924	6.730
2150.1	4.381	4.400
α-D-*Glucose*-3-d_1		
2964.5	0.227	0.400
2944.2	4.146	7.480
2942.5	9.867	11.110
2894.0	6.208	4.440
2891.7	4.532	5.440
2882.0	5.227	4.150
2149.5	6.013	3.760
α-D-*Glucose*-6,6-d_2		
2958.6	2.779	4.920
2942.7	6.732	6.680
2900.1	0.735	0.590
2891.8	7.583	7.520
2879.0	10.836	5.950
2199.4	4.386	6.430
2122.1	2.736	3.190

TABLE VII *(continued)*

ν	*A*	*B*
α-D-Glucose-5,6,6-d_3		
2958.4	2.560	4.680
2942.7	6.677	6.640
2894.2	11.917	9.700
2889.1	0.146	0.090
2199.2	3.851	5.870
2146.9	6.044	3.940
2119.8	3.654	4.090

We have used the *charge flow model*, which can also be employed for the calculation of the rotational strengths[30], and have considered only the intensities of CH- and CD-stretchings for which it is necessary to know the charges of hydrogen atoms and the charge flows due to such vibrations. On the basis of previous studies[6], it was convenient to characterise the different electrical behaviour of the various CH's, assuming (*a*) constant charge flow along CH bonds due to their own stretchings, (*b*) zero charge flow along bonds not stretched, and (*c*) different equilibrium charges.

For (*a*), the value −0.200 e/Å (from C to H) was assumed; different values for the charges relative to the different conformations were used by analogy with

TABLE VIII

CALCULATED FREQUENCIES (cm^{-1}) AND ABSOLUTE INTENSITIES ($esu^2.cm^2 \times 10^{39}$), WITH THE SETS OF CHARGES FOR β-D-GLUCOSES

ν	*A*	*B*
β-D-Glucose		
2975.2	1.920	4.347
2970.1	4.607	7.186
2960.7	0.021	0.040
2940.8	7.225	11.988
2924.7	2.498	2.962
2889.6	10.878	7.203
2877.2	5.187	3.269
β-D-Glucose-2-d_1		
2975.0	1.741	3.990
2970.1	4.645	7.125
2950.9	2.910	4.880
2924.8	3.299	4.100
2889.6	11.077	7.420
2877.2	5.254	3.340
2191.7	3.178	5.300

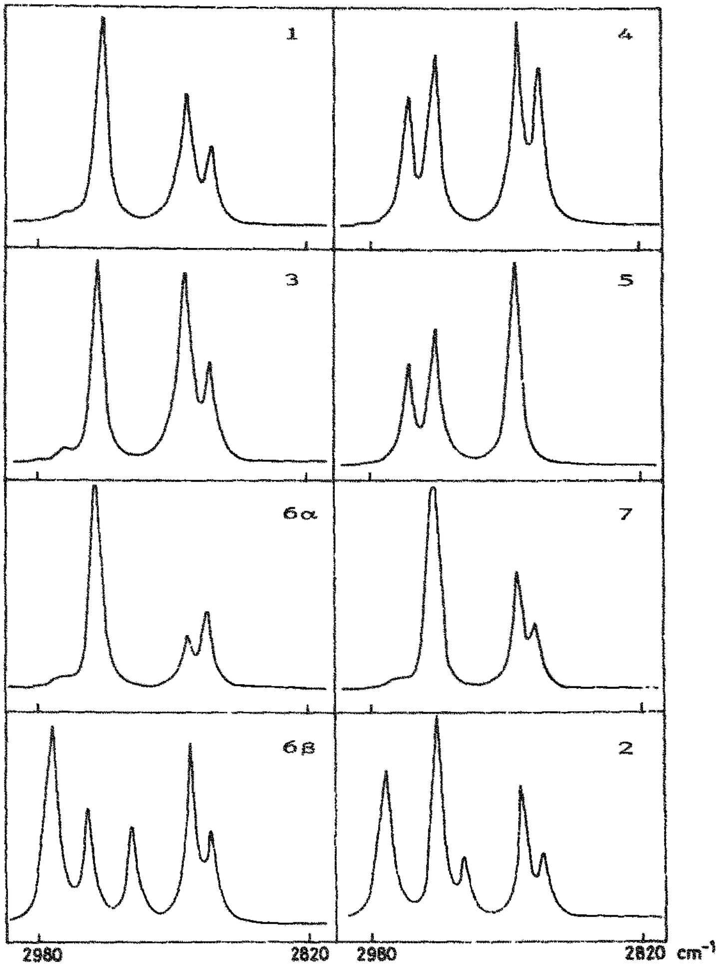


Fig. 6. Calculated i.r. spectra (2800–3000 cm^{-1}) of D-glucoses.

the force constants. For methyl ether and methanol, values of 0.07 and 0.02 e were found[6] for the charge of CH's *gauche* and *trans* to an oxygen lone-pair, respectively. This difference shows that the back-donation is favoured when the CH is in the plane of the lone-pair orbital; both values are different from that of 0.045 e found for paraffins because of the presence of the oxygen. The latter value was used for those orientations in between *gauche* and *trans*, and 0.02 e was used also for CH *cis* to a lone pair*. The results thus obtained are presented in columns A of Tables VII

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*For the full calculations, the charges for oxygens, hydroxyl hydrogens, and carbons are needed. These are not important for the intensities of CH-stretching normal modes. For the sake of completeness, their values are listed: $q_0 = -0.570$ e for hydroxyl oxygens (as derived from methanol); $q_0 = -0.360$ e for the oxygen in the pyranose ring (from methyl ether); $q_H = 0.391$ e for hydroxyl hydrogens (from methanol). Q_C for the different functional groups were obtained by imposing the neutrality separately on the groups CH$_2$OH, C-5–H–O–C-1–H–OH, and CHOH in all the other chiral centres. $\partial q^{OH}/\partial r_{OH} = -0.118$ e/Å from O to H as in methanol[11].

and VIII. From a comparison with Fig. 1, it appears that the intensities of the low-frequency bands have been overestimated relative to those of high frequency. When the charge values of set A were interchanged, the intensities in column B were obtained. The spectra in Fig. 6 were calculated (set B) for the CH-stretching region for the isotopic species of known anomeric composition, ascribing a Lorentzian band-shape to the transitions with 5 cm^{-1} half-height full band-width. In this way, the calculated and experimental spectra compare fairly well even though there is no explanation of why the charges of the weaker CH's should be higher. It is not known whether this fact is general or applies only to some CH's. The experimental finding that, for D-glucose, the higher frequencies correspond to the higher intensities is contrary to what is usually observed[19].

DISCUSSION

Although the calculations reported here cannot be considered as final, they give a better understanding of the vibrational spectra of D-glucose and rationalise the marked differences in the spectra of the α and β forms.

For α-D-glucopyranose, the orientation of C-5–H *trans* to a lone pair on O-5 is defined by the $^4C_1$ conformation of the pyranose ring, which determines its characteristic frequency to be unambiguously low, at 2880 cm^{-1}. Indeed, some modifications in the i.r. and Raman spectra are observed near this frequency for **5** but, as shown by the data in Table V, C-5–H couples with C-3–H which has a similar force constant. Moreover, the calculated C-5–D stretching frequency is at 2147 cm^{-1}, close to the observed value at 2150 cm^{-1}.

C-3–H is almost *trans* to a lone pair on the closest hydroxyl oxygen (Fig. 5) and it is likely that its stretching vibration should be at ~2880 cm^{-1}. This view accords with the observed disappearance of the band at 2883 cm^{-1} in the i.r. and Raman spectra of **7** and with the correspondingly low CD-stretching observed at 2144 cm^{-1}. Moreover, with C-3–H and C-5–H being degenerate, symmetric and antisymmetric motions at 2880 and 2900 cm^{-1}, respectively, are obtained from the force field. This might explain how 5-deuteration causes the disappearance of two i.r. bands (2901 and 2855 cm^{-1}), since the band for C-3–H, now decoupled from C-5–H, is shifted towards the frequency of another CH-stretching, possibly C-2–H. In the i.r., the normal mode C-3–H + C-5–H (which is predicted to be more intense) is calculated at lower frequency (see Table VII and Fig. 6), in contrast to what is observed for **4**. Also, in the Raman, the strongest feature was observed at 2905 cm^{-1} and, in general, symmetric motions are expected to be more intense than antisymmetric. These facts require a reversal of the order of these two frequencies which could be accomplished by changing the sign of the interaction force constants f''_t, if the diagonal force constant of Table IV is maintained. Furthermore, our force field makes it hard to interpret the 2914 cm^{-1} band of **1**, **3**, **6**, and **7**, which seems to correlate to that at 2905 cm^{-1} in **4**.

The C-1–H bond is subject to two opposite interactions since it is *gauche* to the lone pairs on O-5 and *trans* to a lone pair on the closest hydroxyl oxygen. The values for the CH- and CD-stretching frequencies (Table V), obtained by averaging the relevant force constants, approximate quite well the values 2945 and 2196 cm^{-1} assigned previously.

The C-6–H′, C-6–H″, C-4–H, and C-2–H bonds are influenced only by hydroxyl groups, and their orientation is such that it is difficult to establish their force constants (see Fig. 4). A high value was ascribed to C-6–H″ and C-4–H, which are oriented at a small angle from the *cis* position with respect to the OH bond, and a low value to C-2–H and C-6–H′, which are nearly *cis* to a lone pair.

The first two stretchings give rise to two coupled motions at 2965 and 2944 cm^{-1}, the first of which is absent from the i.r. spectrum of the non-deuterated compound, as well as from that of **3**, since it is the antisymmetric combination of the two. Also, it was predicted correctly that there should be an intense i.r. band at ~2960 cm^{-1} when position **6** is dideuterated, as in **4** and **5** (see Tables V and VII, and Fig. 6). Our prediction for these bonds is not as good for **6** and **7**, where a rather intense i.r. and Raman band at 2960 cm^{-1} was observed which was calculated as weak. In the force field, C-2–H and C-6–H′ are strongly mixed with C-3–H and C-5–H, and contribute mostly to the bands at 2892 and 2888 cm^{-1} for **1** (see Table V). The prediction of a low frequency for C-2–H contrasts with the observation for **6** of a C-2–D stretching frequency that is among the highest recorded (see Fig. 3)*. On the other hand, good values were calculated for C-6–D′D″ compared to experiment, even though it is difficult to determine the nature of the bands predicted.

The force field allows no interpretation of the Raman band at ~2990 cm^{-1} for **4**, **5**, and **7**. The fact that this band is not observed in **6** could be associated with the observed high value for C-2–D.

The comparison of the predicted with the experimental data for β-D-glucopyranose was less effective because no data on deuterated derivatives are available. The CH-stretchings can be classified into three groups.

The C-3–H and C-6–H′ bonds are *cis* to the nearby hydroxyl group (Fig. 4) and thus have the highest force constant. It seems reasonable to assign these stretchings to the feature at ~2978 cm^{-1} in the i.r. and Raman spectra. Because of the presence of the two motions, the calculated intensity of this band is too high in the i.r. (Fig. 6) and is supposed to be high also in the Raman.

The C-4–H and C-2–H bonds have almost the same orientation, namely, in between *trans* and *gauche* to a lone pair, and it is predicted that they give a symmetric and an antisymmetric motion, at 2940 and 2960 cm^{-1}, respectively. The C-1–H bond, instead, is influenced by two types of oxygen atoms. Since it is axial,

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*Standard localisation procedures for the oxygen lone-pairs obtained from a STO-3G quantum mechanical calculation on ethanol[31] indicate that the lobes of Fig. 5 are separated by ~127°, which would render the C-2–H stretching force constant higher. Preliminary calculations, fitting ν(C-2–D) to the observed value, give results which are no better than those presented here.

its characteristic frequency is lowered by back-donation from a lone pair on O-5, but, being in a conformation similar to C-2–H and C-4–H with respect to hydroxyl (Fig. 4), its frequency tends to be higher and is calculated as 2924 cm^{-1}. Thus, these motions should give rise to the structured band observed at ~2940 cm^{-1}, the i.r. intensity of which is the highest in the spectrum. The prediction of this band is only achieved partially (Fig. 6), since its centre-frequency seems to be higher than that calculated and the prominent shoulder on the high frequency side was not predicted at all.

The C-6–H″ bond is *cis* to a lone pair (Fig. 4) and a low frequency is attributed to it. The C-5–H bond has the same axial conformation as in the α anomer and is almost degenerate, with C-6–H″ giving rise to symmetric and antisymmetric motions at 2890 and 2877 cm^{-1}, respectively. Two bands in this frequency range are found in the i.r. spectrum. In the Raman spectrum, this feature is the most intense and is at higher frequencies, containing probably also a motion of the group discussed above.

For aqueous solutions of α- and β-D-glucose, the interactions of oxygen lone-pairs with adjacent CH bonds can also be used to define a force field describing the behaviour of CH-stretchings in solution. In this situation, the orientations of the hydroxyl groups are not fixed as in the solid and the possibly large amplitude torsional motions render the influence of oxygen lone-pairs not as specific as in the solid. It is reasonable to assume that the primary factor in the definition of the

TABLE IX

CALCULATED FREQUENCIES (cm^{-1}), EIGENVECTORS (a.m.u.$^{-1/2}$), AND ABSOLUTE INTENSITIES (esu^2.cm^2 × 10^{39}), FOR α-D-GLUCOSE AND β-D-GLUCOSE IN AQUEOUS SOLUTION

ν	*Eigenvectors*	I_A	I_B
α-D-Glucose			
2963.7	1.03C-1–H	5.806	8.647
2961.6	0.71C-6–H′ − 0.74C-6–H″	4.856	4.517
2920.0	−0.69C-2–H + 0.74C-4–H	0.348	0.384
2913.1	−0.10C-2–H + 0.98C-3–H − 0.18C-4–H	5.411	5.939
2901.2	0.74C-2–H + 0.16C-3–H + 0.56C-4–H	6.145	5.670
2887.6	−0.40C-4–H − 0.63C-6–H′ − 0.68C-6–H″	6.127	6.209
2868.6	1.0C-5–H	8.340	5.563
β-D-Glucose			
2955.0	−0.75C-6–H′ + 0.73C-6–H″	6.130	6.137
2920.4	0.72C-2–H − 0.74C-4–H	0.005	0.005
2915.1	−0.12C-2–H + 0.98C-3–H − 0.14C-4–H	2.620	3.364
2900.3	0.69C-2–H + 0.11C-3–H + 0.55C-4–H	12.135	11.343
2898.1	0.23C-2–H + 0.27C-4–H + 0.27C-5–H + 0.63C-6–H′ + 0.63C-6–H″	1.543	1.518
2880.3	−0.76C-1–H + 0.62C-5–H	1.079	0.893
2857.6	0.65C-1–H + 0.74C-5–H	13.850	8.499

TABLE X

COMPARISON OF OBSERVED AND CALCULATED FREQUENCIES FOR D-GLUCOSE (COLUMNS I–III CONTAIN THE I.R., RAMAN, AND CALCULATED FREQUENCIES, RESPECTIVELY; COLUMN IV CONTAINS THE CALCULATED ASSIGNMENTS)

I	*II*	*III*	*IV*	*I*	*II*	*III*	*IV*
α-D-*Glucose*				*α*-D-*Glucose*-1-d_1			
2960 sh	2966	2965	C-4–H − C-6–H″	2958	2964	2965	C-4–H − C-6–H″
2944	2948	2944	C-6–H″ + C-4–H	2946	2948	2944	C-4–H + C-6–H″
		2943	C-1–H	2914	2916	2901	C-3–H − C-5–H
2914	2919	2901	C-3–H − C-5–H	2891	2892	2893	C-2–H
2892	2895	2892	C-2–H	2876	2880	2889	C-6–H′
2877	2883	2888	C-6–H′	(2855)		2877	C-5–H + C-3–H
(2855)		2877	C-5–H + C-3–H				
α-D-*Glucose*-6,6-d_2				*α*-D-*Glucose*-5,6,6-d_3			
	2993 ?				2994 ?		
2963	2968	2959	C-4–H	2964	2968	2958	C-4–H
2938	2941	2943	C-1–H	2937	2941	2943	C-1–H
2920 sh							
2901	2905	2900	C-3–H − C-5–H	2884	2891	2894	C-2–H − C-3–H
2884	2887	2892	C-2–H			2889	C-3–H + C-2–H
2855		2879	C-3–H + C-5–H				
α-D-*Glucose*-3-d_1				*β*-D-*Glucose*			
	2993			2978	2978	2975	C-3–H
2973	2978					2970	C-6–H′
2964	2968	2964	C-4–H − C-6–H″	2947	2948	2961	C-2–H − C-4–H
2936	2939	2944	C-6–H″ − C-4–H	2933	2934	2941	C-2–H + C-4–H
		2943	C-1–H	2920	2910	2925	C-1–H
2924 sh				2898	2901	2890	C-6–H″ + C-5–H
2902	2905	2894	C-6–H′ − C-5–H	2880	2883	2877	C-5–H − C-6–H″
(2888)		2892	C-2–H				
(2856)		2882	C-5–H − C-6–H′				

I	*II*	*αIII*	*IV*	*βIII′*	*IV′*
D-*Glucose*-2-d_1					
	2982				
2974	2973			2975	C-3–H
				2970	C-6–H′
2964		2964	C-4–H − C-6–H″		
	2947	2943	C-6–H″ + C-4–H	2951	C-4–H
2938		2942	C-1–H	2925	C-1–H
2903	2912	2901	C-3–H − C-5–H		
	2892	2889	C-6–H′	2890	C-6–H″ + C-5–H
2883		2877	C-5–H + C-3–H	2877	C-6–H″ − C-5–H

CH-stretching force constants is simply their position in the pyranose ring. In order to transfer force constants, tetrahydropyran should be considered in which, from n.i.r. spectroscopy, a weak band at low frequency, corresponding to axial CH's in the α-position, can be distinguished from an intense band which includes the contributions from all the other CH's[20]. However, these experiments[20] give only a qualitative indication. The actual values of the force constants were obtained as follows. For C-5–H in α- and β-D-glucose and C-1–H in the β form, which are conformationally similar also to axial CH's in dioxane, the value in Table III, obtained from n.i.r. spectroscopy, was used. For C-1–H of α-D-glucose, the force constant relative to the equatorial CH's of 1,4-dioxane (Table III) was used. For C-2–H, C-3–H, and C-4–H, the value of 4.600 mdyne/Å was assumed, which is close to that derived from the most intense n.i.r. band in tetrahydropyran[20]. For the CH_2OH group, the force constant derived for ethanol by Perchard and Josien[32] was used; different conformations of CH's with respect to the OH were not distinguished, thus giving the symmetric and antisymmetric motions typical of the methylene groups of equivalent CH's.

Using this force field for α- and β-D-glucose, the frequencies, normal modes, and intensities reported in Table IX were obtained. There is no detailed experimental data on these vibrations. However, Back *et al.*[33] have monitored the mutarotation of aqueous solutions of α- and β-D-glucose and deduced that C-1–H absorbs at 2948 cm^{-1} in the α form and at 2884 cm^{-1} in the β form. The method adopted here to establish CH-stretching force constants for these compounds reproduces and explains this difference in frequency. Furthermore, it gives three coupled motions in the range 2920–2900 cm^{-1}, involving the centres 2–4. These are the motions which were thought to explain the sign of CH-stretching vibrational c.d. spectra of all aldohexoses[8,9]. The assignments of i.r. and Raman spectra of α- and β-D-glucose, both in the solid and in solution in D_2O, are summarised in Table X.

In conclusion, our assignment to each CH (CD) stretching of a diagonal force constant that is a function of the position of the CH (CD) bond in the pyranose ring and, for solids, of the dihedral angle HCOH provides an explanation of the differences in the i.r. and Raman spectra of α- and β-D-glucose both in the solid state and in solution. The differences are major in the solid, since the spectral features are determined by the conformation of the hydroxyl group at every chiral centre, which is fixed ultimately by the arrangement of the molecules in the crystal. In solution, there is instead only one difference between α and β, reflecting the configuration at C-1. For solutions, the assumption of a common value for the diagonal force constants of C-2–H, C-3–H, and C-4–H justifies the existence of strongly coupled motions which have been thought to be responsible for vibrational c.d. in aldohexoses[8].

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