



Vibrational normal modes calculation in the crystalline state of methylated monosaccharides: Anomers of the methyl-D-glucopyranoside and methyl-D-xylopyranoside molecules



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ABSTRACT

A structural investigation of the organic molecules is being carried out using vibrational spectroscopy. In this study, normal co-ordinate calculations of anomers of the methyl-D-glucopyranoside and methyl- β -D-xylopyranoside in the crystalline state have been performed using the modified Urey–Bradley–Shimanouchi force field (mUBSFF) combined with an intermolecular potential energy function. The latter includes Van der Waals interactions, electrostatic terms, and explicit hydrogen bond functions. The vibrational spectra of the compounds recorded in the crystalline state, in the 4000–500 cm^{-1} spectral region for the IR spectra, and in the 4000–20 cm^{-1} spectral range for the Raman spectra are presented. After their careful examination, several differences in the intensities and frequency shifts have been observed. The theoretical spectra have been obtained after a tedious refinement of the force constants. Thus, on the basis of the obtained potential distribution, each observed band in IR and in Raman has been assigned to a vibrational mode. The obtained results are indeed in agreement with those observed experimentally and thus confirm the previous assignments made for the methyl- α and β -D-glucopyranoside, as well as for the methyl- β -D-xylopyranoside.

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1. Introduction

Sugars are biomolecules used not only in various applications such as the pharmaceutical and food industries, but also in environment domains. Although the number of monosaccharides is small, their association and their combination have led to the existence of a considerable number of oligo- and poly-saccharides. This diversity is due to the presence of the anomeric carbon. This structural feature is the origin of an important number of phenomena and biological behaviors.

The various experimental methods such as spectroscopy applied to sugars have been used as a structural approach to bring about the different pyranose and furanose ring configurations of the monosaccharides or their anomery.

Because the interpretation of the obtained IR and Raman spectra is not too precise, some analysis calculations of the normal modes have been realized in this work in order to obtain more accurate attributions of the bands of vibration. Thus this work consists of obtaining the vibrational molecular force field of three molecules, the methyl- α -D-glucopyranoside (Me- α -D-GLU), the methyl- β -D-glucopyranoside

hemihydrate (Me- β -D-GLU) and the methyl- β -D-xylopyranoside (Me- β -D-XY) in the crystalline state. A normal coordinate analysis has been done in the crystalline state using a modified Urey–Bradley–Shimanouchi force field combined with an intermolecular potential energy function that includes Van Der Walls interactions, some electrostatic terms and an explicit hydrogen bond function. The frequencies calculation of the internal intermolecular vibration has been accomplished using the CVOA (Crystalline Vibrations Optically Active) program [1].

The structures of these molecules can be determined using experimental methods such as X-ray diffraction, neutrons diffusion, nuclear magnetic resonance, Raman diffusion and Infrared absorption, as well as theoretical methods using quantum mechanics such as the *ab-initio*, semi-empirical and empirical methods. The infrared spectra of the three compounds are recorded in the 4000–500 cm^{-1} region while the Raman spectra are recorded in the 4000–20 cm^{-1} region. The calculation consists of fitting the force constants derived from calculations on similar molecules, namely the glucopyranose anomers [2]. The objective is to obtain a good agreement between the calculated frequencies and the observed ones on the IR and Raman spectra. The fitting of the force fields is done in such a way so that the calculated and the observed frequencies are as close as possible, with the aid of the Jacobian matrix. This study has been based on some previous works [2,13] which helped obtaining a better result interpretation and

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that would certainly be exploited in other research works. Moreover, the isotopic derivatives have been very helpful to confirm the reliability of the obtained force field.

2. Normal coordinates analysis

The CVOA program written by Takeuchi [1] has been utilized to calculate the optically active vibrations of the molecules in the crystalline state. The method used to determine the frequencies and normal modes of vibration is derived from the Wilson GF method [14] and has been made assuming that the molecule is inside the crystal and using the intramolecular modified Urey–Bradley–Shimanouchi intramolecular potential combined with an intermolecular function [15].

2.1. Samples

The Me- α -D-GLU and Me- β -D-GLU hemihydrate molecules are obtained from the α and β -D-glucopyranoside molecules respectively. The goal of the substitution of the hydrogen belonging to the anomeric carbon hydroxyl by the tetrahedral methyl group is to study the anomeric effect in the saccharides and to study also the nature of the glycosidic bond. In fact, both of these molecules act as chemical intermediates in the production of many products including emollients, emulsifiers, humectants, moisturizers, thickening agents, plasticizers, surfactants, varnishes, and resins [16,17].

The Me- β -D-XY molecule is a monosaccharide derived from the β -D-glucopyranose when replacing the CH₂OH group of the C₅ carbone by hydrogen. This substitution allows studying the anomeric effect in the saccharides as well as the glycosidic bond nature. It is a monosaccharide used as a carbon source for some mushrooms such as the *Aspergillus tamarii* and used also as a growing substrate to produce enzymes. It is also part of the composition of some oligosaccharides such as pectines [18,19].

The samples of the three molecules have been purchased from the Sigma-Aldrich company as a white crystalline powder with a 98% purity.

2.2. Material

The FT-IR spectra of these compounds were recorded in the 4000–500 cm⁻¹ range, using a Shimadzu FTIR 8300 spectrophotometer with a 2 cm⁻¹ spectral resolution and 64 scans and with KBr pellets. The Raman spectra in the frequency 4000–20 cm⁻¹ range have been obtained using a T64000 Isa/JOBIN Yvon spectrometer with a 514.5 radiation laser and a resolution of about 2 cm⁻¹ with 4 accumulated scans.

These spectra constitute the experimental support for the establishment of a force field for the molecule in the crystalline state through a normal coordinate analysis.

2.3. Geometry

The structures of the Me- α -D-GLU and Me- β -D-GLU molecules differ in the configuration at the carbon labeled C₁ (in the first anomer, the C₁–H bond is equatorial while it is axial in the second one). The conformation of the primary hydroxyl group 'CH₂OH' is also different from one case to the other (it is GT (gauche-trans) for the first anomer and GG (gauche-gauche) for the second one). These molecules have a ⁴C₁ configuration of the pyranose ring [16,17].

The structure of Me- β -D-XY was studied by S. Takagi [18,19] using neutron scattering. This molecule is derived from Me- β -D-GLU when replacing the CH₂OH group of C₅ by one hydrogen. This compound crystallizes in a monoclinic system with two molecules per unit cell with the P2₁ spatial group and has the ¹C₄ configuration of the pyranose ring. The crystallographical data used in the normal mode analysis for the three molecules [16–19] are summarized in Table 1.

Table 1

Crystallographical data used in the normal mode analysis of the Me- α -D-GLU, Me- β -D-GLU and Me- β -D-XY molecules.

	Me- α -D-GLU	Me- β -D-GLU	Me- β -D-XY
Formula	C ₇ H ₁₄ O ₆	C ₇ H ₁₄ O ₆ , 1/2 H ₂ O	C ₆ H ₁₂ O ₅
Conformation of CH ₂ OH	GT	GG	–
Number of atoms (N)	27	29	23
Internal mode (3N-6)	75	76	63
space group	P2 ₁ 2 ₁ 2 ₁	P4 ₁ 2 ₁ 2	P2 ₁
Molecules per cells (Z)	4	8	2
Number of cells considered	27	125	25
Number of hydrogen-bonds	5	5	3
Parameter cells:			
a (Å)	11.311	7.433	7.877
b (Å)	14.781	7.433	6.933
c (Å)	5.281	34.154	7.748
α = 'y' (°)	90	90	90
β (°)	90	90	113.38

These molecules as well as their atom numbering are presented in Fig. 1. The coordinates of cell molecules are shown in Table 2.

2.4. Internal coordinates

In the studied molecules, there are:

88 internal coordinates constituted of 27 stretchings, 48 bendings and 13 torsional angles reduced to 75 internal modes for Me- α -D-GLU.

89 coordinates constituted of 28 stretchings, 48 bendings and 13 torsional angles reduced to 76 internal modes for Me- β -D-GLU hemihydrates.

75 internal coordinates constituted of 23 stretchings, 41 bendings and 11 torsional angles reduced to 63 internal modes Me- β -D-XY.

The geometrical redundancies resulting from the pyranose ring and its substituents were eliminated using the REDUND program. The two redundancies due, respectively, to the CH₂OH and CH₃ (Fig. 2) groups are treated on the basis of local symmetry [20,21]. When the internal modes of vibrations are combined with the six external modes (three translations and three rotations), the irreducible representation in the crystalline state is given by:

$$\begin{aligned} \text{Me-}\alpha\text{-D-GLU : } \Gamma_{\text{crystal}} &= 81A + 80B1 + 80B2 + 80B3 \\ \text{Me-}\beta\text{-D-GLU } \Gamma_{\text{crystal}} &= 87A1 + 86A2 + 86B1 + 86B2 + 86E \\ \text{Me-}\beta\text{-D-XY } \Gamma_{\text{crystal}} &= 68A + 67B. \end{aligned}$$

2.5. Potential energy function

The calculation of normal modes has been achieved assuming that the molecule is inside the crystal using the intramolecular modified Urey–Bradley–Shimanouchi potential [15,22], combined with an intermolecular potential as described in Ref. [23]:

2.5.1. The intramolecular function

For the studied molecules, the selected potential energy function is the Urey–Bradley–Shimanouchi modified one (mUBSFF), given by:

$$\begin{aligned} V(r) = & 1/2 \sum K_i (\Delta r_i)^2 + 1/2 \sum H_{ij} (\Delta \alpha_{ij})^2 + 1/2 \sum F_{ij} (\Delta q_{ij})^2 \\ & + 1/2 \sum Y_i (\Delta \tau_i)^2 + 1/2 \sum F'_{ij} W_{g_{ij}} (\Delta r_i \Delta \alpha_{ij}) \\ & + 1/2 \sum K_t W_t (\Delta \alpha_{ij}) \end{aligned}$$

with:

Δr_i variation of the bond length.
 $\Delta \alpha_{ij}$ variation of the bond angle.

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