European Journal of Applied Sciences – Vol. 9, No. 5
Publication Date: October 25, 2021
DOI:10.14738/aivp.95.10896.
Valentin, A. A., Robert, N. B., & Sawaliho, B. E. H. (2021). DFT Investigation of Carbon Dioxide Effects with Temperature on Hydrated Tetra and Penta-Saccharide Complexes. European Journal of Applied Sciences, 9(5). 142-161.

DFT Investigation of Carbon Dioxide Effects with Temperature on Hydrated Tetra and Penta-Saccharide Complexes

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ABSTRACT

Plantain banana mainly constitutes by water and starch. The latter includes amylopectin and amylose. Glucose represents their core molecule. This work aims to elucidate the temperature and carbon dioxide effects in four (AM4G) or five (AM5G) of its hydrated synthons (basic unit). Ultimately, it wants to identify their role in the deterioration of starch components. The research exploits the resources of quantum chemistry to generate the relevant geometric, thermodynamic, and spectroscopic parameters related to the hydrated tetra and penta-saccharide at the ONIOM level (B3LYP/6–311++G [d, p]: AM1). Their analysis reveals the following results. The temperature maintains the geometries of both complexes. It retains most of the enthalpies, and entropy associated with their formation. Moreover, it lowers the free enthalpies of the latter. Furthermore, it increases the frequency shifts $\Delta\nu_{O-H}$. This work also identifies the action of carbon dioxide. This one almost conserves the geometry of the two complexes and their hydrogen bonds. Its effects on the thermodynamic quantities depend on the temperature. Carbon dioxide maintains the exothermic character of the complexations involved. More, it transforms their entropy. It increases the free enthalpy of fluctuating importance. It keeps the non-spontaneity of complexation reactions. Its effects concern the frequency shifts $\Delta\vartheta_{O-H}$. These rely on the temperature. Dioxide carbon exalts them in function of these latter.

Keywords: temperature, carbon dioxide, amylose and ONIOM

INTRODUCTION

Plantain banana constitutes a source of energy and nutrients [1]. Côte d'Ivoire produces 1.7 million tonnes annually. It deploys various methods to conserve its performance. It

implements different cultivation techniques to improve its productivity. However, it struggles to cover the needs of its inhabitants; post-harvest losses are quantified at nearly 30% of production [2]. The theoretical chemistry team wants to suggest ways to increase the green life of this fruit. Its researchers are trying to understand the degradation modalities of mass-produced foods. Subsequently, they recommend the properties of candidate molecules that could reduce these huge losses. Before, it presents and discuss preceding work.

Starch represents the main constituent of green plantain. It consists of two polysaccharides, amylose and amylopectin. These polymers comprise chains of α-D-glucose linked by osidic bridges. Water hydrolyzes them into disaccharides or monosaccharides during ripening [3.4]. It establishes hydrogen bonds with the hydroxyls of D-glucose [5.6]. It contributes to its rapid alteration. The team's previous work sheds light on this mechanism. Temperature also acts role in this process.

Its increase accelerates the maturing of the banana. Cold plays an important role in retarding its metabolism [7], [8]. It prolongs the duration of the green state and maintains the quality of the fruit [9, 10, 11]. Furthermore, carbon dioxide participates in the preservation process of bananas in a controlled atmosphere [12.13]. Its enzymatic hydrolysis decreases if stored in an environment with 10% CO_2 [14]. But previous works reveal that water, temperature, and carbon dioxide constitute three factors that can elucidate the degradation of green bananas. They remain silent on the mechanisms shaping their effects. This research wants to fill this gap. It targets to answer the following question:

What are the mechanisms underlying the effects of temperature and carbon dioxide on green bananas?

This work aims to explain the role of temperature and carbon dioxide in starch degradation. It generates and analyzes geometric, thermodynamic, and spectroscopic parameters using quantum calculations on complexes of four (AM4G) and five (AM5G) amylose synthons. It calculates and discusses them for the AM4G-H_2O, AM4G-H_2O-CO_2, AM5G-H_2O, and AM5G-H2O-CO_2 complexes. It performs the calculations at 298 K and 286 K. The article includes four main parts.

The first one follows this introduction. It describes the compounds and the method of study. The second presents the results. The third comments on these. It explains the effects of temperature and CO_2 on geometric, thermodynamic, and spectroscopic parameters of the complexes and hydrogen bonds (HB) related to the formation of these. A conclusion closes this presentation in the fourth.

COMPOUNDS AND METHOD

This section deals with the procedures of the calculations. First, it presents the polysaccharides under study and their geometrical, energetic, or spectroscopic parameters.

Compounds

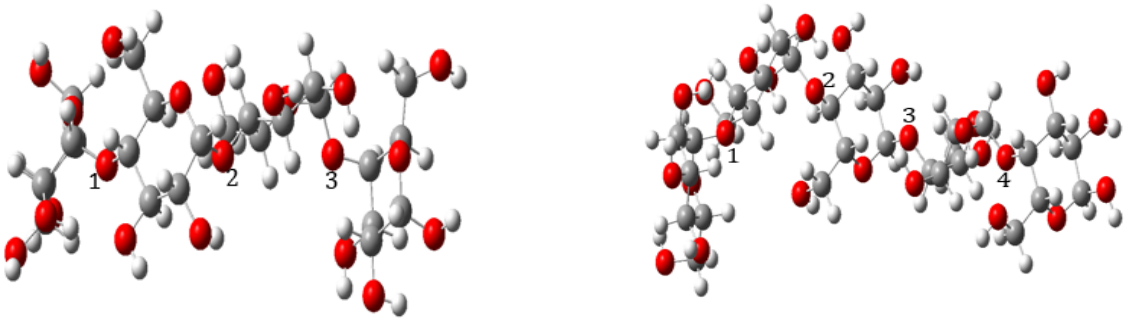
Starch comprises two polysaccharides, amylose, and amylopectin. The first corresponds to a linear polymer of D-glucose in α (1–4). The second is another from D-glucose (1–4). It has branches in α (1–6) amylose. This study focuses on complexes of four or five D-glucose units with water. They have three and four osidic bridges respectively. Figure 1 shows the 3D molecular structure of AM4G (four synthons) and AM5G (five synthons). All oxygen are sp3

hybridized. The bridge is numbered from 1 to 3 for first polysaccharides and to 4 for the second one. These numerals also correspond to the names of the different HB complexes. Quantum Methods permit identifying them.

Method

All calculations perform using the ONIOM (Own N-layered Integrated Molecular Orbital) method developed by Morokuma and all [15]. Our previous work utilizes it to highlight the HB sites of amylose and amylopectin [16]. The ONIOM method suits here for this reason. It consists of splitting any complex into two parts. Each part behaves at different levels of calculation (figure 2).

For AM4G-H_2O and AM5G-H_2O, the water, and the carbons of the osidic bridge and their hydrogen constitute the first (internal) part. This division makes it possible to describe the HB precisely. The calculations carry out at a high level (B3LYP/6–311++G [d, p]). The diffuse and polarization functions consider the isolated pairs of oxygen and their interactions with the hydrogen in water. For the second (external) part, the semi-empirical AM1 approach helps to capture the remainder of the complex environment in a less rigorous way.



AM4G **AM5G**

Fig. 1: 3D image of the AM4G and AM5G

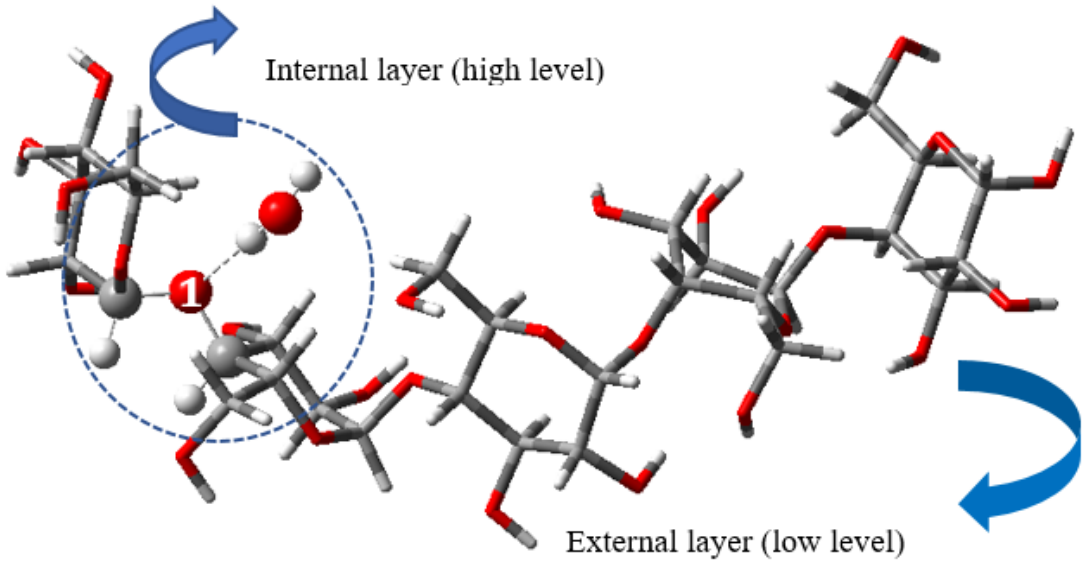


Fig. 2: Calculation scheme according to the ONIOM method

ONIOM uses other data. It calculates the energy of the system at a high level (the part circled in figure 2): E (DFT, model). It estimates that of the real system at a low level of computation (the whole complex in figure 2): E (AM1, complex). It gives that of the model system with identical precision: E (AM1, model). Ultimately, the DFT energy of polysaccharide complex E (DFT, polysaccharide) is obtained with the formula below (Equation 1).

E (DFT, polysaccharide) = E (AM1, complex) +E (DFT, model)—E (AM1, model) (1)

Figure 2 describes the two parts of the four-synthon amylopectin (AM4G) for the ONIOM calculation. All calculations perform utilizing the Gaussian 09 software [17]. They use for generating the geometry of the HB and its thermodynamic or spectroscopic parameters. The following section presents them. The interaction between polysaccharide synthons and water molecules materializes by the HB. The complex builds by connecting hydrogen from water to one osidic bridge oxygen. Three geometric quantities characterize HB (figure 3).

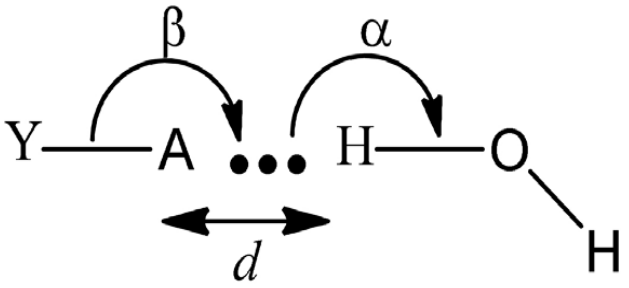
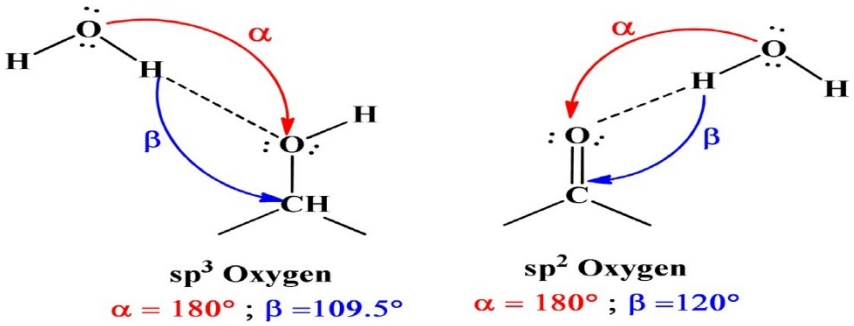


Fig. 3: Geometric parameters α, β, and d of hydrogen bonding [18]

Geometric Parameters of Hydrogen Bonds

Before polysaccharide optimization, the linearity angle α equals 180°. The direction is worth 109.5° for sp3 oxygen and 120° for sp^2 oxygen (figure 4). The distance d to hydrogen is 2 Å. It coincides with the minimum approach length of the latter to oxygen [19]. According to Rowland & Taylor (1996), a HB becomes possible when the distance d doesn't exceed 2.62 Å. This value expresses the sum of Van der Waals oxygen radii (1.52 Å) and hydrogen one (1.1 Å) [20, 21]. It converts strong as d decreases.

The privileged osidic site coincides with the smallest value of d. The parameter α refers to HB's linearity angle. It indicates to the one between the O-H and H-A direction. The atom A represents its acceptor. The parameter β corresponds to the direction angle. It materializes in the corner between the Y-A direction and its A-H axis. The more α and β deviate from their ideal values, the more the HB becomes destabilized. The HB also defines in thermodynamic quantities such as enthalpies, free enthalpies and entropy of formation or reaction. The next section shows the relationships for calculating these parameters.



Hydrogen bonds linearity (α) and directionality (β) angle

Energy and thermodynamic parameters

The HB between an H-X donor and a Y-A proton acceptor carries out according to equation 2. The Y-A… H-X complex constitutes the product.

$$Y - A + H - X \rightarrow Y - A \cdots H - X \quad (2)$$

The variation of the energy at 0 K is obtained with equation 3.

$$\Delta E^0_{elec} = E^0_{elec}(Y - A \cdots H - X) - [E^0_{elec}(Y - A) + E^0_{elec}(H - X)] \quad (3)$$

The internal energy at 298.15 K corresponds to the sum of the electronic, rotational, translational, and vibrational energies. Equation 4 describes its variation.

$$\Delta E^0_{298} = \Delta E^0_{electronique} + \Delta E^0_{rotation} + \Delta E^0_{translation} + \Delta E^0_{vibration} \quad (4)$$

The geometry optimization of the reactants and products gives access to all contributions (including the nuclear repulsion energies). In the ideal gas approximation, equation 5 specifies the expressions for the rotational and translational energies.

$$\Delta E^0_{translation} = \Delta E^0_{rotation} = -\frac{3}{2}RT \quad (5)$$

ΔE° vibration includes the ZPVE (Zero Point Vibrational Energy), i.e., that of the lowest vibrational level. It results from those of the 3 N-6 normal modes (3 N-5 for linear molecules), each with a frequency νi, at 0 K. Equation 6 defines it at this temperature.

$$E^0_{vib.thermal} = R\sum_{i=1}^{3N-6} \frac{h\nu_i/k}{e^{h\nu_i/298K} - 1} \quad (6)$$

Consequently, the change in internal energy of the reaction at 298.15 K is obtained from equation 7:

$$\Delta E^0_{298} = \Delta E^0_{elec} + \Delta ZPVE + \Delta E^0_{vib.thermal} - 3RT \quad (7)$$

These relationships provide the basis for optimizing the geometries of the chemical entities. This work doesn't incorporate the study of energy gaps; it focuses on thermodynamic quantities. Equations 8 and 9 give the enthalpy and free enthalpy variations for the complexation reaction at 298.15 K.

$$\Delta H^0_{298K} = \Delta E^0_{298K} - RT \quad (8)$$

$$\Delta G^0_{298K} = \Delta H^0_{298K} - T\Delta S^0_{298K} \quad (9)$$

$$\Delta S^0_{298K} = \Delta S^0_{trans} + \Delta S^0_{rot} + \Delta S^0_{vib} \quad (10)$$

Equation 10 corresponds to the change in entropy under these conditions. Also, spectroscopic parameters help to specify the HB host sites of polysaccharides.

Spectroscopic Parameters

Spectroscopic descriptors can use as a scale for HB. Its strength is based on that of the H-X bond. The stretching frequency of the latter becomes accessible. When the donor is a water molecule, the offset turns into a scale. For the sp3 osidic oxygen, it's defined by the equation11:

$$\Delta\boldsymbol{\vartheta}_{\boldsymbol{O-H}} = \boldsymbol{\vartheta}_{\boldsymbol{O}_{sp^3-H,libre}} - \boldsymbol{\vartheta}_{\boldsymbol{O}_{sp^3-H,complexe}} \quad \textbf{(11)}$$

At the ONIOM level (B3LYP/6–311++G [d, p]: AM1), the vibrator frequency $\boldsymbol{\vartheta}_{\boldsymbol{O}_{sp^3-H,free}}$ equals to 3923.84 cm-1. If the value of $\Delta\boldsymbol{\vartheta}_{\boldsymbol{O-H}}$ is positive, the value of $\boldsymbol{\vartheta}_{\boldsymbol{O}_{sp^3-H,complex}}$ becomes lower than $\boldsymbol{\vartheta}_{\boldsymbol{O}_{sp^3-H,free}}$; the frequency $\boldsymbol{\vartheta}_{\boldsymbol{O}_{sp^3-H,free}}$ of water decreases. The hydrogen in water approaches the oxygen in the osidic bridge. Simply, as $\Delta\boldsymbol{\vartheta}_{\boldsymbol{O-H}}$ increases, it's likely to become a site susceptible to HB. Furthermore, this work sets criteria for analyzing these parameters. It assumes that significant variations exceed 10%. A difference in angles is discriminating if it surpasses 20°. The next sections present its results.

RESULTS

This part details the results relating to the complexes of four or five amylose synthons with water. Firstly, it presents temperature effects on theses of the geometric, energetic, and spectroscopic parameters of the saccharide-water complexes. The thermodynamic aspect focuses on enthalpy, free enthalpy, and energy gaps. the last component interests in the frequency shifts of the band $\Delta\boldsymbol{\vartheta}_{\boldsymbol{O-H}}$ of HB surroundings O1sp3, O2sp3 and O3sp3. Before, this article presents its effects on the geometry of the complex.

Effects of Temperature on Saccharide-Water Complexes

The geometric aspect focuses on the distance d, the angle alpha and beta. The temperature effects concern AM4G-H_2O-CO_2, AM5G-H_2O, AM5G-H_2O-CO_2, and AM4G-H_2O.

Effects of Temperature on AM4G—H_2O

Tables 1 and 2 present the effects of temperature on the geometric data. Table 1 shows the bond length and valence angle results for the osidic bridges of AM4G at 298 K and 286 K. Table 2 summarizes the HB parameters that may exist between AM4G and water.

Table 1. Bond length and valence angle related to the osidic bridges of AM4G-H_2O at 298K and 286 K

Distances (Å)	Angles (°C)	T= 298 K			T= 286 K		
		AM4G	AM4G-H_2O	Variation	AM4G	AM4G-H_2O	Variation
d (C-O1sp3)		1.42	1.43	1%	1.43	1.44	1%
d (O1sp3-C)		1.44	1.45	1%	1.44	1.45	1%
	θ (C-O1sp3-C)	117.58	120.07	2%	117.58	120.07	2%
d (C-O_{2sp3})		1.42	1.43	1%	1.42	1.43	1%
d (O2sp3-C)		1.43	1.45	2%	1.43	1.45	1%
	θ (C-O2sp3-C)	115.23	116.29	1%	115.23	116.29	1%
d (C-O3sp3)		1.42	1.43	1%	1.42	1.43	1%
d (O3sp3-C)		1.43	1.44	1%	1.43	1.44	1%
	θ (C-O3sp3-C)	116.86	120.07	1%	116.86	120.07	3%

Table 2. Hydrogen bonds geometries of AM4G-H_2O at 298K and 286K

HB anchor	T= 298 K	T=286 K	Variation
	α (°)	**α (°)**	
O1sp3	172,55	172,48	0%
O2sp3	168,22	159,27	5%
O3sp3	159,27	168,22	-5%
	β (°)	**β (°)**	
O1sp3	112,62	112,65	0%
O2sp3	108,47	108,47	0 %
O3sp3	118.5	118.5	0%
	d (Å)	**d (Å)**	
O1sp3	1.92	1.92	0%
O2sp3	1.84	1.84	0%
O_{3sp3}	1.88	1.88	0%

Effects of temperature on the thermodynamic parameters of AM4G-H_2O

Table 3 presents the thermodynamic quantities related to the HB around the oxygen O_{1sp3}, O_{2sp3} and O_{3sp3} of the polysaccharide AM4G at 298 K and 286 K. It concentrates on the enthalpy and free enthalpy.

Table 3. Thermodynamic quantities of AM4G-H_2O at 298 K and 286 K

HB anchor	**AM4G-H_2O**		
	$\Delta_r H°_{298}$ (kcal/mol)	**$\Delta_r H°_{286}$ (kcal/mol)**	**Variation**
O1sp3	-6,983	-7,003	0%
O2sp3	-7.52	-7,538	0%
O3sp3	-7,072	-7,082	0%
	$\Delta rS°_{298}$ (cal/mol.K^{-1})	**$\Delta rS°_{286}$ (cal/mol.K^{-1})**	
O1sp3	-34.6	-34.67	0%
O2sp3	-30,976	-31,016	0%
O3sp3	-35,374	-35,407	0%
	$\Delta rG°_{298}$ (kcal/mol)	**$\Delta rG°_{286}$ (kcal/mol)**	
O1sp3	3,334	2,913	13%
O2sp3	1,709	1,332	25%
O3sp3	3,475	3,045	13%

<u>Effects of temperature on the spectroscopic parameters of the AM4G—H_2O complex</u>

Table 4 collects the effects of temperature on the $\Delta\vartheta_{O-H}$ frequency shifts of HB surroundings O1sp3, O2sp3 and O3sp3 at 298 K and 286 K. Furthermore, the research treats the case of AM5G-H_2O.

Table 4. Displacement frequencies $\Delta\vartheta_{O-H}$ of the AM4G-H_2O complex at temperatures 298K and 286K

HB anchor	**$\Delta\vartheta_{O-H}$298 (cm^{-1})**	**$\Delta\vartheta_{O-H}$286 (cm 1)**	**Variation**
O1sp3	260.96	260.95	0%
O2sp3	281.45	271.41	-4%
O3sp3	280.11	314.12	+11%

Effects of temperature on AM5G—H_2O

This section presents the effects of temperature on AM5G-H_2O geometrical, thermodynamic, and spectroscopic parameters. Tables 5 to 8 collected their calculated values at 298K and 286K.

<u>Effects of temperature on the geometrical parameters of the AM5G—H_2O complex</u>

Table 5 shows the bond length and valence angle results for the osidic bridges of AM5G at 298 K and 286 K. Table 6 summarizes the HB geometric parameters that may exist between AM4G and water.

Table 5. Bond length and valence angle related to the osidic bridges of AM5G-H_2O at 298 K and 286 K

Distances (Å)		T =298 K	T=286 K	
	Angles	AM5G-H_2O	AM5G-H_2O	Variation
d (C-O1sp3)		1.43	1.43	0%
d (O1sp3-C)		1.45	1.45	0%
	θ (C-O1sp3-C)	120.11	120.11	0%
d (C-O2sp3)		1.43	1.43	0%
d (O2sp3-C)		1.45	1.45	0%
	θ (C-O2sp3-C)	116.45	116.45	0%
d (C-O3sp3)		1.44	1.44	0%
d (O3sp3-C)		1.44	1.44	0%
θ (C-O3sp3-C)		117.36	117.36	0%
d (C-O4sp3)		1.43	1.43	0%
d (O4sp3-C)		1.45	1.45	0%
	θ (C-O4sp3-C)	119.30	119.30	0%

Effects of temperature on the thermodynamic parameters of the AM5G-H_2O complex

Table 7 presents the thermodynamic quantities related to the HB around the oxygen O1sp3, O2sp3 O3sp3 and O4sp3 of the polysaccharide AM5G at 298 K and 286 K. It explains the values of enthalpy, free enthalpy and the energy gap associated with the two search temperatures.

Table 6. Geometric parameters of the AM5G-H_2O hydrogen bond at 298 K and 286 K

HB anchor	α (°) 298	α (°) 286	Variation
O1sp3	172.57	172.57	0%
O2sp3	169.27	169.27	0%
O3sp3	159.37	159.37	0%
O4sp3	168.59	168.59	0%
	β (°)	β (°)	
O1sp3	126.63	126.63	0%
O2sp3	108.08	108.08	0%
O3sp3	114.09	114.09	0%
O4sp3	113.11	113.11	0%
	d (Å)	d (Å)	
O1sp3	1.92	1.92	0%
O2sp3	1.84	1.84	0%
O3sp3	1.87	1.87	0%
O4sp3	1.88	1.88	0%

Table 7. Thermodynamic quantities of AM5G-H_2O at 298 K and 286 K

HB anchor	AM5G-H2O		
	$\Delta_rH°_{298}$ (kcal/mol)	**$\Delta_rH°_{298}$ (kcal/mol)**	**Variation**
O1sp3	-7,025	-7,043	0%
O2sp3	-8,251	-7,677	7 %
O3sp3	-7,084	-7,094	0 %
O4sp3	-8,939	-7,183	22 %
	$\Delta rS°_{298}$ (cal/mol.K^{-1})	**$\Delta rS°_{286}$ (cal/mol.K^{-1})**	
O1sp3	-34,591	-34,636	0 %
O2sp3	-29,593	-29,655	0 %
O3sp3	-35,316	-35,072	1%
O4sp3	-36,279	-29,886	19%
	$\Delta rG°_{298}$ (kcal/mol)	**$\Delta rG°_{286}$ (kcal/mol)**	
O1sp3	3,288	2,863	14%
O2sp3	1,164	0.804	37%
O3sp3	3,364	2,937	14%
O4sp3	1,878	1,365	32%

Effects of temperature on the spectroscopic parameters of the AM5G—H2O complex

Table 8 collects the effects of temperature on the $\Delta\vartheta_{O-H}$ frequency shifts of HB surroundings O1sp3, O2sp3 and O3sp3 at 298 K and 286 K. Furthermore, research focuses on those of carbon dioxide in saccharide-water complexes.

Table 8. Shift frequencies $\Delta\vartheta_{O-H}$ of the AM5G-H_2O complex at 298K and 286K

HB anchor	$\Delta\vartheta_{O-H}$ 298 (cm^{-1})	$\Delta\vartheta_{O-H}$ 286 (cm^{-1})	Variation
O1sp3	261.07	260.97	0%
O2sp3	284.36	264.20	-7%
O3sp3	280.52	315.60	+12%
O4sp3	264.66	264.66	0%

Effects of carbon dioxide on saccharide-water complexes

This part presents the carbon dioxide effects in saccharide complexes geometric, thermodynamic, and spectroscopic parameters. First, it illustrates those of CO2 in the AM4G-H2O complex.

Effects of Carbon Dioxide in the AM4G—H_2O Complex

Tables 9 to 12 detail the effects of carbon dioxide in the geometrical, energetic, and spectroscopic parameters of the AM4G-H_2O complex.

Effects of carbon dioxide in the AM4G-H_2O geometry and its hydrogen bonds

Table 9 shows the CO2 effects on the bond lengths and valence angles around the AM4G-H2O osidic bridges at 298 K and 286 K. Table 10 summarizes these associated with the HB at the same temperatures.

Table 9. Bond length and valence angle related to the osidic bridges of AM4G-H_2O and AM4G-H_2O-CO_2 at 298 K and 286 K

		T= 298 K			T= 286 K		
Distances (Å)	**Angle**	**AM4G-H_2O**	**AM4G-H_2O-CO_2**	**Variation**	**AM4G-H_2O**	**AM4G-H2O-CO_2**	**Variation**
d (C-O1sp3)		1.43	1.43	0%	1.44	1.44	0%
d (O1sp3-C) (Å)		1.45	1.45	0%	1.45	1.45	0%
	θ (C-O1sp3-C)	120.07	119.25	-1%	120.07	119.25	-1%
d (C-O2sp3)		1.43	1.43	0%	1.43	1.43	0%
d (O2sp3-C)		1.45	1.45	0%	1.45	1.45	0%
	θ (C-O2sp3-C)	116.29	116.08	0%	116.29	116.09	0%
d (C-O3sp3)		1.43	1.44	1%	1.43	1.44	1%
d (O3sp3-C)		1.44	1.44	0%	1.44	1.44	0%
	θ (C-O3sp3-C)	120.07	116.77	-3%	120.07	116.77	-3%

Table 10. Geometric parameters of AM4G-H_2O and AM4G-H_2O-CO_2 hydrogen bonding at 298 K and 286 K

	AM4G-H_2O-CO_2		**AM4G-H2O**		**Variation**	
Temperature	**298K**	**286 K**	**298K**	**286 K**	**298K**	**286 K**
HB anchor	**α (°)**	**α (°)**	**α (°)**	**α (°)**	**α var (°)**	
O1sp3	172,55	172,48	176,16	176,16	-2 %	-2 %
O2sp3	168,22	159,27	168,74	157,62	0%	1%
O3sp3	159,27	168,22	157,2	167,54	1%	0%
	β (°)	β (°)	β (°)	β (°)	β var	
O1sp3	112,86	112,65	112,62	112,65	0%	0%
O2sp3	106,02	108,47	108,47	108,47	-2%	0%
O3sp3	118.39	118.5	118.5	118.5	0%	0%
	d (Å)	**d (Å)**	**d (Å)**	**d (Å)**	**d var**	
O1sp3	1.95	1.95	1.92	1.92	2%	2%
O2sp3	1.87	1.87	1.84	1.84	2%	2%
O3sp3	1.89	1.89	1.88	1.88	1%	1%

Effects of carbon dioxide in the AM4G-H2O thermodynamic parameters

Table 11 presents the thermodynamic quantities related to the HB around the oxygen O1sp3, O2sp3 and O3sp3 of the AM4G-H_2O and AM4G-H_2O-CO_2 complexes at 298 K and 286 K. Table 12 details $\Delta\vartheta_{O-H}$ shifts frequencies of AM4G-H_2O and AM4G-H_2O-CO_2 at 298 K and 286 K.

Effects of carbon dioxide in the AM5G—H_2O complex

The effects of carbon dioxide are evaluated on the geometric, thermodynamic, and spectroscopic parameters of the AM5G-H_2O complexes. Tables 13 to 16 present the results of this calculation.

Effects of carbon dioxide on the geometric parameters of AM5G—H_2O

Table 13 shows the CO_2 effects on the bond length and valence angles about AM5G-H_2O's osidic bridges at 298 K and 286 K. Table 14 summarizes these related to the geometric parameters of HB between AM5G and water at these temperatures.

Table 11. Thermodynamic quantities of AM4G-H2O and AM5G-H2O-CO2 at 298K and 286 K

T= 298 K			**T= 286 K**		
AM4G-H_2O	**AM4G-H_2O-CO_2**	**Variation**	**AM4G-H_2O**	**AM4G-H_2O-CO_2**	**Variation**
ΔrH° T (kcal/mol)					
-6,983	-10,147	-37 %	-6,983	-10,197	-32 %
-7,52	-9,701	-25 %	-7,52	-9,747	-23 %
-7,072	-8,909	-23 %	-7,072	-8,639	-18 %
ΔrS° T (cal/mol. K^{-1})					
-34.6	-65,864	-62%	-34.67	-61.85	-56%
-30,976	-59,892	-64%	-31,016	-60,048	-64%
-35,374	-58,896	-50%	-35,407	-63.16	-56%
ΔrG° T (kcal/mol)					
3,334	8,239	-85 %	3,045	7,492	-84 %
1,709	8,155	-131 %	3,045	7,427	-84 %
3,475	8,651	-85 %	3,045	7,934	-89 %

Table 12. $\Delta\vartheta_{O-H}$ shifts frequencies of AM4G-H_2O and AM4G-H_{20}-CO_2 at 298 K and 286 K

AM4G-H_2O		**AM4G-H_2O-CO2**		**Variation**	
298 K	**286K**	**298 K**	**286K**	**298 K**	**286K**
$\Delta\vartheta_{O-H}$ (cm-1)					
260,96	260,95	268,75	268,99	-3 %	-3 %
281,45	271,41	262,25	262,25	7 %	3 %
280,11	314,12	301,5	300,97	-7 %	4 %

Carbon Dioxide Effects on the thermodynamic parameters of AM5G-H_2O

Table 15 presents the thermodynamic quantities related to the HB around the oxygen O1sp3, O2sp3 O3sp3 and O4sp3 of the AM5G-H_2O and AM5G-H_2O-CO_2 at 298 K and 286 K.

Table 13. Bond lengths and valence angle associated with the osidic bridge atoms of AM5G-H_2O and AM5G-H_2O-CO_2 at 298 K and 286 K

		T= 298 K			T= 286 K		
Distances (Å)	**Angles (°)**	**AM5G-H_2O**	**AM5G-H_2O-CO_2**	**Variation**	**AM5G-H_2O**	**AM5G-H2O-CO2**	**Variation**
d (C-O_{1sp3})		1.43	1.43	0%	1.43	1.43	0%
d (O_{1sp3}-C)		145	145	0%	1.45	1.45	0%
	θ (C-O_{1sp3}-C)	120.11	119.89	0%	120.11	119.89	0%
d (C-O_{2sp3})		1.43	1.43	0%	1.43	1.43	0%
d (O_{2sp3}-C)		1.45	1.45	0%	1.45	1.45	0%
	θ (C-O2sp3-C)	116.45	116.01	0%	116.45	116.01	0%
d (C-O_{3sp3})		1.44	1.43	-1%	1.44	1.43	-1%
d (O_{3sp3}-C)		1.44	1.44	0%	1.44	1.44	0%
	θ (C-O3sp3-C)	117.36	116.83	0%	117.36	116.83	0%
d (C-O_{4sp3})		1.43	1.43	0%	1.43	1.43	0%
d (O_{4sp3}-C)		1.45	1.45	0%	1.45	1.45	0%
	θ (C-O4sp3-C)	119.3	119.02	0%	119.3	119.02	0%

Table 14. Geometric parameters of AM5G-H_2O or AM5G-H_2O-CO_2 hydrogen bonding at 298 K and 286 K

	AM5G-H_2O-CO_2		AM5G-H_2O		Variation	
Temperature	**298K**	**286 K**	**298K**	**286 K**	**298K**	**286 K**
HB anchor	**α (°)**				**α var (°)**	
O1sp3	173,94	173,94	172,57	172,57	1 %	1 %
O2sp3	160,7	158,57	169,27	159,37	-5 %	-1 %
O3sp3	158,57	160,67	159,37	169,27	-1 %	-5 %
O4sp3	164,87	164,87	168,59	168,59	-2 %	-2 %
	β (°)				**β var**	
O1sp3	126,48	126,48	126,63	126,63	0%	0%
O2sp3	107,1	107,1	108,08	108,08	-1%	-1%
O3sp3	116.27	116.27	114.09	114.09	2%	2%
O4sp3	125.84	125.84	113.11	113.11	11%	11%
	d (Å)				**d var (Å)**	
O1sp3	1.92	1.92	1.92	1.92	0%	0%
O2sp3	1.89	1.89	1.84	1.84	3%	3%
O3sp3	1.89	1.89	1.87	1.87	1%	1%
O4sp3	1.90	1.90	1.88	1.88	1%	1%

Table 15. Thermodynamic quantities of the AM5G-H_2O and AM5G-H_2O-CO_2 at 298K and 286 K

	T= 298 K			**T= 286 K**		
HB anchor	**AM5G-H_2O**	**AM5G-H_2O-CO_2**	**Variation**	**AM5G-H_2O**	**AM5G-H_2O-CO_2**	**Variation**
	ΔrH° T (kcal/mol)			**ΔrH° T (kcal/mol)**		
O1sp3	-7,025	-8,061	-14 %	-7,043	-8,109	-13 %
O2sp3	-8,251	-7,78	6 %	-7,677	-10,099	-24 %
O3sp3	-7,084	-9,187	-26 %	-7,094	-9,18	-23 %
O4sp3	-8,939	-7,966	12 %	-7,183	-8,025	-10 %
	ΔrS° T (cal/mol.K^{-1})			**ΔrS°T (cal/mol.K^{-1})**		
O1sp3	-34,591	-57,818	-50%	-34,636	-57,999	-110%
O2sp3	-29,593	-49,343	-50%	-29,655	-58,548	-115%
O3sp3	-35,316	-63,436	-57%	-35,072	-61,541	-113%
O4sp3	-36,279	-53,504	-38%	-29,886	-53,741	-111%
	ΔrG° T (kcal/mol)			**ΔrG°T (kcal/mol)**		
O1sp3	3,288	9,176	94%	2,863	8,479	99%
O2sp3	1,164	6,931	42%	0.804	6,646	157%
O3sp3	3,364	9,727	97%	2,937	8,421	97%
O4sp3	1,878	7,987	124%	1,365	7,346	137%

Effects of carbon dioxide on spectroscopic parameters

Table 16 shows the values of the frequency shifts $\Delta\vartheta_{O-H}$ (O-H) for the AM5G-H_2O-CO_2 and AM5G-H_2O complexes at temperatures of 298 K and 286 K.

Table 16. Frequency shift $\Delta\vartheta_{O-H}$ (O-H) of AM5G-H2O-CO_2 and AM5G-H_2O at 298K and 286K at 298K and 286K

	AM5G-H_2O-CO_2		**AM5G-H_2O**			
Calculated quantity	**$\Delta\vartheta_{O-H}$**				**Variation**	
Temperature	**298 K**	**286 K**	**298 K**	**286 K**	**298 K**	**286 K**
O1sp3	280.96	275.05	261.07	260.97	-7%	-5%
O2sp3	267.01	281.51	284.36	264.2	6%	-6%
O3sp3	286.97	286.89	280.52	315.6	-2%	10%
O4sp3	250.75	250.75	264.66	264.66	5%	5%

DISCUSSION

This section comments on the geometric, thermodynamic, and spectroscopic parameters calculated on the complexes. It's interested in the carbon dioxide or temperature effects of these.

Effects of Temperature on Saccharide-Water Complexes

The discussion of the temperature effects concerns the complexes of four or five amylose synthons with water at 298K and 286K. The analysis starts with the AM4G-H_2O complexes.

Effects of Temperature on AM4G—H_2O

This part comments on the geometrical, energetic, and spectroscopic parameters of AM4G-H_2O complex. The discussion bases on data from tables 1 to 4.

Effects of Temperature on the Geometrical Parameters of AM4G-H_2O

The table 1 data show that the C-O lengths and C-O-C bond angles remain insensitive to a decrease in temperature. The latter doesn't transform the geometry of the AM4G-H_2O complex between that of the ambient (298 K) and the banana conservation (286 K). Table 2 summarizes the geometric parameters of the probable HB between AM4G and water. According to these data, temperature weakly impact on them. It doesn't modify the HB geometry of the AM4G-H_2O complex between 298 K and 286 K. This research also interests in the thermodynamic aspects linked to the HB formation.

Effects of Temperature on the Thermodynamic Parameters of AM4G-H_2O

Table 3 presents the thermodynamic quantities connected with the formation of HB around the oxygen O1sp3, O2sp3 or O3sp3 of AM4G. Data indicating that temperature doesn't influence their entropy and enthalpies. By decreasing, the free enthalpies linked with O1sp3, O2sp3 and O3sp3 diminish respectively by 13%, 25% and 13%. But the variations of the latter remain positive; the change in temperature doesn't transform the non-spontaneous character of AM4G-H_2O associated with its formation reaction. On the other hand, the study emphasizes the vibrational frequencies $\Delta\vartheta_{O-H}$ within AM4G; the latter contributes to HB.

Effects of temperature on the spectroscopic parameters of the AM4G—H_2O complex

Table 4 collects the $\Delta\vartheta_{O-H}$ frequency shifts of HB surroundings O1sp3, O2sp3 and O3sp3. These remain insensitive to temperature changes for HB around O1sp3. They increase by 11% for O3sp3 and decrease in O2sp3.This table collects the frequency offsets $\Delta\vartheta_{O-H}$ of the HB environments O1sp3, O2sp3 and O3sp3. These remain insensitive to temperature changes for HB around O1sp3. They increase by 11% for O3sp3 and decrease in O2sp3. Temperature influences the frequency shifts $\Delta\vartheta_{O-H}$ of AM4G-H_2O, especially around O3sp3. It goes from 280.11 cm-1 to 314.12 cm-1 for 298 K and 286 K respectively; As the temperature increases, the frequency shift decreases. More, this work analyzes the effects of temperature on the AM5G-H_2O.

Effects of Temperature on AM5G—H_2O

This section analyzes the effects of temperature on the AM5G-H_2O geometric, energetic and spectroscopic parameters. The discussion bases on data from tables 5 to 8 at 298K and 286K.

Effects of temperature on the geometrical parameters of the AM5G—H_2O complex

This section analyzes the effects of temperature on the AM5G-H_2O geometric, energetic and spectroscopic parameters. The discussion bases on data from tables 5 to 8 at 298K and 286K. Table 5 displays that the bond lengths and valence angles related to the AM5G osidic bridges at 298 K and 286 K. According to its data, the C-O bond lengths, and the C-O-C valence angles of the latter conserves their initial values when the temperature decreases. In other words, this doesn't modify the geometry of AM5G—H_2O. Moreover, this work analyzes the parameters of the HB. Table 6 summarizes their parameters. Its data prove that α, β and don't vary. Simply, the HB parameters of AM5G-H_2O remain insensitive to its variation between 298 K and 286 K.

Effects of temperature on the thermodynamic parameters of the AM5G-H_2O complex.

According to the data in Table 7, the formation enthalpy of HB on O4sp3 rises by 22%. Those of the other sites don't change. The thermodynamic quantity always stays positive. The temperature maintains the exothermic character associated HB formation surroundings O4sp3. This work examines its effects on entropy. The temperature conserves the formation entropy of HB. It remains negative. The level of order related to this process doesn't vary between 298K and 286K. The research focuses on the free enthalpy. This one declines by 14% during the formation of HB around O1sp3 and O3sp3. It diminishes by 37% of the atom near O2sp3. For O4sp3, it decreases by 32%. It remains always positive. Temperature influences it. However, it doesn't promote any spontaneous reactions to establish these HB. Furthermore, the research analyzes its effects on the spectroscopic parameters of the AM5G-H_2O complex.

Effects of temperature on the spectroscopic parameters of the AM5G—H_2O complex

Table 8 collects the $\Delta\vartheta_{O-H}$ frequency shifts of HB surroundings O1sp3, O2sp3, O3sp3 and O4sp3. These remain insensitive to temperature changes for HB around O4sp3. They increase by 12% for O3sp3 and decreases by 7% for O2sp3. Temperature influences the frequency shifts $\Delta\vartheta_{O-H}$ of AM5G-H_2O, especially around O3sp3. It goes from 280.52 cm-1 to 315.60 cm-1 for 298 K and 286 K respectively: As the temperature decreases, $\Delta\vartheta_{O-H}$ increases. More, the comments relate to the effects of carbon dioxide on saccharide-water complexes.

Effects of Carbon Dioxide on Saccharide-Water Complexes

This section analyzes the effects of carbon dioxide in the geometric, energetic, and spectroscopic parameters on AM5G-H20 complex. Before, it discusses the effects of CO_2 on the AM4G-H_2O complex.

Effects of Carbon Dioxide in the AM4G—H_2O

The analysis of CO2 effects relates to the geometric, energetic, and spectroscopic parameters of the AM4G-H_2O complex. The discussion is based on data from tables 9 to 12.

Effects of carbon dioxide in the AM4G-H_2O geometry and its hydrogen bonds

Table 9 shows the bond lengths and valence angles related to the osidic bridges of AM4G-H_2O at temperatures of 298 K and 286K. Its data reveal little variation in CO bond lengths and C-O-C valence angles of this latter. CO_2 maintains the geometry of AM4G-H_2O.

Table 10 presents the HB geometric aspects of AM4G-H_2O-CO_2-AM4G-H_2O at 298 K and 286 K. It specifies the variations generated by the first complex about the second. Its data indicate that the HB characteristics remain constant there.

Effects of Carbon Dioxide on the AM4G-H2O thermodynamic Parameters Table 11 displays the thermodynamic quantities of AM4G-H2O and AM4G-H2O-CO2 complexes at 298 K and 286 K. For AM4G-H2O, CO2 modifies the enthalpy of complexation by -28% at 298K and by -24% at 286 K. The maximum decreases are observed for the HB around the O1sp3 atom. They're -37% at 298 K. Furthermore, the work examines the effects of CO2 on the AM4G-H2O.K thermodynamic parameters, and -32% at 286 K. Carbon dioxide causes the HB enthalpy of formation to vary significantly. However, this thermodynamic quantity persists negative. CO_2 retains the exothermic character of this reaction. This work analyzes the evolution of its entropy.

Effects of Carbon Dioxide on the Spectroscopic Parameters of AM4G-H_2O

Table 12 describes the frequency shifts $\Delta\vartheta_{O-H}$ of AM4G-H_2O and AM4G-H_2O-CO_2 at 298 K and 286 K. It details their variations induced by carbon dioxide. According to its data, CO_2 preserves the $\Delta\vartheta_{O-H}$ values for AM4G-H2O. This research also elucidates the role of carbon dioxide in AM5G—H_2O complexes.

Effects of Carbon Dioxide in the AM5G—H_2O

The effects of carbon dioxide are evaluated on the geometric, thermodynamic, or spectroscopic parameters of the AM5G—H_2O complexes. The comment is based on data from tables 13 to 16 at temperatures of 298K and 286K.

<u>Effects of carbon dioxide on the geometric parameters of AM5G—H_2O</u>

Table 13 shows the bond lengths and valence angles of the atoms bound to the osidic bridges of AM5G-H_2O at 298 K and 286 K. According to its data, CO_2 doesn't change them. Table 14 collects the HB geometric parameters of AM5G-H_2O-CO_2 and AM5G-H_2O at 298 K and 286 K. Its data prove that CO_2 only influences its β angle related to oxygen O4sp3. This angle increases from 113.11° to 125.84 °; however, CO_2 maintains its hybridization state. It destabilizes the HB without modifying the geometry of the associated HB. The study also concerns about the effects of CO_2 on the thermodynamic parameters of AM5G—H_2O.

<u>Carbon Dioxide Effects on the Thermodynamic Parameters of AM5G-H_2O</u>

Table 15 shows the thermodynamic quantities of the AM5G-H_2O-CO_2 and AM5G-H_2O complexes at 298 K and 286 K. It incorporates the changes in the relative enthalpy of the reaction between the latter and AM5G-H_2O-CO_2. At 298 K, carbon dioxide changes the complexation enthalpy of AM5G-H_2O from -26% (O3sp3) to 12% (O4sp3). At 286 K, this thermodynamic quantity varies from 24% (O2sp3) to -10% (O4sp3).

The sign of the enthalpy remains negative. Carbon dioxide retains the exothermic nature of the reaction associated with the formation of AM5G-H_2O hydrogen bonding. At 298 K, it lowers its entropy from -57% (O3sp3) to -38% (O4sp3). At 286K, these proportions become -115% (O2sp3) to -110% (O1sp3). These sharp decreases in entropy show that complexation with CO_2 increases the disorder correlated with the formation of AM5G-H_2O. Furthermore, the analysis extends to the free enthalpy.

Carbon dioxide grows the free enthalpy. At 298 K, the largest increase corresponds to the HB on O4sp3. It reaches 124%. The least is 42%. It's achieved with the HB associated with O2sp3. At 286 K, its variation evolves from 157% (O2sp3) to 97% (O3sp3). Its value remains positive.

CO_2 hardly transforms the non-spontaneity underlying its complexation with AM5G-H_2O. Moreover, this work concerns about its effects on $\Delta\vartheta_{O-H}$ bands.

Carbon Dioxide Effects on Spectroscopic Parameters

Table 16 provides the frequency shifts $\Delta\vartheta_{O-H}$ for the AM5G-H_2O-CO_2 and AM5G-H_2O complexes at 298 K and 286 K. It details the changes caused by carbon dioxide. According to its data, carbon dioxide retains the $\Delta\vartheta_{O-H}$ shifts of AM5G-H_2O. But it exalts that of HB associated with O3sp3 at 286 K; its band goes from 286.89 cm-1 to 315.6 cm-1. This last spectroscopic aspect leads to conclude this article.

CONCLUSION

The work aims to identify the carbon dioxide and temperature roles in the preservation process of plantain banana. To do so, it uses reduced chains of amylose with four or five D-glucose synthons. It mobilizes the two-layer ONIOM method at the level (B3LYP/6–311++G [d, p]: AM1). It generates geometric, energetic, and spectroscopic parameters related to amylose-water complexes. Besides, water establishes HB with amylose synthons [6], [16]. The latter represents focus of this research. Its approach leads to the following results. This work clarifies the effect of temperature on AM4G—H_2O complexes. Temperature conserves the geometries of AM4G-H_2O and their HB. It maintains their entropy and complexation enthalpies. It lowers the free enthalpies associated with the creation of HB near O1sp3, O2sp3 and O3sp3. It increases the frequency shifts $\Delta\vartheta_{O-H}$ around O3sp3 from 298 K to 286 K. It influences the parameters of the AM5G—H_2O in diverse ways.

The temperature doesn't impact the geometries of AM5G-H2O and its HB. The complexation entropy remains unchanged. Decreasing from 298 K to 286K, this variable only increases the enthalpy of the HB associated with O4sp3. It declines the free enthalpies connected with O1sp3, O2sp3 and O3sp3. It increases the $\Delta\vartheta_{O-H}$ frequency shifts of the O3sp3 associated HB. Moreover, carbon dioxide transforms some features on the saccharide-water complexes.

Carbon dioxide preserves the geometry of AM4G-H_2O and that of its HB. It lowers mainly the entropy related to the formation of the latter. It consolidates their orders. It strongly modifies their free enthalpies. But it conserves their non-spontaneity. CO_2 keeps intact the $\Delta\vartheta_{O-H}$ for AM4G-H_2O. It also impacts AM5G—H_2O parameters.

Carbon dioxide doesn't change the geometry of AM5G-H_2O. For its HB, it only increases the β-angle related to the oxygen O4sp3. But it maintains its hybridization state. In other words, it destabilizes the HB without distorting its basic geometry. Its effect on the enthalpy of complexation depends on temperature. At 298 K, it reduces the enthalpy around O3sp3. It grows it near O4sp3. At 286 K, it heightens it for the HB surrounding O2sp3. It diminishes the one close to O4sp3. It always keeps the exothermic nature of the AM5G-H_2O complexation.

Its effect on entropy is related to temperature. At 298 K, CO_2 lowers the entropy correlated with O3sp3 and O4sp3. At 286 K, it robustly decreases the entropy associated with O2sp3 and O1sp3; Carbon dioxide increases the disorder within AM5G-H_2O. It heightens the free enthalpy. Its magnitude is linked to temperature. The largest corresponds to HB around O4sp3. The least is achieved with the HB near O2sp3. At 286 K. Its values related to O2sp3 and O3sp3 augment

strongly. However, carbon dioxide maintains the non-spontaneity underlying its complexation with AM5G-H_2O. Its effect on the $\Delta\vartheta_{O-H}$ frequency shifts is temperature dependent.

At 298 K, carbon dioxide conserves them. At 286 K, AM5G-H_2O band moves from 286.89 cm-1 to 315.6 cm-1. These results establish ambient, or storage temperatures of banana and carbon dioxide play a different role in the degradation of hydrated amylose in this fruit. The work, associated with the previous ones [6] [16], allows us to propose a mechanism for the rotting of bananas. This aspect constitutes one of the research team's goals.

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