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Original research article

Computational Investigation of Bond Strength in α-D-Glucose under Strong Electric Fields: Implications for Plasma-Induced Starch Cross-Linking

Withoon Chunwachirasiri*

Department of Physics, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

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ABSTRACT

Plasma technology offers a promising, environmentally friendly approach for starch modification, including cross-linking, which can significantly alter its functional properties. While macroscopic changes in plasma-treated starch are observable, the underlying molecular mechanisms, particularly the specific sites of cross-linking, remain challenging to elucidate experimentally. Starch is a complex polysaccharide composed primarily of glucose units. Understanding how individual glucose molecules respond to the plasma environment at the atomic level is crucial for revealing these mechanisms. This study employs Density Functional Theory (DFT) calculations to investigate the effect of strong static electric fields on the bond strength of α-D-glucose, a fundamental building block of starch. By systematically varying the applied electric field, we aim to simulate a key interaction experienced by starch molecules within a plasma environment. We will analyze changes in key molecular descriptors, such as bond lengths, bond orders, and vibrational frequencies, to quantify alterations in bond strength. We hypothesize that specific bonds within the glucose molecule will exhibit significant and consistent weakening under the influence of electric fields applied in certain orientations and strengths. Identifying these vulnerable locations computationally is expected to provide valuable theoretical insights into the preferred sites for bond cleavage or rearrangement—crucial initial steps in plasma-induced cross-linking—and offer molecular-level clues to complement experimental characterizations of cross-linking behavior in plasma-modified starch.

Keywords: Bond Strength; Cross-linking; DFT; Glucose; Plasma; Starch Modification

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***Corresponding author:** withoon.chu@mahidol.ac.th
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1. Introduction

Starch, a vital biopolymer, serves as a primary dietary energy source and a renewable feedstock for diverse industrial applications [1]. Native starch often requires physicochemical modifications, with cross-linking being a key process to enhance properties like thermal stability and shear resistance [1]. While traditional chemical cross-linking is effective, it raises safety and environmental concerns [2]. Plasma technology offers an eco-friendly alternative for starch modification [3, 4]. This physical process can alter material structures without harsh chemical reagents. Studies by Zou et al. [5] demonstrated plasma's efficacy for starch cross-linking, proposing pathways involving activation of hydroxyl (O-H) groups on glucose units. The focus of this computational study is α-D-glucose, the fundamental repeating unit of starch. Its molecular structure and the specific carbon numbering are detailed in Fig. 1. Of particular importance is the C-2 position, which is implicated by experimental data and the model advanced by Zou et al. as a primary site of high reactivity for these processes.

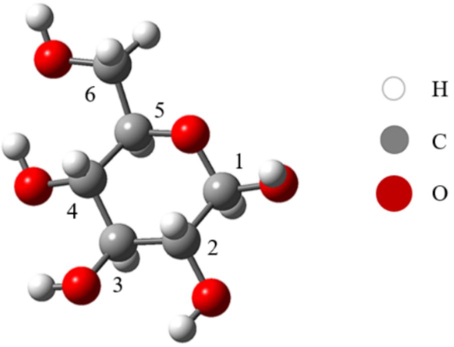

Fig. 1. Molecular structure of α-D-glucose with carbon atom numbering.

Despite these advancements, a detailed understanding of the molecular-level mechanisms, especially the initial bond activation steps on glucose units under plasma conditions, remains incomplete. This study aims to bridge this gap by employing molecular simulations, specifically focusing on α-D-glucose. Recognizing that plasma environments are highly energetic and can potentially induce electronic excitations in molecules, our approach considers molecular characteristics pertinent to such conditions. This work focuses on investigating the effects of strong static electric fields—a key component of the plasma environment—on O-H bond characteristics of α-D-glucose. Density Functional Theory (DFT) was utilized for analyzing key molecular descriptors such as bond lengths, bond orders, and IR intensities of O-H stretching vibrations (the latter providing insights related to the vibrational frequencies analysis). We hypothesize that specific O-H bonds, particularly at the C-2 position, will exhibit significant sensitivity to the applied electric field, providing a theoretical basis for the experimentally observed site preference in plasma-induced cross-linking. Given the involvement of C1-OH and C4-OH groups in glycosidic linkages within polymeric starch, our primary comparative analysis will center on the C2-OH and C3-OH groups, with C6-OH group also considered, to identify sites particularly sensitive to electric field perturbation.

2. Methodology

The study involved a two-stage computational approach. Initially, the geometries of the first electronically excited state (S_1) of α-D-glucose were optimized using Configuration Interaction Singles (CIS) within the Gaussian 09 software package [6]. These CIS/S_1 optimizations employed the 6-31+G(d,p) basis set and were performed both in the absence of an electric field and under static electric fields of 0.002 a.u. (~1.03×10^9 V/m) and 0.004 a.u. (~2.06×10^9 V/m) applied along the positive and negative x, y, and z molecular axes. O-H bond lengths reported are from these CIS-optimized S_1 state geometries.

Electric field strengths of 0.002 a.u., and 0.004 a.u. were selected to approximate the strong fields in cold plasma environments, such as dielectric barrier discharge, which range from 10^8 to 10^{10} V/m [1, 3]. These values also bridge to lower-field PEF studies (10^6 − 10^7 V/m) used in starch modification [7], allowing exploration of both subtle and pronounced molecular responses.

To further characterize these CIS-optimized S_1 excited-state geometries under each electric field condition, subsequent quantum chemical analyses were performed using the ORCA quantum chemistry package (Version 6.0.1) [8]. For these property calculations, Density Functional Theory (DFT) was employed, specifically using the B3LYP hybrid functional in conjunction with the def2-SVP basis set. All DFT calculations were carried out on the previously determined, fixed CIS S_1 geometries. To derive the bond strength indicators and molecular characteristics outlined in our objectives, two distinct types of DFT calculations were conducted: single-point DFT energy calculations were performed on each CIS geometry to obtain electronic properties, from which Mayer bond orders for the O-H bonds were specifically extracted; additionally, harmonic vibrational frequency calculations at the same B3LYP/def2-SVP level of theory on these fixed CIS geometries yielded vibrational frequencies and their corresponding IR intensities, with the latter being a key focus for analyzing changes in vibrational properties. Therefore, the primary molecular characteristics analyzed in this study are: O-H bond lengths; bond orders; and IR intensities. This combined CIS (for generating relevant excited-state geometries) and DFT (for detailed property on these excited-state geometries) approach was adopted to assess molecular characteristics within an excited-state framework, which is considered highly pertinent for molecules subjected to the energetic conditions found in plasma environments. The impact of the electric field on the different hydroxyl groups (specifically those at C-2, C-3, and C-6, denoted C2-OH, C3-OH, etc.) was then assessed, with a particular focus on comparing the C2-OH and C3-OH groups.

The combined CIS/DFT approach was adopted to balance computational feasibility with accuracy for modeling the S_1 excited state of α-D-glucose under strong electric fields. CIS, implemented in Gaussian 09, efficiently optimizes S_1 geometries, capturing field-induced structural changes relevant to plasma environments. This method is suitable for systems dominated by single excitations, such as glucose's S_1 state, and has been used in prior field-perturbation studies [9, 10]. Subsequent DFT calculations (B3LYP/def2-SVP) on fixed CIS geometries provide robust electronic properties and vibrational characteristics. While CIS neglects dynamic electron correlation, potentially overestimating excitation energies by 1–2 eV, focusing on relative changes in bond descriptors (e.g., % change in IR intensity) mitigates absolute errors. This hybrid approach is a practical compromise given the computational cost of optimizing multiple geometries under varied field conditions ($\pm x$, $\pm y$, $\pm z$; 0.002–0.004 a.u.).

3. Result and Discussion

The application of an external static electric field induced notable changes in the O-H bond lengths, bond orders, and IR intensities of the first excited state of α-D-glucose. The S_1 state itself, even at zero field, possesses a geometry distinct from the ground state. Our analysis focuses on how the electric field further perturbs the O-H characteristics of this already excited state, aiming to identify specific bonds that exhibit weakening or heightened sensitivity. Baseline values without the applied electric field and data under applied fields for the C2-OH, C3-OH, and C6-OH groups are presented in Table 1.

3.1 Geometry validation

To validate our computational model, the optimized geometries of α-D-glucose in the S_1 state (CIS/6-31+G(d,p), no field) and ground state (B3LYP/def2-SVP) were compared to X-ray crystallographic data [11]. Key bond lengths, such as C2-OH (exp: 1.41 $\mathring{A}$, S_1: 1.40 $\mathring{A}$, ground: 1.41 $\mathring{A}$) and C1-O5 (exp: 1.43 $\mathring{A}$, S_1: 1.42 $\mathring{A}$, ground: 1.43 $\mathring{A}$), and the C1-O5-C5 ring angle (exp: 112.5°, S_1: 113.1°, ground: 112.8°) agree within 0.02 $\mathring{A}$ and 1°. These results confirm that both CIS and DFT geometries retain structural fidelity to experimental data, providing a reliable foundation for field-perturbation studies.

3.2 Bond lengths and bond orders

In the S_1 excited state, the O-H bond lengths of the C2-OH and C3-OH groups predominantly exhibited contraction when an external electric field was applied, compared to the S_1 no-field geometry (Table 1). For example, the C2-OH bond length (S_1 state) decreased from 0.96743 $\mathring{A}$ (no field) to as low as ~0.943 $\mathring{A}$ under fields of 0.004 a.u. The bond orders for these bonds generally showed slight increases or minor variations, consistent with this bond contraction. This indicates that for these secondary hydroxyls in the S_1 state, the electric field induces further polarization leading to O-H bond compression. Similar trends were noted for the O-H bonds of the C1-OH and C4-OH groups (data not shown).

The C6-OH bond showed a distinct anisotropic response. While contracting in some field directions (e.g., -x field), it exhibited clear elongation (e.g., from 0.96497 $\mathring{A}$ to 0.987 $\mathring{A}$ with a +y field) and a corresponding decrease in bond order in other specific directions (+x, +y, +z). This indicates that the C6-OH group, even in the S_1 state, can undergo further field-induced bond weakening (elongation) depending on orientation.

3.3 IR intensities of O-H stretching vibrations: differentiating C2-OH and C3-OH sensitivity

The IR intensities of O-H stretching vibrations provided key distinctions in the electric field's impact on the C2-OH versus C3-OH groups S_1 state. The C2-OH stretch demonstrated a consistent and often substantial increase in IR intensity across nearly all applied field directions and strengths. For instance, its intensity (baseline 38.92 arb. units no-field) increased to 87.10 (-y direction, 0.004 a.u.).

In contrast, the C3-OH stretch showed a more complex, direction-dependent response in its IR intensity. While its intensity (baseline 52.79 arb. units) increased in several orientations, it exhibited a marked decrease in others, notably along the -x axis (to 27.75) and +y axis (to 42.70) at 0.004 a.u. The C6-OH stretch also generally showed increased IR intensity under field perturbation.

3.4 Relative site sensitivity in the excited state for cross-linking initiation

Our initial hypothesis considered that electric fields would induce bond weakening. Based on bond length and order analysis of the S_1 state, direct weakening via O-H bond elongation was not the primary observation for the C2-OH or C3-OH groups; they mostly contracted. However, the IR intensity data offers a significant perspective on field-induced ”activation” or ”sensitization” of these sites within the excited state. The consistent and significant enhancement of the C2-OH stretching IR intensity implies a more reliable and pronounced electronic perturbation of this bond during its vibration when the field is active. Such an alteration could render the C2-OH group, once electronically excited, more susceptible to interactions or reactions (e.g., deprotonation, radical attack) that are precursors to bond cleavage and possible cross-linking.

The enhanced C2-OH IR intensity under electric fields aligns with experimental observations of plasma-treated starch. Zou et al. [5] reported preferential reactivity at the C-2 position, likely due to field-induced activation facilitating deprotonation or radical formation. IR spectroscopy of plasma-modified starch shows broadened O-H stretching bands (~3400 cm^{-1}), suggesting bond polarization or altered hydrogen bonding [12], consistent with our computed C2-OH IR intensity increases (up to 123% in –y). The field-induced elongation of C6-OH (up to 2.2% in +y) correlates with plasma-driven oxidation at primary hydroxyls [13], supporting its role as a cross-linking site.

The mixed intensity response of the C3-OH group suggests its interaction with the field in the S_1 state is less uniformly ”activating” in terms of its vibrational characteristics. Although the C6-OH site shows potential for direct field-induced bond elongation in specific orientations, the C2-OH site stands out due to its consistently enhanced IR activity when compared to C3-OH. This suggests the hydroxyl group at C2 is more favorably sensitized by the electric field for subsequent reactions once the molecule is in an excited state.

Prior computational studies provide context for our findings. DFT analyses of α-glucan models identified C2-OH and C6-OH as flexible due to hydrogen bonding [14], consistent with their sensitivity to electric fields in our S_1 state calculations. However, these studies focused on ground-state conformations without external fields. Our work extends this by demonstrating that plasma-like fields enhance C2-OH IR intensity and induce C6-OH elongation, revealing unique reactivity in the excited state not captured previously [2, 10].

3.5 Summary of field effects

Table 2 summarizes the relative changes in bond length, bond order, and IR intensity for C2-OH, C3-OH, and C6-OH at 0.004 a.u., grouped by site to highlight their differential responses to electric field directions (+x, +y, +z). C2-OH exhibits consistent IR intensity increases (up to 123% in -y) with slightly positive bond order changes (up to +0.5% in +z), indicating field-induced sensitization and bond strengthening, likely enhancing polarity for cross-linking interactions. C6-OH shows significant bond elongation (up to 2.2% in +y) and reduced bond order (up to -2.0% in +y), suggesting bond weakening favorable for covalent cross-linking. C3-OH displays minimal changes, with stable bond lengths, small bond order reductions, and variable IR intensity.

Table 1. Selected O-H bond characteristics in the CIS-optimized S_1 state of α-D-glucose under varying electric field conditions. Field "0"/"20"/"40" = 0/0.002/0.004 a.u. The columns with no electric field are repeated for convenient references and relative comparisons.

Direction/ E-field	O-H Sites	Bond Length			Bond Order			IR Intensities (arb. units)		
		0	20	40	0	20	40	0	20	40
-3*+x	C-2	0.96743	0.94404	0.94385	0.9745	0.9777	0.9794	38.92	70.86	71.7
	C-3	0.96903	0.94588	0.94546	0.9610	0.9700	0.9693	52.79	54.16	61.08
	C-6	0.96497	0.98263	0.97948	0.9733	0.9646	0.9638	44.92	55.82	65.65
-3*–x	C-2	0.96743	0.96573	0.96295	0.9745	0.9708	0.9707	38.92	41.82	56.28
	C-3	0.96903	0.94455	0.94484	0.9610	0.9801	0.9823	52.79	68.22	7.75
	C-6	0.96497	0.94299	0.94323	0.9733	0.9800	0.9808	44.92	43.30	38.65
-3*+y	C-2	0.96743	0.94465	0.94511	0.9745	0.978	0.9797	38.92	56.80	48.58
	C-3	0.96903	0.9461	0.94597	0.9610	0.9729	0.9755	52.79	49.82	42.70
	C-6	0.96497	0.98718	0.98682	0.9733	0.9652	0.9655	44.92	58.01	55.51
-3*–y	C-2	0.96743	0.94386	0.94349	0.9745	0.9797	0.9737	38.92	94.33	87.10
	C-3	0.96903	0.94645	0.94667	0.9610	0.9755	0.9639	52.79	57.73	70.23
	C-6	0.96497	0.98425	0.98146	0.9733	0.9655	0.9622	44.92	55.12	64.64
-3*+z	C-2	0.96743	0.94433	0.94428	0.9745	0.9776	0.9795	38.92	82.97	77.05
	C-3	0.96903	0.94597	0.94559	0.9610	0.9714	0.9714	52.79	53.31	60.98
	C-6	0.96497	0.98128	0.98406	0.9733	0.9675	0.9643	44.92	55.81	93.22
-3*–z	C-2	0.96743	0.96497	0.96331	0.9745	0.9713	0.9706	38.92	65.63	77.02
	C-3	0.96903	0.94454	0.94435	0.9610	0.9798	0.9803	52.79	70.90	59.70
	C-6	0.96497	0.94284	0.94283	0.9733	0.9790	0.9787	44.92	52.49	56.71

Table 2. Relative Changes in O-H Bond Characteristics (0.004 a.u. vs. No Field).

Site	Direction	% Change in Bond Length	% Change in Bond Order	% Change in IR Intensity
C2-OH	+x	–2.4%	+0.3%	+84.2%
	+y	–2.3%	+0.2%	+24.8%
	+z	–2.3%	+0.5%	+98.0%
C3-OH	+x	–2.4%	–0.3%	+15.7%
	+y	–2.3%	–0.4%	–19.1%
	+z	–2.4%	–0.5%	+15.5%
C6-OH	+x	+1.5%	–1.0%	+46.2%
	+y	+2.2%	–2.0%	+23.6%
	+z	+1.9%	–1.5%	+107.6%

4. Conclusion

This study employed a combined CIS and DFT approach to investigate the effect of strong static electric fields on the bond characteristics of α-D-glucose, focusing on its first electronically excited state (S_1), a condition relevant to energetic plasma environments. Geometries of the S_1 state were optimized using CIS under various fields, and O-H bond lengths, Mayer bond orders, and IR intensities were subsequently analyzed using DFT on these S_1 geometries. Analysis of the S_1 state revealed that the O-H bonds of the C2-OH and C3-OH groups predominantly undergo slight contraction under field perturbation. However, the C6-OH group exhibited orientation-dependent elongation, suggesting direct field-induced weakening at this site within the excited manifold. The most critical distinction between the C2-OH and C3-OH sites arose from their IR intensity responses. The C2-OH stretching vibration showed a consistent and significant increase in IR intensity under most field conditions. In contrast, the C3-OH stretch displayed a mixed response, including significant intensity decreases in certain orientations.

The consistent enhancement of C2-OH IR intensity in the S_1 state suggests it is a primary site for field-induced sensitization, aligning with experimental evidence of C-2 hydroxyl reactivity in plasma-induced starch cross-linking [5]. In starch's polymeric structure, C2-OH and C6-OH remain accessible, unlike C1-OH and C4-OH, which form glycosidic linkages. The orientation-dependent elongation of C6-OH indicates its potential as a cross-linking site, particularly in amylopectin's branched regions. These findings provide a molecular basis for plasma treatments targeting C2 and C6 hydroxyls, facilitating cross-linking via deprotonation or radical-mediated pathways [12, 13].

Based on its more reliable and pronounced increase in IR intensity—indicative of a greater and more consistent electric field-induced perturbation of its vibrational electronic character within the first excited state—we conclude that the hydroxyl group at C2 of S_1 α-D-glucose is more favorably and consistently sensitized by an external static electric field compared to the hydroxyl group at C3. This suggests that if glucose is electronically excited by plasma, the C2-OH site becomes particularly responsive to the plasma's electric field component, potentially facilitating its involvement in the initial steps of cross-linking. This computational outcome, highlighting the particular sensitivity of the C2-OH group to electric field perturbation, aligns with and provides further theoretical support for the experimental findings and mechanisms proposed by Zou et al. [5], which identified the C-2 position as a primary site for plasma-induced cross-linking in starch.

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