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Electron collisions with α-D-glucose and β-D-glucose monomers

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The development of new alternative routes for production of second generation ethanol from sugarcane biomass poses a challenge to the scientific community. Current research in this field addresses the use of a plasma-based pretreatment of the lignocellulosic raw material. With the aim to provide a theoretical background for this experimental technique we investigate the role of low-energy electrons from the plasma in the rupture of the matrix of cellulosic chains. In this paper, we report calculated cross sections for elastic scattering of low-energy electrons by the α- and β-D-glucose monomers. The calculations employed the Schwinger multichannel method with pseudopotentials and were carried out at the static-exchange and static-exchange plus polarization levels of approximation. Through the comparison of the results obtained with inclusion of polarization effects we discuss the influence of the different conformations of the hydroxyl group linked to the anomeric carbon on the resonance spectra of these molecules. Resonant structures appearing at different energies for α- and β-glucose at the low-energy regime of impact energies can be understood as a fingerprint of an "isomeric effect" and suggest that distinct fragmentation mechanisms proceeding via σ^* shape resonances may become operative depending on the glucose anomer under consideration. For energies above 15 eV the integral elastic cross sections are very similar for both monomers. Differential cross sections for the glucopyranose anomers considered in this work are typically dominated by a strong forward scattering due to the molecules' large electric dipole moments and, for energies close to the resonances' positions, they display particular features at the intermediate angular region, notably a pronounced f-wave scattering pattern, that are probably associated with the presence of those structures. © *2010 American Institute of Physics*.

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I. INTRODUCTION

The control of global warming is currently considered as one of the greatest challenges to be faced by humanity. In order to achieve this goal and to prevent dangerous anthropogenic interference with the climate system, an important issue to be addressed is the reduction of the greenhouse gas emissions on the Earth's atmosphere. Within that context, the replacement of fossil fuels by biofuels obtained from renewable resources plays a rather special role. Efforts in this area have focused on developing alternative technologies, as well as in the improvement of the existing ones, with a particular interest on generating the scientific knowledge necessary to support new developments. The production of cellulosic ethanol has attracted much attention in this scenario due to its potential as a substitute for gasoline in the supply of automotive vehicles.[1] Although meaningful progress regarding sustainable production and use of cellulosic biomass has been achieved in the last years, it is worth noting that there are still many drawbacks to be overcome in almost all stages of the bioethanol lifecycle: feedstock growth, fuel production, distribution, and combustion, to mention only a few.

Recently, Amorim *et al.*[2,3] proposed a microplasma source based on the use of atmospheric-pressure (AP) plasmas that may be used for selective treatment of lignocellulosic material from sugarcane. Nonequilibrium plasmas have been widely used to promote, with high efficiency, the modification or treatment of surfaces for a variety of industrial applications.[4–6] The development of a plasma-based pretreatment for the processing of sugarcane biomass may represent a very important step towards the industrial production of second generation ethanol considering that: (i) the plasma attack is a short-time and low-cost process; (ii) the use of a plasma-based treatment implies a low environmental impact; (iii) the plasma is a finely controlled environment and its action on the treated material can, in principle, be directed to the molecular region of interest; and (iv) these plasmas may

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be used not only in the breaking down of the matrix of cellulose and lignin which protects cellulose but also to produce fermentable sugars.

The present study is carried out with the aim to provide the theoretical foundations supporting the development of the new method for selective treatment of sugarcane biomass based on the use of AP plasmas. In order to accomplish this task the interaction of the plasma electrons with lignocellulosic biomass should be better understood and we begin this investigation by studying the scattering of low-energy electrons from the biologically active α- and β-D-glucopyranose (or simply α- and β-D-glucose) monomers, the sugar units that compose starch and cellulose polymeric chains, respectively.

Low-energy electrons are known to interact with biological polymers in a very complex way. In particular, it has been shown that secondary electrons generated from ionizing radiation can be trapped into specific sites of DNA and RNA strands, giving rise to temporary anions.[7] These metastable ions have lifetimes comparable to typical vibrational periods and provide a very efficient way to release energy into nuclear degrees of freedom. This effect is most dramatic when the resonant potential surface is dissociative since it can lead to mutagenic strand breaks in nucleic acids. The fact that electron capture takes place in specific DNA sites, such as sugars and bases, has motivated an intense effort to understand electron interactions with DNA components.[8–18] Considering that even simple DNA units such as uracil or thymine display a very rich spectra of resonant states, it is important to relate the appearance of those resonances, i.e., to assign them, to possible dissociative pathways triggered out by electron attachment in order to put some light into the discussion about the breakage of chemical bonds that could be induced. In short, at very low energies (<1 eV) anion states supported by dipole interactions usually prevail, while electrons in the energy range of 1–3 eV are usually trapped into π^* resonances. It has been proposed[19–21] that π^* resonances couple to dissociative σ^* resonances in a non Born–Oppenheimer fashion (i.e., the resonant states are diabatically coupled), although a direct capture into a σ^* resonance is also possible, as discussed by Scheer *et al.*,[22] Gallup *et al.*,[23,24] and Rescigno *et al.*[25] At higher energies, direct capture into σ^* resonances is also possible and core-excited resonant states become operative.

As long as the reaction mechanisms described above are concerned, polysaccharides and nucleic acids differ in the sense that the former have saturated rings lacking of π electrons. On the other hand, σ^* resonances could be expected for polysaccharides, and these might lead to dissociation of O—H, C—H, C—O, and C—C chemical bonds. Recent experimental studies of dissociative electron attachment (DEA) to saturated cyclic alcohols have indicated a very rich σ^* resonance spectra (either shape or core excited) leading to the cleavage of several bonds.[26,27] The shape resonances were seen to mostly yield OH fragmentation, while more complex dissociation pathways could arise from core-excited (Feshbach) resonances. In addition, recent DEA measurements for gas-phase fructose in the pyranose form observed the formation of the light fragments OH^-, H^-, and O^- above 5eV.[18] These authors suggested that the first two anions can be formed by simple bond cleavage whereas the former must be expelled from the C—O—H unit with a possible subsequent formation of a new C—H bond.

In the present work we carry out a comparative study of low-energy electron scattering from α-D-glucose and β-D-glucose monomers in order to investigate the influence of the different conformations of the hydroxyl group linked to the anomeric carbon on the resonance spectra of these molecules. We expect these results to elucidate the similarities and differences in the resonant processes responsible for the breakage of the respective $(\alpha 1\rightarrow 4)$ and $(\beta 1\rightarrow 4)$ linkages. Of paramount importance is to get a deeper insight about the role of electron capture on the hydrogen bond network of cellulose through the identification of resonances and possible dissociation pathways for the glycosidic bonds. In particular, the resonance energies should provide invaluable information for optimizing the plasma-based pretreatment of lignocellulosic raw material (i.e., by tuning electron energies in the atmospheric plasma).

The paper is organized as follows: in Sec. II, we briefly review the main theoretical aspects of the Schwinger multichannel method (SMC) and its implementation with pseudopotentials (SMCPP). Section III provides information about the computational details on target and scattering calculations. In Sec. IV, we present and discuss our results, while in Sec. V, we summarize our findings.

II. THEORY

Since the SMC (Ref. 28) and SMCPP (Ref. 29) methods have been widely discussed previously, we present here only those aspects relevant to the discussion that follows. In the SMC method the scattering amplitude (in the body reference frame) is given by

$$f(\vec{k}_f,\vec{k}_i) = -\frac{1}{2\pi}\sum_{m,n}\langle S_{\vec{k}_f}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V|S_{\vec{k}_i}\rangle, \qquad (1)$$

where the χ_m's, also known as configuration state functions (CSFs), are $(N+1)$-electron Slater determinants constructed from products of target states with one-particle wave functions. From these products, only overall doublet states are retained if the target is a closed shell system.[30]

The d_{mn} matrix elements are given by

$$d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle, \qquad (2)$$

where the $A^{(+)}$ operator can be written as

$$A^{(+)} = \frac{1}{2}(PV+VP) - VG_P^{(+)}V + \frac{\hat{H}}{N+1} - \frac{1}{2}(\hat{H}P + P\hat{H}). \qquad (3)$$

In the above equations, $S_{\vec{k}_{i(f)}}$ is an eigenstate of the unperturbed Hamiltonian H_0, given by the product of a target state and a plane wave with momentum $\vec{k}_{i(f)}$; V is the interaction potential between the incident electron and the target; $\hat{H} \equiv E-H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H=H_0+V$; P is a projection operator onto the open-channel space

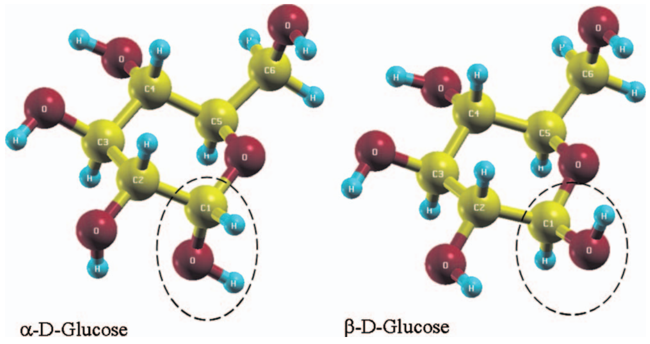

FIG. 1. Optimized geometrical structure and atoms labeling for α-D-glucose (left) and β-D-glucose monomers (right).

$$P = \sum_{l \in \text{open}} |\Phi_l\rangle\langle\Phi_l|, \tag{4}$$

and $G_P^{(+)}$ is the free-particle Green's function projected on the P-space.

In this work, we are specifically dealing with elastic scattering of electrons by molecules at the static-exchange (SE) and the SE plus polarization (SEP) levels of approximation. For calculations carried out in both approximations the P operator is given by

$$P = |\Phi_0\rangle\langle\Phi_0|. \tag{5}$$

For calculations carried out at the SE approximation, the configuration space is composed by CSFs of the type

$$|\chi_m\rangle = \mathcal{A}[|\Phi_0\rangle \otimes |\varphi_m\rangle], \tag{6}$$

where $|\Phi_0\rangle$ is the target ground state (represented by a single N-electron Slater determinant), $|\varphi_m\rangle$ is the one-electron wave function, and $\mathcal{A}$ is the antisymmetrizer. For calculations carried out at the SEP level of approximation, the above set is augmented by CSFs constructed as

$$|\chi_{mn}\rangle = \mathcal{A}[|\Phi_m\rangle \otimes |\varphi_n\rangle], \tag{7}$$

where $|\Phi_m\rangle$ are N-electron Slater determinants obtained by single excitations from the occupied (hole) orbitals to a set of unoccupied (particle) orbitals. As before, $|\varphi_n\rangle$ is represented by a one-electron wave function and $\mathcal{A}$ is the antisymmetrizer.

The numerical stability of calculations presented in this paper was checked with the procedure developed by Chaudhuri and co-workers,[31] as adapted to electron-molecule scattering.[30] This procedure has been successfully applied to the removal of spurious structures arising from numerical linear dependence among basis set functions (see, for instance, Ref. 32).

III. COMPUTATIONAL DETAILS

For both systems the ground state molecular geometry was optimized using the GAMESS package[33] at the RHF level with the use of a DZP++ basis set in the C_1 point group. The geometrical structures of α- and β-D-glucose monomers are shown in Fig. 1. The D-pyranose form is biologically active, and the anomers differ by the axial (α) or equatorial (β) orientation of the hydroxyl group linked to the C1 atom with respect to the ring. Although over 700 conformers may occur in view of the rotational freedom of hydroxyl and hydroxymethyl groups,[34] the scattering properties would not be expected to significantly depend on these orientational changes, in principle. However, the dipole moments are strongly affected by the conformation of the hydroxymethyl group.[35] As a result, the dipole-supported states at very low energies as well as the magnitude of differential cross sections (DCSs) at low scattering angles would be conformer-dependent (strictly, many conformations would be accessible at finite temperatures). In the present work, we mainly focus on shape resonances whose position and widths should be little affected by internal rotational degrees of freedom. Employing the terminology of Ref. 35, the α and β anomers addressed here are classified as αG-g and βG-g, abundant in the gas phase.

Our bound state and scattering calculations were performed using the pseudopotentials developed by Bachelet, Hamann, and Schlüter (BHS) (Ref. 36) in order to represent the nuclei and the 1s core electrons of carbon and oxygen atoms. The BHS pseudopotential V^{PP} is a nonlocal operator given by

$$\hat{V}^{PP}(r) = \hat{V}_{\text{core}}(r) + \hat{V}_{\text{ion}}(r), \tag{8}$$

with

$$\hat{V}_{\text{core}}(r) = -\frac{Z_v}{r}\left[\sum_{i=1}^{2} c_i^{\text{core}} \operatorname{erf}[(\alpha_i^{\text{core}})^{1/2} r]\right], \tag{9}$$

and

$$\hat{V}_{\text{ion}}(r) = \sum_{n=0}^{1}\sum_{j=1}^{3}\sum_{l=0}^{2} A_{njl} r^{2n} e^{-\alpha_{jl} r^2} \sum_{m=-l}^{+l} |lm\rangle\langle lm|. \tag{10}$$

In the above equations, Z_v is the valence charge of the atom and in this application it is equal to 4 to carbon and 6 to oxygen. The coefficients c_i^{core}, A_{njl}, and the decay constants α_i^{core} and α_{jl} are tabulated in Ref. 36. The implementation of the BHS pseudopotentials in the Hartree–Fock and in the Schwinger multichannel methods has been described in Ref. 29.

The basis set employed in bound state and scattering calculations consists of functions generated by a variational method, as described in Ref. 37. For carbon atoms labeled as C2 to C6 the basis set consists of 4s4p uncontracted Cartesian Gaussian (CG) functions with exponents: 3.236 886 0, 0.717 066 00, 0.329 964 00, and 0.067 576 000 for the s-type functions and 4.911 060 0, 1.339 766 0, 0.405 869 00, and 0.117 446 00 for the p-type functions. Oxygen atoms labeled as O1 and O3 to O6 are described by a 4s4p basis set of uncontracted CG functions with exponents: 4.887 651 0, 1.147 849 0, 0.337 743 00, and 0.066 792 00 for s-type functions and 10.141 200, 2.782 999 0, 0.841 004 00, and 0.232 939 00 for p-type functions. For the hydrogen atoms we used a 2s basis set composed by CG functions with exponents: 1.309 757 0 and 0.233 136 00. Since the difference between α-glucose and β-glucose is precisely the orientation of the hydroxyl group linked to the C1 atom, these carbon and the O2 atoms are described by a 5s5p2d basis set of uncontracted CG functions with exponents: 12.496 280, 2.470 286 0, 0.614 028 00, 0.184 028 00, and 0.039 982 00 for the *s*-type functions; 5.228 869 0, 1.592 058 0, 0.568 612 00, 0.210 326 00, and 0.072 250 00 for the *p*-type functions and 0.603 592 00 and 0.156 753 00 for the *d*-type functions in the case of the carbon atom and exponents: 16.058 780, 5.920 242 0, 1.034 907 0, 0.316 843 00, and 0.065 203 00 for the *s*-type functions; 10.141 270, 2.783 023 0, 0.841 010 00, 0.232 940 00, and 0.052 211 00 for the *p*-type functions and 0.756 793 00 and 0.180 759 00 for the *d*-type functions in the case of the oxygen atom.

As mentioned before, to take polarization effects into account, we considered single excitations from the hole (occupied) orbitals to a set of particle (unoccupied) orbitals. Recent calculations on electron-molecule collisions performed by Winstead *et al.*[38] and Bettega *et al.*[39] indicated that an efficient way to describe the distortion of the molecular target due to the presence of the incident electron is through the use of modified virtual orbitals (MVOs).[40] In the present work, these MVOs are obtained as follows: by freezing the occupied orbitals, we have diagonalized the cation Hamiltonian (more precisely, a +4 cationic Fock operator where four electrons are subtracted from the two highest occupied orbitals) and generated MVOs from the remaining virtual orbitals. We considered single excitations from all valence occupied orbitals to the MVOs with energies less than 15 eV as a cutoff criterion for selection of the particle orbital space. The same set of MVOs was then used as scattering orbitals. We included singlet and triplet excitations which resulted in a total of 8852 doublet CSFs. Recent calculations on electron-propane collisions showed that it is important to consider both singlet- and triplet-coupled excitations in order to obtain good results for low energies.[41]

The computed values of permanent dipole moments are 4.4912 and 3.0898 D for α- and β-glucose monomers, respectively. The long-ranged dipole interaction is accounted for with the Born-closure procedure described in Ref. 42. The highest angular momenta computed with the SMC method in the present SEP calculations were $\ell_{\mathrm{SMC}}=4$ at 3 eV and $\ell_{\mathrm{SMC}}=5$ at 5 and 7 eV, $\ell_{\mathrm{SMC}}=7$ at 9, 10, and 15 eV and $\ell_{\mathrm{SMC}}=10$ at 20 eV. These values were chosen to provide the best matching between the DCSs obtained with and without the Born closure for scattering angles above ~40°. The present integral cross sections (ICSs) were not Born-corrected, though.

IV. RESULTS AND DISCUSSION

In Fig. 2, we show the ICSs for both glucose monomers obtained in the SE and SEP approximations without the Born correction. The Born correction would only increase the magnitude of the ICS without changing the resonances locations. Since we are interested in discussing the resonances, we chose to omit this additional calculation regarding the ICS. The energies considered in this work range from 3 to 20 eV. The SE and SEP cross sections for α-D-glucose (top panel) display two structures, a weak peak at 4.5 eV and a broad structure around 12 eV. For β-D-glucose (bottom panel) we note the appearance of four structures in the SE results: two sharp peaks with maximum at 3.7 and 5 eV, a less pronounced peak at 7.6 eV and a broad structure centered at 14 eV. Cross sections obtained in the SEP approximation follows the same pattern with the exception of the first structure that is not present at this level of calculation, or may have been shifted to lower energies. We discuss these points based on the following considerations. The cross sections obtained with the SMC method may be affected by the presence of unphysical resonances. The occurrence of these spurious structures is related to numerical linear dependence in the trial basis set used in the expansion of the configuration state space. In order to investigate the numerical stability of present scattering calculations we performed an analysis consisting of the steps briefly described in the last paragraph of Sec. II (for more details, see Refs. 31 and 32). The procedure was used to check only the results obtained in the SE approximation since the analysis for calculations carried out at the SEP level would be computationally demanding. Our conclusions are that in general the results are stable except for the lowest structure of β-D-glucose, which is sensitive to the removal of few CSFs, suggesting that this structure is in fact spurious. Besides, our results obtained in the SE and SEP approximations are quite similar, implying that the contribution of polarization effects would not be so important due to the large dipole moments values of α- and β-D-glucose.

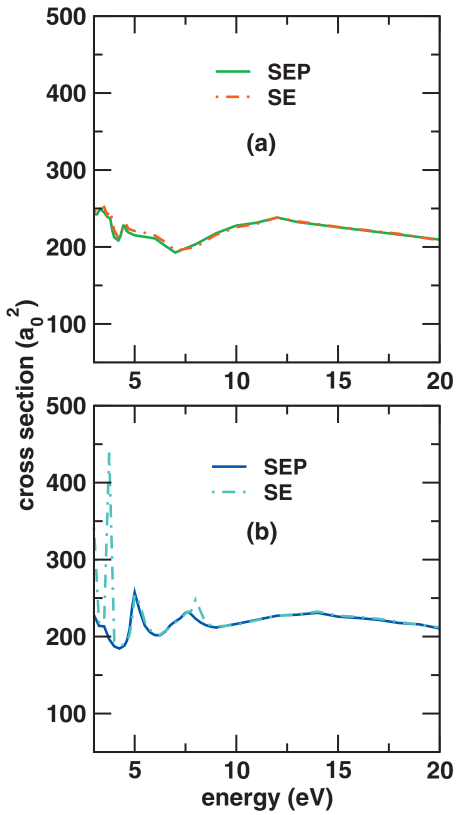

FIG. 2. ICSs for (a) α-D-glucose and (b) β-D-glucose monomers at the SE and SEP levels of approximation. From the structures appearing at the SE and SEP cross sections, those at 4.5 and 12 eV for α-D- and those at 5, 7.6, and 14 eV for β-D- glucose are considered as physical resonances related to the capture of the incident electron on a temporary anion state. The peak at 3.7 eV was unstable under our numerical analysis and is ascribed as an unphysical structure. See text for more details.

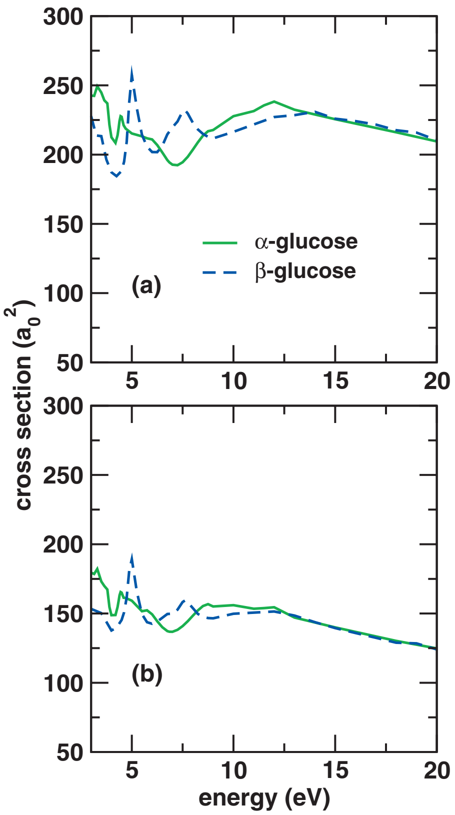

FIG. 3. (a) Integral and (b) momentum transfer cross sections at the SEP level of approximation.

Figure 3 compares the SEP integral and momentum transfer cross sections for the two glucose monomers. For energies below 15 eV, the resonances seen in both ICSs are located at different energies, indicating a strong isomeric effect. As a consequence the two molecules may dissociate by electron impact at different energies. For energies above 15 eV the ICSs for both monomers become very similar. The same behavior can be viewed in the momentum transfer cross sections, which agree above 15 eV and show remarkable differences for energies below this value. The isomeric effect can also be seen in the DCSs. The SEP DCSs for α and β-glucose monomers from 3 to 20 eV are shown in Figs. 4 and 5. At 3, 5, and 7 eV the DCSs for the two monomers differ, showing the isomeric effect. For energies above 9 eV the DCSs become similar. At 9, 10, 15, and 20 eV the DCSs present an oscillatory pattern that is characteristic of f-wave scattering.

Finally, we make some additional comments based on a qualitative analysis of the isosurfaces of the energy pseudoeigenstates obtained from the square-integrable basis set used for the scattering calculations. More specifically, we choose those states with the energy eigenvalue closer to the position of the resonances that appear in our ICS results. Following this criterion we found for the α-D-glucopyranose a state around 4.46 eV, which has the most relevant contributions for the electronic density localized on the ring oxygen (O1), on the C1—C2 chemical bond, on the C3—O4—H6, and C4—O5—H8 moieties and also on the hydroxymethyl group, as displayed in Fig. 6. The β-pyranosic anomer, in turn, has a 4.92 eV energy pseudoeigenstate with significant density on the O1, O3, and O6 oxygen atoms, on the C2—C3 and C4—C5 bonds and on the C3—O4—H6 moiety, as can be seen in Fig. 6(b). From the above considerations we can say that from a general point of view such resonances, i.e., those appearing at 4.5 eV for α- and at 5 eV for β-glucose, have at least partial C—C, C—O, and O—H σ^* dissociative character. Thus our results suggest that, for both glucose monomers, the formation of transient states in this energy range would lead to the breakage of chemical bonds at the ring as well as to elimination of OH^- and H^- fragments from some specific groups. As mentioned before, the β-glucose also has a resonant structure located at the energy of 7.6 eV. In Fig. 6(d), it is shown that the pseudoeigenstate with the closest eigenvalue (7.56 eV) has significant density contributions located on the O1, O2, and O5 oxygen atoms, on the C2—O3—H4 and C3—O4—H6 moieties and, finally, on the C6 carbon. An important feature that occurs only in this case is related to the fact that the formation of a transient state at this energy can, in principle, give rise to dissociation of the OH^- fragment linked to the anomeric carbon. It is worth noting that, according to the results obtained in the present calculations, such fragmentation pathway has no analog in the case of the α-glucose, since the resonance present in the ICS for the β-glucose at the energy of 7.6 eV has no counterpart for the other monomer. Only for comparison purposes, we present in Fig. 6(c), the isosurface for the 7.46 eV energy state of the α-glucose which has considerable electronic density on the O3, O4, and O6 oxygen atoms, on the C4—O5—H8 moiety and on the hydroxymethyl group.

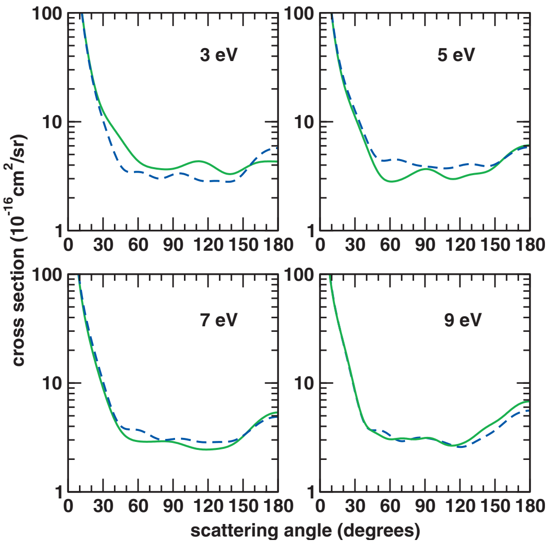

FIG. 4. DCSs at the SEP level of approximation. Solid-line (green): α-glucose and dashed-line (blue): β-glucose.

V. CONCLUSIONS

We presented elastic integral, momentum transfer and DCSs for scattering of electrons from the biologically active α- and β-D-glucose monomers. The cross sections were computed using the SMC method with pseudopotentials for energies from 3 to 20 eV in the SE and SEP approximations. Our results show a strong isomeric effect for energies below

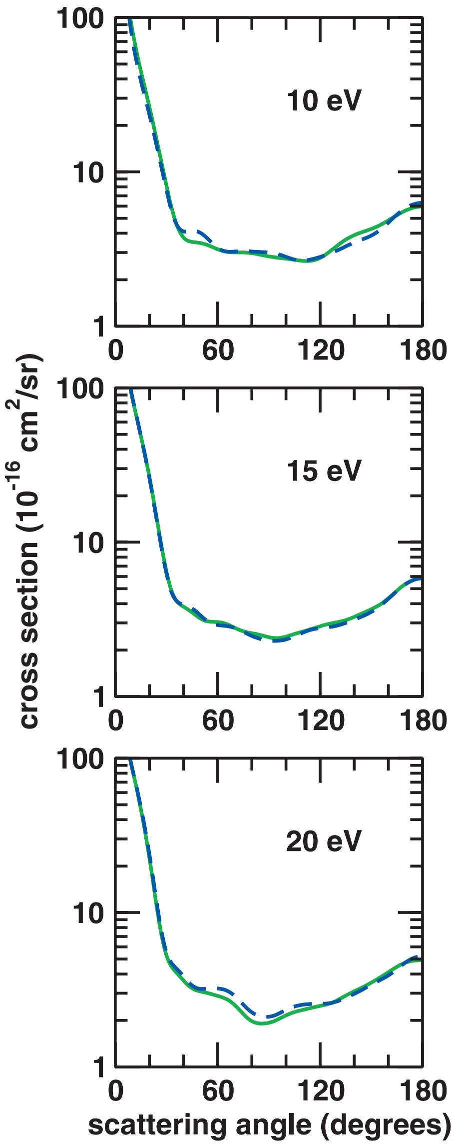

FIG. 5. DCSs at the SEP level of approximation. Solid-line (green): α-glucose and dashed-line (blue): β-glucose.

15 eV. The ICSs for both monomers present shape resonances located at different positions. As a consequence, low-energy electron may dissociate these two monomers at different energies.

These results have considerable bearing with regard to the discussion about what happens when cellulosic biomass is exposed to a plasma treatment since they suggest the fact that low-energy electrons display a specific bond-selective behavior depending on whether the interaction takes place with α-D-glucose or β-D-glucose monomers. In the light of these findings it appears to be highly desirable to study in a next step the electron scattering by the D-glucopyranose dimmers so as to investigate possible influence of electron capture in the rupture of the ($\alpha 1 \rightarrow 4$) and ($\beta 1 \rightarrow 4$) linkages.

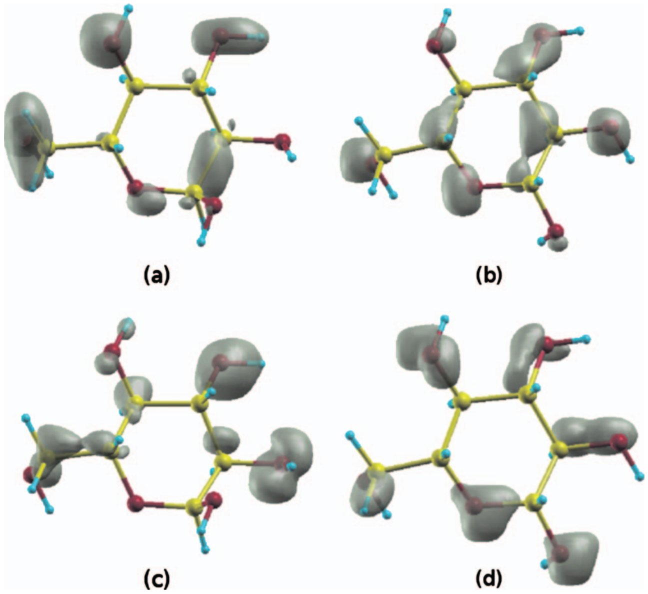

FIG. 6. Electronic density isosurface for the energy pseudoeigenstate: (a) α-glucose at 4.46 eV, (b) β-glucose at 4.92 eV, (c) α-glucose at 7.46 eV, and (d) β-glucose at 7.56 eV.

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[1] R. C. D. Leite, M. R. L. V. Leal, L. A. B. Cortez, W. M. Griffin, and M. I. G. Scandiffio, Energy **34**, 655 (2009).
[2] J. Amorim, J. A. S. Corrêa, and C. A. Oliveira, Patent No. 018080043419 (10 July 2008).
[3] C. Oliveira, J. A. Souza Corrêa, M. P. Gomes, B. N. Sismanoglu, and J. Amorim, Appl. Phys. Lett. **93**, 041503 (2008).
[4] A. Garscadden, Z. Phys. D: At., Mol. Clusters **24**, 97 (1992).
[5] W. M. Huo and Y. K. Kim, IEEE Trans. Plasma Sci. **27**, 1225 (1999).
[6] L. G. Christophorou, and J. K. Olthoff, Appl. Surf. Sci. **192**, 309 (2002).
[7] See, for example, B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Science **287**, 1658 (2000); L. Sanche, Eur. Phys. J. D **35**, 367 (2005); M. A. Huels, B. Boudaïffa, P. Cloutier, D. Hunting, and L. Sanche, J. Am. Chem. Soc. **125**, 4467 (2003); F. Martin, P. D. Burrow, Z. Cai, P. Cloutier, D. Hunting, and L. Sanche, Phys. Rev. Lett. **93**, 068101 (2004) (and references therein).
[8] P. Mozejko and L. Sanche, Radiat. Phys. Chem. **73**, 77 (2005).
[9] C. König, J. Kopyra, I. Bald, and E. Illenberger, Phys. Rev. Lett. **97**, 018105 (2006).
[10] C. Winstead and V. McKoy, J. Chem. Phys. **125**, 244302 (2006).
[11] C. Winstead and V. McKoy, J. Chem. Phys. **125**, 074302 (2006).
[12] D. Bouchiha, J. D. Gorfinkiel, L. G. Caron, and L. Sanche, J. Phys. B **39**, 975 (2006).
[13] C. S. Trevisan, A. E. Orel, and T. N. Rescigno, J. Phys. B **39**, L255 (2006).
[14] C. J. Colyer, V. Vizcaino, J. P. Sullivan, M. J. Brunger, and S. J. Buckman, N. J. Phys. **9**, 41 (2007).
[15] M. H. F. Bettega and M. A. P. Lima, J. Chem. Phys. **126**, 194317 (2007).
[16] See, for instance, T. Fleig, S. Knecht, and C. Hättig, J. Phys. Chem. A **111**, 5482 (2007) (and references therein).
[17] A. Modelli and P. W. Burrow, J. Phys. Chem. A **108**, 5721 (2004).
[18] P. Sulzer, S. Ptasinska, F. Zappa, B. Mielewska, A. R. Milosavljevic, P. Scheier, T. D. Märk, I. Bald, S. Gohlke, M. A. Huels, and E. Illenberger, J. Chem. Phys. **125**, 044304 (2006).
[19] J. Gu, Y. Xie, and H. F. Schaefer III, J. Am. Chem. Soc. **127**, 1053 (2005).

[20] J. Berdys, P. Skurski, and J. Simons, J. Phys. Chem. B **108**, 5800 (2004).

[21] T. N. Rescigno, C. S. Trevisan, and A. E. Orel, Phys. Rev. Lett. **96**, 213201 (2006).

[22] A. M. Scheer, P. Mozejko, G. A. Gallup, and P. D. Burrow, J. Chem. Phys. **126**, 174301 (2007).

[23] G. A. Gallup, P. D. Burrow, and I. I. Fabrikant, Phys. Rev. A **79**, 042701 (2009).

[24] G. A. Gallup, P. D. Burrow, and I. I. Fabrikant, Phys. Rev. A **80**, 046702 (2009).

[25] T. N. Rescigno, C. S. Trevisan, and A. E. Orel, Phys. Rev. A **80**, 046701 (2009).

[26] T. Skalický and M. Allan, J. Phys. B **37**, 4849 (2004).

[27] B. C. Ibănescu, O. May, A. Monney, and M. Allan, Phys. Chem. Chem. Phys. **9**, 3163 (2007).

[28] K. Takatsuka and V. McKoy, Phys. Rev. A **24**, 2473 (1981); **30**, 1734 (1984).

[29] M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, Phys. Rev. A **47**, 1111 (1993).

[30] R. F. da Costa, F. J. da Paixão, and M. A. P. Lima, J. Phys. B **37**, L129 (2004); **38**, 4363 (2005).

[31] P. Chaudhuri, M. T. do N. Varella, C. R. C. Carvalho, and M. A. P. Lima, Nucl. Instrum. Methods Phys. Res. B **221**, 69 (2004); Phys. Rev. A **69**, 042703 (2004).

[32] R. F. da Costa, M. H. F. Bettega, and M. A. P. Lima, Phys. Rev. A **77**, 012717 (2008).

[33] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[34] C. J. Cramer and D. G. Truhlar, J. Am. Chem. Soc. **115**, 5745 (1993).

[35] J. C. Corchado, M. L. Sánchez, and M. A. Aguilar, J. Am. Chem. Soc. **126**, 7311 (2004).

[36] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[37] M. H. F. Bettega, A. P. P. Natalense, M. A. P. Lima, and L. G. Ferreira, Int. J. Quantum Chem. **60**, 821 (1996).

[38] C. Winstead and V. McKoy, Phys. Rev. A **57**, 3589 (1998); C. Winstead, V. McKoy, and M. H. F. Bettega, *ibid.* **72**, 042721 (2005).

[39] M. H. F. Bettega, C. Winstead, and V. McKoy, Phys. Rev. A **74**, 022711 (2006).

[40] C. W. Bauschlicher, J. Chem. Phys. **72**, 880 (1980).

[41] M. H. F. Bettega, R. F. da Costa, and M. A. P. Lima, Phys. Rev. A **77**, 052706 (2008).

[42] M. A. Khakoo, J. Blumer, K. Keane, C. Campbell, H. Silva, M. C. A. Lopes, C. Winstead, V. McKoy, R. F. da Costa, L. G. Ferreira, M. A. P. Lima, and M. H. F. Bettega, Phys. Rev. A **77**, 042705 (2008).