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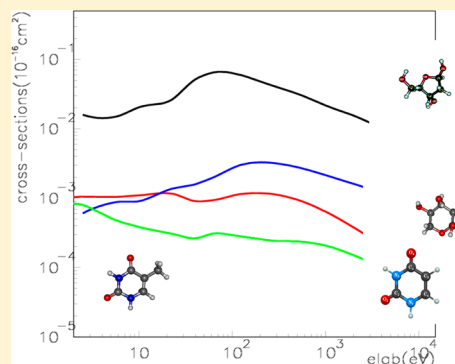
Looking at Radiation Damage on Prebiotic Building Blocks

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S Supporting Information

ABSTRACT: A number of complex organic molecules have been detected in the interstellar medium, as well as in meteorites or comets. Among them, some exobiologic-relevant molecules have attracted particular interest. In the hypothesis of an exogen transport of prebiotic building blocks at the origin of life, the survival of such species and particularly their resistance to the solar UV radiation or cosmic rays is a key issue. For that purpose, we have performed a theoretical approach of the charge transfer dynamics induced by collision of protons with nucleobases and the 2-deoxy-D-ribose sugar moiety in a wide collision energy range. Calculations have been carried out by means of ab initio quantum chemistry molecular methods and compared to previous theoretical results using carbon projectile ions. Qualitative trends can be exhibited on DNA or RNA building blocks damage, which may concern studies on prebiotic species under spatial radiation.



1. INTRODUCTION

Prebiotic organic chemistry may have started in the interstellar medium (ISM), on icy grains of interstellar clouds where fundamental molecules could be formed. Accretion of icy bodies or comet bombardments may provide those organic compounds necessary for the origin of life. In that sense, building a DNA world, or more likely an RNA world^{1,2} has been one of the main concerns of prebiotic chemistry since the first theories developed on the origin of life and the first experiments of Miller and Hurey to produce amino acids from simple molecule mixtures.^{3,4} Specific interest has thus been devoted to complex organic molecules that could be prebiotic precursors,⁵ in that sense attention has been focused on the DNA and RNA building blocks, nucleobases, sugar moiety, or phosphate group, which may drive the formation of DNA or RNA. Since the discovery of amino acids in the Murchison meteorite,⁶ the hypothesis of an exogen origin of life has been widely discussed. In such an approach, survival and transport of prebiotic building blocks, desorption from the icy mantle by the thermic effect, VUV photons, or cosmic rays and especially their resistance to the spatial radiation are extremely important questions which remain still open.^{7,8}

Within a more general context, ionizing radiations have been shown to induce lesions to DNA,⁹ which may be due not only to the high-energy photon radiation but also to secondary particles, electrons, radicals, or ions, generated on the track of the ionizing radiation by interaction with the biomolecule.¹⁰ We have been concerned especially with interactions with ions, which may be present in space in a very wide collision energy range.¹¹ With regard to the astrophysical environment, the temperature and, consequently, the energy involved in the collision processes may be effectively very different, from 10 K (\sim meV) in the interstellar medium, to more than 10^4 K (\sim 10 eV) in some evolved stars, and we can even reach MeV energies

for a highly energetic charged nucleus in cosmic rays. Taking into account the abundance of hydrogen in space, we have considered as a starting point the collisions with protons, focusing our attention on the processes with DNA and RNA building blocks. Nucleobase targets have indeed been particularly investigated in gas-phase experiments using time-of-flight technique, more generally in the keV energy range^{12–15} as well as theoretically in a wide collision energy range.^{16–21} Recently, experiments have also been developed on base–sugar complex nucleosides²² and the determinant role of the deoxyribose sugar moiety has been exhibited by measurements on protonated oligonucleotides²³ and isolated molecules.^{24,25} Such studies have shown an almost complete fragmentation of the sugar part corroborated by a theoretical analysis of the mechanism.²⁶ The fragmentation process has, however, been shown to be less efficient in collisions with protons; we have thus investigated jointly the collision of protons on the 2-deoxy-D-ribose sugar part, as well as on nucleobases, considering more specifically the pyrimidine nucleobases uracil and thymine of RNA and DNA, respectively.

Reactions of ions with (bio)molecular species may induce different processes: excitation and fragmentation of the biomolecule, direct ionization of the target, and possible charge transfer from the projectile ion toward the biomolecular target. Excitation and fragmentation processes are mainly investigated experimentally¹² and theoretical treatments on fragmentation dynamics proceed on ionized species considering almost instantaneous electron removal with regard to the fragmentation time.^{21,27} However, analysis of the ionization of the molecular target by charge transfer is an important process that

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may be performed theoretically in the molecular representation of the collisions. We have indeed developed for these systems a quantum chemistry treatment with *ab initio* molecular calculations of the potentials and nonadiabatic couplings between the different molecular states involved in the process, followed by a collision dynamics valid in a wide energy domain.^{20,28–30} Pyrimidine nucleobases, uracil, and thymine presenting similar structures with different substituents may permit consideration of the steric effects induced in the charge transfer process. Such reactions may be compared to the behavior of the 2-deoxy-D-ribose with a detailed analysis of the inner orbital excitations. For each molecular target, a more global comparison is also performed for collisions with carbon ions to extract general features for radiation damage.

2. THEORETICAL TREATMENT

2.1. Molecular Calculations. In the molecular description of the collisions, the charge transfer reaction may be described as the evolution of a quasi-molecular system formed by the projectile ion and the biomolecular target. A model for the analysis of this collision system may be developed, even for complex polyatomic molecules, by means of the one-dimension reaction coordinate approximation.^{31–33} The ion–biomolecule collision system may thus be treated as a pseudodiatom molecule that evolves along the reaction coordinate associated with the distance between the center-of-mass of the biomolecule and the projectile ion. Such a simple approach does not take into account the internal motions of the biomolecule, but it has been shown to be acceptable for very fast collision processes where nuclear vibration and rotation movements are much slower than the collision time.

For pyrimidine nucleobases uracil and thymine, the geometry is constructed around a six-membered planar ring,³⁰ with out-of-the-plane substituents as in thymine. The anisotropy of the charge transfer process can thus be considered for different orientations of the projectile ion toward this ring plane, as shown on Figure 1a,b for the collision of H^+ with thymine. Different orientations, from perpendicular ($\theta = 90^\circ$) to planar geometries may thus be investigated. The problem is more complex for the 2-deoxy-D-ribose (dR, $C_5H_{10}O_4$) as this monosaccharide can be found under three different conformations, a linear form, a furanose form constructed around a five-membered ring with CH_2OH and OH substituents (Figure

2a), and a pyranose form with a six-membered ring (Figure 2b). In the DNA backbone, 2-deoxy-D-ribose is in the furanose form

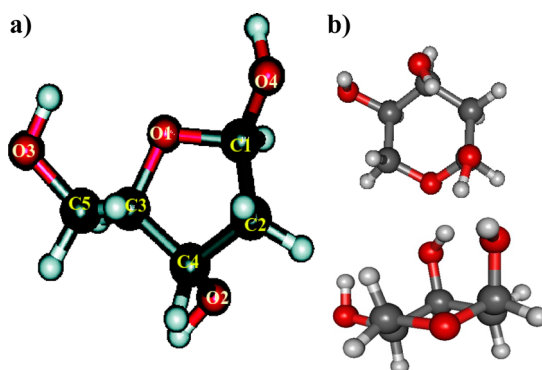


Figure 2. (a) Geometry of 2-deoxy-D-ribose (dR) in the furanose form. (b) Geometry of 2-deoxy-D-ribose (dR) in the pyranose form.

and this conformation has to be investigated with regard to the behavior of DNA building blocks. However, as assessed in recent works,^{34–36} the pyranose form is dominant in gas-phase experiments and comparison with experimental data has to take this geometry into account. Calculations have thus been performed with both conformations, at the same theoretical level of theory, to compare both behaviors. At variance with the pyrimidine nucleobases, the 2-deoxy-D-ribose, whatever the configuration, is clearly a nonplanar molecule. A mean xy plane can, however, be defined, as shown in Figure 3 for the five-

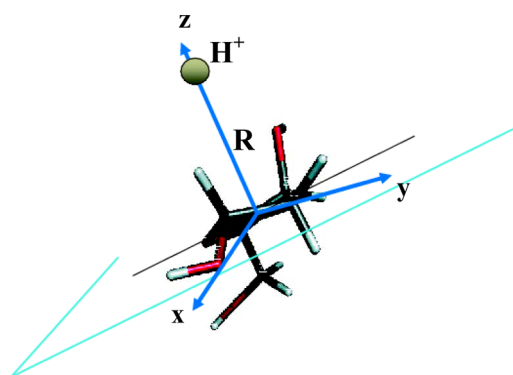


Figure 3. Geometry of the H^+ -dR system (furanose form) in the perpendicular approach.

membered ring, and the orientation of the projectile ion with regard to this mean plane may be analyzed, in particular in the perpendicular orientation along the z axis, or in planar approaches along the x and y coordinates. In the present study, both orientations have been investigated, focusing, however, our attention on collisions in the perpendicular geometry, as this orientation has been clearly shown to be favored for uracil and thymine targets in collisions with carbon ions.^{37,38}

The potential energy curves of the different molecular states involved in the process are determined along the reaction coordinate R for a large number of R values from 0.5 to 9 au. The potentials are then extrapolated to reach the asymptotic region. All biomolecular targets are considered in their ground state geometry and kept frozen during the collision process. The geometry of the ground state of thymine and uracil have been optimized at the CASSCF (complete active space self-

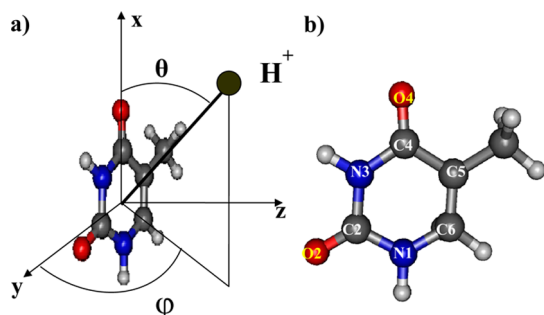


Figure 1. (a) Internal coordinates for the H^+ + thymine system. The six-membered ring is in the xy plane, the x axis is along the $C4O4$ bond, and the z axis is perpendicular to the ring plane with origin at the center of the ring. The angle φ corresponds to the angle between the y axis and the projection of H^+ on the yz plane. (b) Geometry of the thymine molecule. The CH_3 group would be replaced by H in uracil.

consistent field) level of theory with the 6-311G** basis set and with DFT (density functional theory) approaches³⁰ (Supporting Information, Tables S1 and S2). DFT calculations using the gradient-corrected BLYP functional^{39,40} have been developed to optimize the 2-deoxy-D-ribose ground state geometry in furanose and pyranose form⁴¹ (Supporting Information, Tables S3 and S4), in relation to fragmentation theoretical treatment.^{21,27} The quantum chemical calculations have been carried out by means of the MOLPRO code.⁴² The 6-311G** basis set has been used for all atoms; calculations have been performed in Cartesian coordinates with no symmetries, taking account of all the electrons. The potential energies and nonadiabatic coupling matrix elements (NACME) have been determined at the state-averaged CASSCF level of theory. Such calculations do not take into account the dynamical correlation effects, but the relative energies between the different excited states may be expected to be correctly described as confirmed in our previous studies with carbon ion projectiles.³⁰ Similar active spaces have been considered for the different targets to compare each system at the same level of accuracy. A series of different active spaces have been investigated in a detailed study of collisions of 2-deoxy-D-ribose in the furanose form to analyze the weight of inner excitations and their influence on the charge transfer process.²⁷ Such study has shown clearly that a limit for the calculation of the charge transfer cross section could be reached for the (6,5) active space corresponding to 6 electrons in 5 orbitals centered mainly on the 1s orbital on hydrogen and 2p_z orbitals centered on oxygen O3 of the CH₂OH group, together with the corresponding 2p_{xy}^{O3} in-the-plane orbital, and the 2p_z and 2p_{xy} orbitals on the oxygen O1 of the ring. Such active space has been shown to provide quite accurate results, and including further inner orbitals does not significantly modify the charge transfer cross sections. Similar active spaces have thus been considered for the collisions of protons with the 2-deoxy-D-ribose in the pyranose form, as well as for collisions with uracil and thymine. Taking into account the geometry presented in Figure 1b, active spaces for pyrimidine nucleobases are constructed mainly on the 2p_z and 2p_{xy} orbitals centered on oxygen O4, on the π_{C4O4} (noted π_{CO}) orbital and on the 2p_z^{C5} and 2p_z^{C6} orbitals (describing the molecular orbital called by extension π_{C5C6} , see Figure 1b) with, of course, the 1s orbital on hydrogen. The 1s orbitals of carbon, nitrogen and oxygen are treated as frozen core.

The charge transfer process is mainly driven by the nonadiabatic interactions in the vicinity of the avoided crossings.⁴³ The corresponding nonadiabatic radial coupling matrix elements between all pairs of states of the same symmetry have been calculated numerically by means of the finite difference technique:⁴⁴

$$g_{KL}(R) = \langle \psi_K | \partial / \partial R | \psi_L \rangle \\ = \langle \psi_K(R) | \lim_{\Delta \rightarrow 0} \frac{1}{\Delta} | \psi_L(R + \Delta) - \psi_L(R) \rangle$$

Taking into account the orthogonality of the eigenfunctions $|\psi_K(R)\rangle$ and $|\psi_L(R)\rangle$ for $K \neq L$, the present expression reduces to

$$g_{KL}(R) = \langle \psi_K | \partial / \partial R | \psi_L \rangle = \lim_{\Delta \rightarrow 0} \frac{1}{\Delta} \langle \psi_K(R) | \psi_L(R + \Delta) \rangle \quad (2-1)$$

The step Δ has been widely tested in previous works and a value of $\Delta = 0.0012$ au has been shown to give accurate stability

of the differentiation procedure.⁴⁵ A three-point numerical differentiation method has been used for numerical accuracy, with the center of mass of the biomolecular target chosen as origin of electronic coordinates.

2.2. Collision Dynamics. The collision dynamics has been treated by means of the semiclassical method in the framework of the sudden approximation hypothesis. Effectively, electronic transitions being much faster than vibration and rotation motions, the molecular target can be considered to be frozen during the collision time. The total and partial cross sections, corresponding to purely electronic transitions, are then calculated by solving the impact-parameter equation as in the usual ion-atom approach, assuming the geometry of the molecular target fixed in its ground state. Such an approach is, of course, rather crude, but it has been proved to provide quite accurate results for ion-diatomics collisions⁴⁶ as well as in ion-polyatomics processes for energies higher than ~ 10 eV/amu. Effectively, at these collision energies, the collision time is shown to be much shorter than typical vibration time and of course typical rotation time, as previously pointed out for collisions of carbon ions with uracil.^{17,47} The present treatment has been extended to collision energies in the eV domain,^{20,48} taking into account a recent compared study of time-dependent quantum wave packet and semiclassical methods in ion-atom charge transfer processes.^{28,29} We can thus expect a semiclassical approach to provide a correct order of magnitude of the charge transfer cross sections in a wide collision energy range.

The collision dynamics has been performed by means of the EIKONXS code using an efficient propagation method.⁴⁹ An accuracy of 10^{-4} for the symmetry of the S matrix has been required in the resolution of the collision coupled equations. The calculations have been performed in the ~ 10 eV to ~ 10 keV laboratory energy range for both collision systems, taking into account all the transitions induced by radial couplings.

3. RESULTS

The behavior of pyrimidine nucleobases and 2-deoxy-D-ribose in collisions with protons is analyzed to check the resistance of the different DNA or RNA building blocks in ion-induced collisions in a wide energy range. Protons have been chosen as hydrogen is clearly recognized as the most important element in space. But the comparison may be extended to collisions with other ions; we have investigated in particular the reactions with carbon ions with regard to radiation damage.^{16–19}

In a first step, the two most important configurations of 2-deoxy-D-ribose, the furanose form present in DNA, and the pyranose form expected in the gas phase, have been investigated to point out their differences. The potential energy curves for the pyranose are presented in Figure 4 for both perpendicular and in-plane orientations of the H⁺ projectile. In the perpendicular orientation, the nonadiabatic interactions appear significantly weaker than in the furanose form.²⁶ They are markedly shifted toward longer internuclear distances in the planar collision, and important avoided crossings are exhibited between the entrance channel and charge transfer levels with successive single excitations. The corresponding charge transfer cross sections in planar and perpendicular collisions are presented in Figure 5 for both configurations. Globally speaking, the charge transfer cross sections appear lower in the pyranose configuration than in the furanose form, by roughly a factor 10. Considering the potential energy curves in Figure 4, such a result could be expected as the nonadiabatic

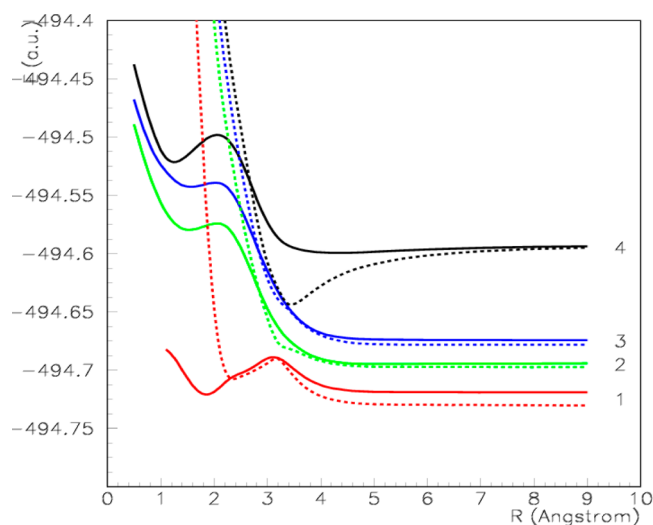


Figure 4. Adiabatic potential energy curves of the 1A states of the H^+ + dR-pyranose collision system in the perpendicular (full lines) and in-the-plane (dashed lines) orientations for the (6,5) active space. 1-red, $\{2p_z^{O2} 1s^H\}$; 2-green, $\{2p_z^{O1} 1s^H\}$; 3-blue, $\{2p_{xy}^{O2} 1s^H\}$; 4-black, $\{(2p_z^{O2})^2\}$, entrance channel H^+ + dR (O1, oxygen of the ring; O2, oxygen of OH group).

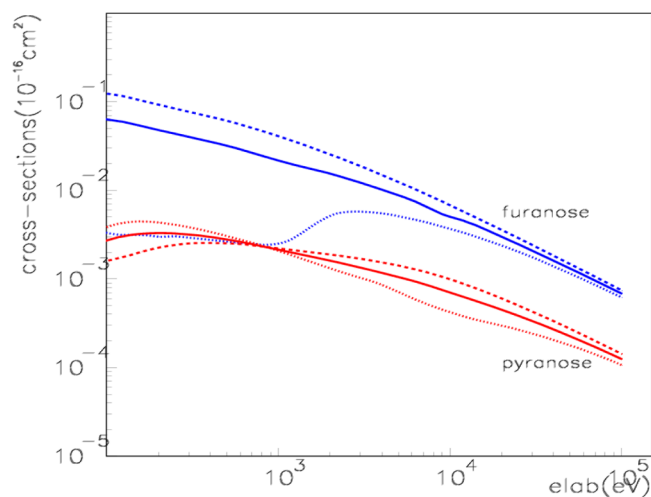


Figure 5. Charge transfer cross sections in H^+ + dR collision systems for furanose (blue) and pyranose (red) configurations: dashed lines, perpendicular approach; dotted lines, in-the-plane approach; full lines, mean value.

interactions between the molecular states involved in the process have been shown to be smoother than with the furanose form. However, even if the perpendicular approach is globally preferred as in the collision with furanose, the charge transfer cross sections between pyranose and H^+ are close in both perpendicular and planar collision orientations in the whole collision domain. We do not observe a significant decrease at lower energies, as in furanose. Such a result could be applied to the much more regular structure of the pyranose, which shows only H and OH groups around the six-membered ring, whereas the furanose form presents an extension to a CH_2OH chain.

To compare such results with the pyrimidine nucleobases, similar calculations have been performed with uracil and thymine. The potential energy curves of the different molecular states involved in H^+ + uracil and H^+ + thymine collision

systems are presented in Figure 6a,b. Successive single excitation levels are observed, with, in particular, a strong avoided crossing around $R = 4$ au between the entry channel and the charge transfer state corresponding to a double excitation from the $2p_{xy}$ and π_{C5C6} orbitals to the $2p_z$ orbital on oxygen O4 and the $1s$ orbital on hydrogen. Taking into account these molecular data, the charge transfer cross sections have been calculated in the $[\sim 10 \text{ eV to } 10 \text{ keV}]$ laboratory energy range. The results presented in Table 1 and Figure 7 are compared to the charge transfer cross sections in the collision of protons with the 2-deoxy-D-ribose in both pyranose and furanose configurations. For both pyrimidine nucleobases, the charge transfer cross sections are globally of the same order of magnitude, from about $10^{-3} \times 10^{-16} \text{ cm}^2$ for uracil to around $10^{-4} \times 10^{-16} \text{ cm}^2$ for thymine, and decrease slowly with increasing collision energy. The cross section values for uracil and thymine are lower than previously observed for the 2-deoxy-D-ribose in its furanose form by about a factor 10–100.²⁶ However, they are almost of the same order of magnitude as the dR in its pyranose configuration. This may bring implication on resistance of DNA building blocks in ion-induced collisions. Effectively, taking account that the relative fragmentation yield for a molecular target after impact with a projectile ion can be assumed to be inversely proportional to the electron capture cross section,²⁴ a point that has been widely exhibited in our previous theoretical studies,³⁰ lower values for the charge transfer cross sections would suggest that uracil and thymine would be more likely destroyed in collisions with protons than the 2-deoxy-D-ribose sugar moiety in furanose configuration in the DNA backbone. This would induce a weakness in either DNA or RNA structure on nucleobase sites or a difficulty for nucleobases to resist to collisions with protons. On the contrary, the pyranose configuration expected to be dominant in gas-phase experiments appears to be more sensitive in collision with protons than the furanose form and thus would be more likely destroyed, as observed experimentally.^{22–25}

The present result on collisions with protons is relatively puzzling by comparison with our previous studies of collisions of carbon ions with biomolecular targets.^{30,50} As presented in Figure 8, collisions with C^{4+} projectiles show indeed quite higher charge transfer cross sections with uracil and thymine targets, up to $10 \times 10^{-16} \text{ cm}^2$. The cross sections are lower for collisions with C^{6+} nucleus but remain around 10^3 times higher than in collisions with protons. This would suggest that nucleobases would be more likely destroyed in collisions with protons than with carbon ions. The probability to react with a proton being far much higher than with a carbon ion in astrophysical environments, both effects move in the same sense and ion-induced damage is more likely to be induced by proton collisions. For 2-deoxy-D-ribose, on the contrary, the charge transfer cross sections are lower in collisions with carbon ions than in reaction with protons, which is relatively surprising, but for both projectiles, the charge transfer cross sections are very low, about $10^{-4} \times 10^{-16} \text{ cm}^2$ for C^{4+} ions and about $10^{-2} \times 10^{-16} \text{ cm}^2$ for protons, and even less, around $10^{-3} \times 10^{-16} \text{ cm}^2$ for pyranose. Such low values would suggest almost complete disintegration of the 2-deoxy-D-ribose molecule in ion-induced collisions whatever the projectile ion considered, a fortiori in the pyranose configuration, in agreement with experimental measurements.^{22,24} As far as collisions with protons are concerned, both nucleobases and the sugar moiety appear thus to present significant sensitivity to spatial radiations, in

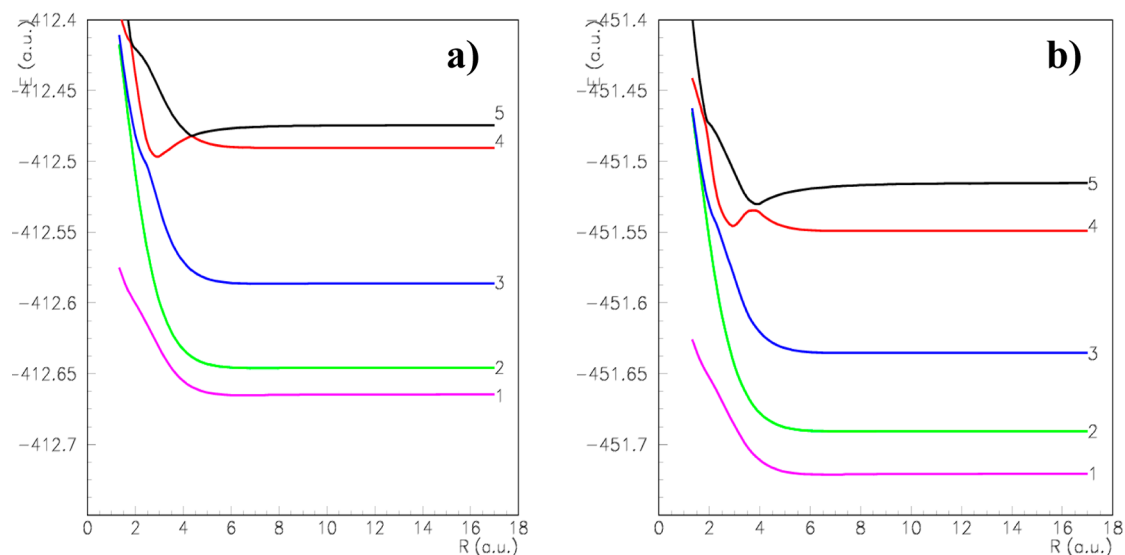


Figure 6. Adiabatic potential energy curves of the $1A$ states in the collision of H^+ with (a) uracil, (b) thymine in the perpendicular geometry. 1-magenta, $\{(\pi_{CO})^2(2p_{xy})^2\pi_{CSC6}1s_H\}$; 2-green, $\{(\pi_{CO})^22p_{xy}^0(\pi_{CSC6})^21s_H\}$; 3-blue, $\{\pi_{CO}(2p_{xy})^0(\pi_{CSC6})^21s_H\}$; 4-red, $\{(\pi_{CO})^22p_{xy}^0\pi_{CSC6}2p_z^01s_H\}$; 5-black, $\{(\pi_{CO})^2(2p_{xy})^0(\pi_{CSC6})^2\}$ configuration, entrance channel $H^+ + U/T$.

Table 1. Charge Transfer Cross Sections for the Collision of Biomolecules with H^+ (in 10^{-16} cm^2)

velocity (m/s)	E_{lab} (eV)	uracil	thymine	dR furanose	dR pyranose
4.4×10^4	10	1.10×10^{-3}	3.86×10^{-4}	0.020	9.08×10^{-4}
6.6×10^4	22.6	1.17×10^{-3}	3.08×10^{-4}	0.026	1.37×10^{-3}
8.8×10^4	40	9.07×10^{-4}	2.65×10^{-4}	0.051	1.59×10^{-3}
1.1×10^5	63	9.42×10^{-4}	3.11×10^{-4}	0.065	2.01×10^{-3}
1.54×10^5	123.4	1.15×10^{-3}	2.82×10^{-4}	0.060	3.02×10^{-3}
2.2×10^5	251.8	1.16×10^{-3}	2.46×10^{-4}	0.043	3.26×10^{-3}
3.3×10^5	566.5	8.97×10^{-4}	2.36×10^{-4}	0.030	2.69×10^{-3}
4.4×10^5	$1. \times 10^3$	6.38×10^{-4}	2.07×10^{-4}	0.022	2.15×10^{-3}
6.6×10^5	2.26×10^3	3.43×10^{-4}	1.41×10^{-4}	0.014	1.53×10^{-3}
8.8×10^5	$4. \times 10^3$	2.09×10^{-4}	9.95×10^{-5}	0.010	1.17×10^{-3}
1.1×10^6	6.3×10^3	1.40×10^{-4}	7.54×10^{-5}	7.48×10^{-3}	9.36×10^{-4}
1.32×10^6	9.1×10^3	1.00×10^{-4}	6.01×10^{-5}	5.37×10^{-3}	7.53×10^{-4}
1.54×10^6	12.34×10^3	7.52×10^{-5}	4.91×10^{-5}	4.46×10^{-3}	6.20×10^{-4}

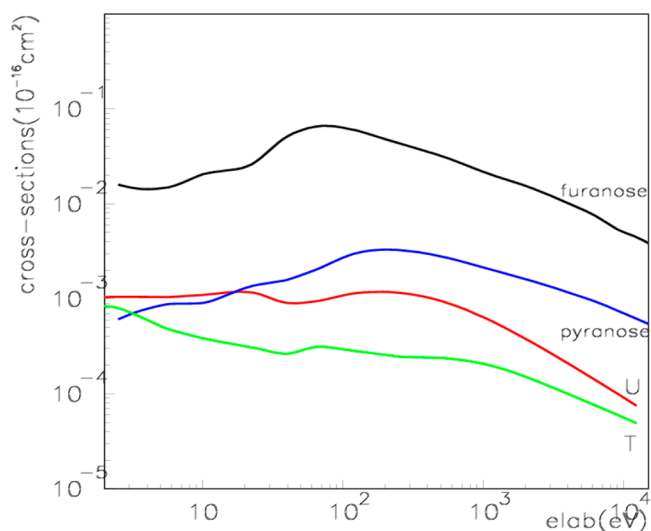


Figure 7. Charge transfer cross sections in H^+ + biomolecule collisions: green, thymine; red, uracil; blue, dR-pyranose form; black, dR-furanose form.

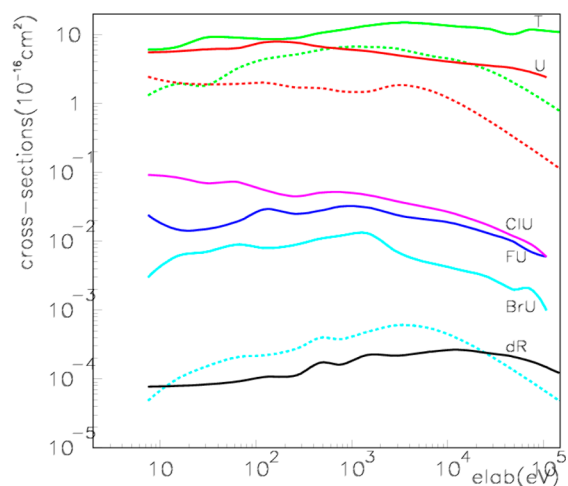


Figure 8. Charge transfer cross sections averaged over the different orientations for collisions of C^{4+} (full lines) and C^{6+} (broken lines) with biomolecules: green, thymine; red, uracil; blue, 5-fluorouracil; magenta, 5-chlorouracil; light blue, 5-bromouracil; black, dR-furanose form.

particular in the gas phase, which would induce important damage.

4. CONCLUDING REMARKS

A comparative analysis of the charge transfer process in collisions of protons with pyrimidine nucleobases and 2-deoxy-D-ribose in both furanose and pyranose configurations has been performed in a wide collision energy range using ab initio molecular calculations. Some qualitative tendency may be pointed out that would suggest a clear weakness of pyrimidine nucleobases under spatial radiations in the DNA backbone. However, even if the 2-deoxy-D-ribose in the furanose DNA conformation could be more resistant in collisions with protons than pyrimidine nucleobases, it presents a strong sensitivity to radiations, with an expected almost disintegration in ion-induced collisions, in particular, in the gas phase. Such features provide significant importance for the resistance of prebiotic species under spatial radiations and further investigations have to be developed.

■ ASSOCIATED CONTENT

● Supporting Information

The optimized geometries of the different biological targets are available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Joyce, G. F. The Antiquity of RNA-Based Evolution. *Nature* **2002**, *418*, 214–221.
- (2) Powner, M. W.; Gerland, B.; Sutherland, J. D. Synthesis of Activated Pyrimidine Ribonucleotides in Prebiotically Plausible Conditions. *Nature* **2009**, *459*, 239–242.
- (3) Miller, S. L. Production of Some Organic Compounds under Possible Primitive Earth Conditions. *J. Am. Chem. Soc.* **1953**, *77*, 2351–2361.
- (4) Miller, S. L.; Hurey, H. C. Organic Compound Synthesis on the Primitive Earth. *Science* **1959**, *130*, 245–251.
- (5) Lattelais, M.; Pauzat, F.; Pilmé, J.; Ellinger, Y. Electronic Structure of Simple Phosphorus Containing Molecules [C_xH₄O₂P] Candidate for Astrobiology (x=1, 3, 5). *Phys. Chem. Chem. Phys.* **2008**, *10*, 2089–2097.
- (6) Cooper, G. W.; Onwo, W. M.; Cronin, J. R. Alkyl Phosphoric Acids and Sulfonic Acids in the Murchison Meteorite. *Geochim. Cosmochim. Acta* **1992**, *56*, 4109–4115.
- (7) Ehrenfreund, P.; Bernstein, M.; Dworkin, J.; Sandford, S. A.; Allamandola, L. J. The Photostability of Amino Acids in Space. *Astrophys. J.* **2001**, *550*, L95–L99.
- (8) Ehrenfreund, P.; Irvine, W.; Becker, L.; Blank, J.; Brucato, R.; Colangeli, L.; Derenne, S.; Despois, D.; Dutrey, A.; Fraaije, H.; Lazcano, A.; Owen, T.; Robert, F. Astrophysical and Astrochemical Insights into the Origin of Life. *Rep. Prog. Phys.* **2002**, *65*, 1427–1488.
- (9) von Sonntag, C. *The Chemical Basis for Radiation Biology*; Taylor and Francis: London, 1987.
- (10) Michael, B. D.; O'Neill, P. D. A Sting in the Tail of Electron Tracks. *Science* **2000**, *287*, 1603–1604.
- (11) Bacchus-Montabonel, M. C. Radiative and Collisional Processes in Space Chemistry. *Rend. Fis. Acc. Lincei* **2011**, *22*, 95–103.
- (12) de Vries, J.; Hoekstra, R.; Morgenstern, R.; Schlathölder, T. C⁹⁺-Induced Excitation and Fragmentation of Uracil: Effects of the Projectile Electronic Structure. *J. Phys. B* **2002**, *35*, 4373–4382.
- (13) Coupier, B.; Farizon, B.; Farizon, M.; Gaillard, M. J.; Gobet, F.; de Castro Faria, N. V.; Jalbert, G.; Ouaskit, S.; Carré, M.; Gstir, B.; et al. Inelastic Interactions of Protons and Electrons with Biologically Relevant Molecules. *Eur. Phys. J. D* **2002**, *20*, 459–468.
- (14) de Vries, J.; Hoekstra, R.; Morgenstern, R.; Schlathölder, T. Multiple Ionization and Fragmentation of the DNA Base Thymine by Interaction with C⁹⁺ Ions. *Eur. Phys. J. D* **2003**, *24*, 161–164.
- (15) Deng, Z.; Imhoff, M.; Huels, M. A. Fragmentation Dynamics of Condensed Phase Thymine by Low-Energy (10–200 eV) Heavy-Ion Impact. *J. Chem. Phys.* **2005**, *123*, 144509/9.
- (16) Bacchus-Montabonel, M. C.; Łabuda, M.; Tergiman, Y. S.; Sienkiewicz, J. E. Theoretical Treatment of Charge-Transfer Processes Induced by Collision of C⁹⁺ Ions with Uracil. *Phys. Rev. A* **2005**, *72*, 052706/9.
- (17) Bacchus-Montabonel, M. C.; Tergiman, Y. S. Anisotropic Effect in the Charge Transfer of C⁹⁺ Ions with Uracil. *Phys. Rev. A* **2006**, *74*, 054702/4.
- (18) Bacchus-Montabonel, M. C.; Tergiman, Y. S.; Talbi, D. An-Initio Molecular Treatment of Charge-Transfer Processes Induced by Collision of Carbon Ions with 5-halouracil Molecules. *Phys. Rev. A* **2009**, *79*, 012710/7.
- (19) Bacchus-Montabonel, M. C.; Tergiman, Y. S. An Ab-Initio Study of Ion Induced Charge Transfer Dynamics in Collision of Carbon Ions with Thymine. *Phys. Chem. Chem. Phys.* **2011**, *13*, 9761–9767.
- (20) Bacchus-Montabonel, M. C.; Tergiman, Y. S. Charge Transfer Dynamics of Carbon Ions with Uracil and Halouracil Targets. *Chem. Phys. Lett.* **2011**, *503*, 45–48.
- (21) López-Tarifa, P.; Hervé du Penhoat, M. A.; Vuilleumier, R.; Gaigeot, M. P.; Tavernelli, I.; Le Padellec, A.; Champeaux, J. P.; Alcamí, M.; Moretto-Capelle, P.; Martín, F.; Politis, M. F. Ultrafast Nonadiabatic Fragmentation Dynamics of Doubly Charged Uracil in a Gas Phase. *Phys. Rev. Lett.* **2011**, *107*, 023202/4.
- (22) Deng, Z.; Bald, I.; Illenberger, E.; Huels, M. A. Beyond the Bragg Peak: Hyperthermal Heavy Ion Damage to DNA Components. *Phys. Rev. Lett.* **2005**, *95*, 153201/4.
- (23) González-Magaña, O.; Tiemens, M.; Reitsma, G.; Boschman, L.; Door, M.; Bari, S.; Lahaie, P. O.; Wagner, J. R.; Huels, M. A.; Hoekstra, R.; Schlathölder, T. Fragmentation of Protonated Oligonucleotides by Energetic Photons and C⁹⁺ Ions. *Phys. Rev. A* **2013**, *87*, 032702/13.
- (24) Alvarado, F.; Bari, S.; Hoekstra, R.; Schlathölder, T. Quantification of Ion-Induced Molecular Fragmentation of Isolated 2-deoxy-D-ribose Molecules. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1922–1928.
- (25) Alvarado, F.; Bernard, J.; Lin, B.; Brédy, R.; Chen, L.; Hoekstra, R.; Martin, S.; Schlathölder, T. Precise Determination of 2-deoxy-D-ribose Internal Energies after keV Proton Collisions. *ChemPhysChem* **2008**, *9*, 1254–1258.
- (26) Bacchus-Montabonel, M. C. Ab-Initio Treatment of Ion-Induced Charge Transfer Dynamics of Isolated 2-deoxy-D-ribose. *J. Phys. Chem. A* **2013**, DOI: 10.1021/jp408570b.
- (27) López-Tarifa, P.; Gaigeot, M. P.; Vuilleumier, R.; Tavernelli, I.; Alcamí, M.; Martín, F.; Hervé du Penhoat, M. A.; Politis, M. F. Ultrafast Damage Following Radiation-Induced Oxidation of Uracil in Aqueous Solution. *Angew. Chem.* **2013**, *125*, 3242–3245; *Angw. Chem. Int. Ed.* **2013**, *52*, 3160–3163.

- (28) Chenel, A.; Mangaud, E.; Justum, Y.; Talbi, D.; Bacchus-Montabonel, M. C.; Desouter-Lecomte, M. Quantum Dynamics of the Charge Transfer in $C^+ + S$ at Low Collision Energies. *J. Phys. B* **2010**, *43*, 245701/11.
- (29) Linguerri, R.; Hochlaf, M.; Bacchus-Montabonel, M. C.; Desouter-Lecomte, M. Characterization of the MgO^{2+} Dication in the Gas Phase: Electronic States, Spectroscopy and Atmospheric Implications. *Phys. Chem. Chem. Phys.* **2013**, *15*, 824–831.
- (30) Bacchus-Montabonel, M. C.; Tergiman, Y. S. Radiation Damage on Biomolecular Systems: Dynamics of Ion Induced Collision Processes. *Comput. Theor. Chem.* **2012**, *990*, 177–184.
- (31) Salem, L. *Electrons in Chemical Reactions: First principles*; Wiley Interscience: New York, 1982.
- (32) Bacchus-Montabonel, M. C.; Talbi, D.; Persico, M. Quantum Chemical Determination of the Rate Coefficients for Radiative Association of CH_3^+ and H_2 . *J. Phys. B* **2000**, *33*, 955–959.
- (33) Bene, E.; Vibók, Á.; Halász, G. J.; Bacchus-Montabonel, M. C. Ab Initio Molecular Treatment of Charge Transfer Processes Induced by Collision of C^{2+} Ions with the OH Radical: A Linear Approach. *Chem. Phys. Lett.* **2008**, *455*, 159–163.
- (34) Guler, L. P.; Yu, Y. Q.; Kenttämää, H. I. An Experimental and Computational Study of the Gas-Phase Structures of Five-Carbon Monosaccharides. *J. Phys. Chem. A* **2002**, *106*, 6754–6764.
- (35) Ha, D. T.; Huels, M. A.; Huttula, M.; Urpelainen, S.; Kukk, E. Experimental and Ab Initio Study of the Photofragmentation of DNA and RNA Sugars. *Phys. Rev. A* **2011**, *84*, 033419/11.
- (36) Almeida, D.; Ferreira da Silva, F.; Garcia, G.; Limão-Vieira, P. Dynamic of Negative Ions in Potassium-D-Ribose Collisions. *J. Chem. Phys.* **2013**, *139*, 114304/6.
- (37) Bacchus-Montabonel, M. C. Action of Secondary Ions on Biomolecules: Anisotropy and Radio-Sensitization Properties. *J. Phys. Conf. Series* **2012**, *373*, 012002/8.
- (38) Bacchus-Montabonel, M. C. Anisotropy and charge effect in collisions of ions with biomolecules. *Appl. Radiat. Isot.* **2014**, *83*, 95–99.
- (39) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (40) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (41) López-Tarifa, P.; Jeanvoine, Y.; Salpin, J. Y.; Hervé du Penhoat, M. A.; Gaigeot, M. P.; Politis, M. F. Optimized Geometries of Furanose and Pyranose, Private Communication.
- (42) Werner, H. J.; Knowles, P. J. *MOLPRO* Package of Ab Initio Programs (version 2010.1).
- (43) Bene, E.; Martínez, P.; Halász, G. J.; Vibók, Á.; Bacchus-Montabonel, M. C. Charge Transfer in Collisions of C^{2+} Carbon Ions with CO and OH Targets. *Phys. Rev. A* **2009**, *80*, 012711/8.
- (44) Baloitcha, E.; Desouter-Lecomte, M.; Bacchus-Montabonel, M. C.; Vaack, N. Wave Packet Methods for Charge Exchange Processes in Ion-Atom Collisions. *J. Chem. Phys.* **2001**, *114*, 8741–8751.
- (45) Bacchus-Montabonel, M. C. Ab Initio Potential-Energy Curves and Radial and Rotational Couplings for the Process $N^{5+} + He \rightarrow N^{4+} + He^+$. *Phys. Rev. A* **1987**, *36*, 1994–2001.
- (46) Stancil, P. C.; Zygelman, B.; Kirby, K. *Photonic, Electronic, and Atomic Collisions*; Aumayr, F., Winter, H.P., Eds.; World Scientific: Singapore, 1998; p 537.
- (47) Sidis, V. Vibronic Phenomena in Collisions of Atomic and Molecular Species. *Adv. At. Mol. Opt. Phys.* **1990**, *26*, 161–208.
- (48) Bacchus-Montabonel, M. C.; Tergiman, Y. S. Charge Transfer Rate Coefficients in Collision of C^{2+} Ions with CO and N_2 Molecular Targets. *Chem. Phys. Lett.* **2010**, *497*, 18–21.
- (49) Allan, R. J.; Courbin, C.; Salas, P.; Wahnon, P. State-Selective effects in the Differential Cross section for Electron capture from Laser-Excited Sodium Atoms by protons. *J. Phys. B* **1990**, *23*, L461–L466.
- (50) Bacchus-Montabonel, M. C. Theoretical Study of Charge Transfer Dynamics in Collisions of C^{6+} Carbon Ions with Pyrimidine Nucleobases. *Eur. Phys. J. D* **2012**, *66*, 175/7.