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Theoretical ionization and capture cross sections for DNA nucleobases impacted by light ions

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Abstract

Purpose: **Although DNA lesions are considered of prime importance for describing the post-irradiation cellular survival, they still remain rarely studied on both experimental and theoretical sides. Under these conditions, we here propose different theoretical models for predicting the single ionization and single capture total cross sections for DNA bases impacted by protons.**

Material and methods**: Three theoretical approaches are developed: a first classical one based on a classical trajectory Monte Carlo (CTMC) model and two quantum mechanical ones, namely, a Coulomb Born (CB1) and a continuum-distorted wave eikonal-initial-state (CDW-EIS) model.**

Results: **Ionization and capture processes induced by protons on DNA bases (adenine, cytosine, thymine and guanine) are here studied in terms of total cross sections.**

Conclusions: **A very good agreement is obtained between the different models at high enough impact velocities but discrepancies are observed between them at low impact energies ($E_i \leq 100$ keV). Furthermore, it is shown that the theoretical cross sections underestimate the rare existing experimental data in particular for adenine and thymine whereas a reasonable agreement is found for cytosine.**

Keywords: DNA, ionization, capture, cross sections, ion impact

Introduction

DNA lesions and more particularly those involved in clustered damages are nowadays considered of prime importance for describing the post-irradiation cellular survival. Indeed, these complex radio-damages may induce critical DNA lesions like double-strand breaks whose relevance has been clearly identified in the radio-induced cellular death process (Nikjoo and Lindborg 2010). Under these conditions, it clearly appears that further theoretical models as well as experimental measurements on ion-induced collisions at the DNA level are crucial. However, to the best of our knowledge only few works exist. Let us cite for example the works of Moretto-Capelle and co-workers who have studied the ionization and fragmentation of isolated DNA/RNA bases and uridine nucleoside induced by protons (see for example Le Padellec et al. 2008). Additionally, Alvarado et al. (2007) have reported measurements on collisions of keV-H^+, He^{2+} and C^+ ions with DNA building blocks. Schalthölter and co-workers have also studied the fragmentation modes induced by heavy ions like Xe^{q+} ($q = 5$–25) and C^{q+} ions ($q = 1$–6) (see for example de Vries et al. 2003 and references therein) on isolated nucleobases and more recently on nucleobase clusters (Schalthölter et al. 2006). Finally, let us mention the works of Brédy and co-workers on adenine fragmentation induced by F^{2+} and Ar^{8+} ions (see Brédy et al. 2007 and references therein).

On the theoretical side, ion-induced collisions on DNA bases have been rarely investigated and we essentially find two approaches in the literature: a first (semi)-classical one generally based on a classical-trajectory Monte Carlo (CTMC) description (see for example the study of Bacchus-Montabonel et al. 2005) and a second one developed in the quantum-mechanical framework and essentially limited to the use of the first Born approximation (see for example the recent work of Dal Cappello et al. 2008 where ionization of cytosine molecules induced by protons was investigated). Finally, it is worthwhile to note that in both approaches, the DNA entities are considered as isolated molecules contrary to the recent studies of Abril et al. (2010, 2011) where inelastic interactions as well as electronic energy loss induced by protons in dry DNA were described within the dielectric formalism.

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We simultaneously here report total cross section calculations provided by both a classical model combining a classical trajectory Monte Carlo (CTMC) approach with a classical over-barrier (COB) criterion (Abbas et al. 2008, Lekadir et al. 2009) and two quantum mechanical approaches, namely, a first developed within the first-order Born approximation (CB1) (Champion et al. 2010), and a second computed within the continuum distorted wave-eikonal initial state (CDW-EIS) model (Fainstein et al. 1988).

Theoretical models

First of all, let us note that the description of the impacted nucleobases is – in the CTMC approach (Abbas et al. 2008, Lekadir et al. 2009) – reduced to the knowledge of the binding energies of the different molecular subshells of the biological targets (ranging from 24–28 according to the DNA base investigated), whereas a linear combination of atomic orbitals (LCAO) is used in the two quantum approaches, namely, that reported by Bernhardt and Paretzke (2003) based on the restricted Harthree-Fock method with geometry optimization (RHF/3-21G) in which the DNA bases are described by means of their five highest occupied molecular orbitals.

The classical approach

In our home-made CTMC model, all the particles are classically described via Newtonian laws and the occurrence of ionizing processes (single as well as multiple) are seen as dependent on both classical over-barrier (COB) and time matching criteria (see Abbas et al. 2008 and Lekadir et al. 2009 for more details). Within the impact parameter approximation, the initial conditions of the numerical simulations are the projectile velocity $\vec{v}$ the impact parameter $\vec{b}$ and the molecular binding energies of the subshells involved in the collision. The calculation starts and stops at sufficiently large time t (or inter-nuclear distance, namely, R ≅ 100 a.u.). At the end of the collision, we finally determine the type k of the ionizing process induced and then provide total cross sections (TCS) defined as:

$$\sigma_k(v) = 2\pi \int_0^{b_{max}} db b.\mathrm{P}_k(b), \tag{1}$$

where,

$$P_k(b) = \frac{N_k(b)}{N(b)}, \tag{2}$$

the numerator $N_k(b)$ and the denominator $N(b)$ refer to the k-type process number scored and to the total number of trajectories simulated at the impact parameter b, respectively.

The quantum mechanical models

Total cross sections are calculated using the CDW-EIS and CB1 models for single electron ionization and the CDW-EIS model for single electron capture. They are obtained by using the expression:

$$\sigma = \sum_{j=1}^{N} \sigma_j, \tag{3}$$

where N is the number of molecular orbitals used in the description of the target. σ_j refers to the total cross section for the jth-orbital of the molecular target, this latter being obtained as a weighted sum of atomic total cross sections corresponding to the different atomic components involved in the target description, namely,

$$\sigma_j = \sum_i g_i \xi_i \sigma_{at,i}, \tag{4}$$

where g_i and ξ_i denote the weight factor and the effective number of electrons of the *ith*-atomic orbital, respectively. According to the target description given by Bernhardt and Paretzke (2003), the five highest occupied orbitals ($N = 5$) are here only considered (see Champion et al. 2010 for more details).

Results and discussions

Present CDW-EIS, CB1 and CTMC-COB theoretical ionization TCS are shown in Figure 1 for proton beams colliding with the four DNA bases.

The overall behavior obtained is similar for the four cases considered and we clearly observe that the two sets of quantum mechanical results are both in close agreement for impact energies larger than 70 keV and in accordance with the CTMC-COB predictions provided that the impact energies are greater than 200 keV.

However, at low impact energies CDW-EIS results present a different behavior than CB1 predictions. This must be attributed to the fact that more complete two-center initial and final wave functions (which include the action of the combined fields of the projectile and target on the active electron) are considered in CDW-EIS. Also, we should mention that the validity of classical calculations is doubtful at low impact velocities.

Furthermore, the only one existing experimental data taken from Tabet et al. (2010) is also reported for comparison. Theoretical predictions are in reasonable agreement with experiments for cytosine whereas underestimation of measurements is pointed out for adenine and thymine. We should note that only one experimental value for each one of the DNA bases was measured.

For single electron capture, CDW-EIS and CTMC-COB give similar total cross sections at high enough projectile velocities (see Figure 2). As for single ionization, the best agreement between the theoretical predictions and the experimental measurements is found for cytosine while huge underestimations are reported for adenine and thymine. Formation of hydrogen in final states with principal quantum numbers $n = 1$ and $n = 2$ was considered in the CDW-EIS calculations. Moreover, we have verified that capture to higher bound states gives a negligible contribution to total cross sections.

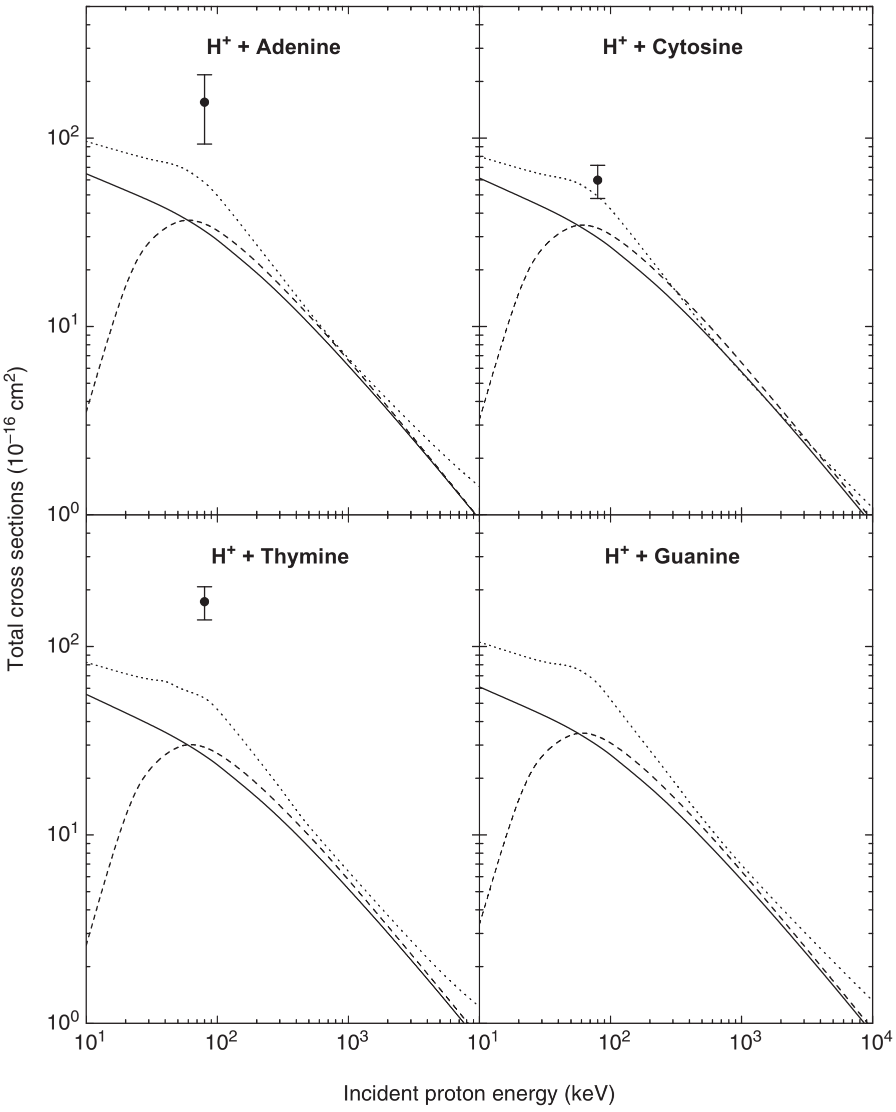

Figure 1. CDW-EIS, CB1 and CTMC-COB TCS (dashed, solid and dotted line, respectively) for single ionization of DNA bases impacted by protons. Experimental data taken from Tabet et al. (2010) are also reported for comparison (circles).

Conclusions

Total cross sections for single ionization and single electron capture of DNA bases by proton impact have been theoretically determined by using classical and quantum mechanical descriptions, showing that all calculations agree at high enough projectile velocities.

A systematic underestimation of experiments is found when comparing with the rare existing measurements at 80 keV in particular for adenine and thymine where the disagreement is of about one order of magnitude while for cytosine it is of about 4. A possible way to improve the theoretical description of the scarce existing experimental data could reside in the inclusion of a larger basis of target orbitals within the quantum mechanical calculations. An investigation on this line is a matter of our present interest. However, new and more extended measurements appear as necessary for further conclusions.

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Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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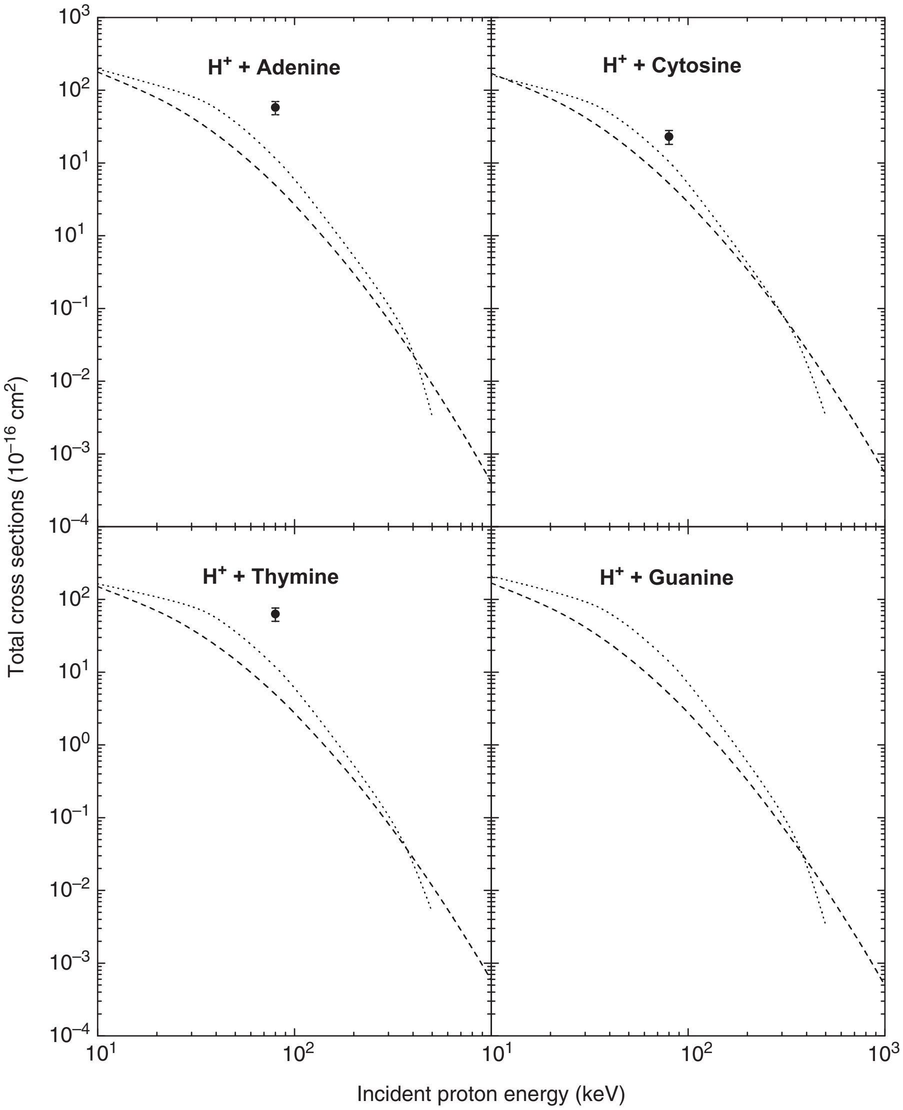

Figure 2. CDW-EIS and CTMC-COB TCS (dashed and dotted line, respectively) for single electron capture on DNA bases impacted by protons. Experimental data taken from Tabet et al. (2010) are also reported for comparison (circles).

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