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Monte Carlo simulation of electronic energy loss for proton impact on nucleobases

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ABSTRACT

Electronic energy loss distributions for the intermediate velocity protons interacting with the nucleobases is simulated under the local density approximation using classical trajectory *Monte Carlo* method. Peak energy loss in the range of 50–70 eV is observed irrespective of the target species with strong orientation dependence. The energetics of the energy loss process is discussed in the context of ionization and fragmentation thresholds for all the nucleobases. Using these threshold values, geometric cross sections are calculated and compared with the previously reported experimental and theoretical investigations. Though the models were in reasonable agreement with each other, the experimental data showed large deviation with present as well as previously reported models.

1. Introduction

The ionization and fragmentation processes as a consequence of the ion–molecule collisions are active research topics in diverse areas of science. This research contributes to the understanding of ion collision with large molecules, clusters and biomolecules like nucleobases. Apart from their terrestrial significance, the presence of nucleobases is evident in the interstellar regions [1,2] as well as in meteorites [3–5]. The radiation induced damage to these molecules could be direct or due to the secondary particles like low energy secondary electrons and ions produced along the track of radiation during the interaction with target [6]. It is shown that the single and double strand breaks in supercoiled DNA are caused by electrons between 3 and 20 eV [7]. In addition to this the understanding of the energy deposition due to the projectile beam in the biological environment bears primary significance in medicine and more specifically in cancer therapy. Here the need of delivering highly localized doses using focused ion beam within tumors while avoiding damage to the surrounding normal tissue is very crucial.

In proton therapy, the incident energy ranges from 10 to 250 MeV and this beam experiences a severe deceleration within the target medium, and deposit a large dose at a given depth, in a well-defined volume, i.e. the so-called the Bragg peak. It is found that the 100 keV proton beam gives maximum stopping for liquid water acting as a prototype for human cell [8]. Hence 100 keV proton beam deposits the maximum energy with a Linear Energy Transfer (LET) of about 80 keV per micron [9] and therefore gives maximum ionization cross section. Hence many experimental and theoretical investigations have been performed at kinetic energies in the keV range [10–17]. A simulation of proton-nucleobase collision is therefore essential to define or refine the best radiotherapy strategy. The literature is enriched with the experimental fragmentation studies for nucleobases using keV proton impact [9,11,18–22], multicharged ion impact [23–27], 3 keV neutral fluorene impact for adenine [28], electron spectroscopy using keV proton impact [29–31].

In collision induced dissociation, the energy gained by the system can only be determined by estimating the average energy deposited into the molecule unlike the photoionization mass spectrometry [32] where the excitation energy of the systems upon photon absorption is well defined giving very accurate estimate of the appearance energy of a specific fragment. Therefore, actual measurement of the initial internal energy of a fragmented system becomes a complex task in many experiments. The present investigation is dedicated to proton interaction with the purine molecule; adenine ($C_5H_5N_5$) and guanine ($C_5H_5N_5O$), and the pyrimidines; cytosine ($C_4H_5N_3O$), thymine ($C_5H_6N_2O_2$) and uracil ($C_4H_4N_2O_2$). We have here done the Classical trajectory *Monte Carlo* (CTMC) simulation within the frame work of the Local Density Approximation (LDA) to calculate the mean electronic energy loss. To highlight some specific attributes, we have compared the result with the case of naphthalene ($C_{10}H_8$). The geometric cross sections for a range of energy loss distribution were calculated using the

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above mentioned CTMC-LDA model. The other theoretical approaches which have been probed in past for nucleobases, are based on models like first-order Born approximation (CB1-CWB), continuum distorted wave-eikonal initial state (CDW-EIS), CTMC with classical over the barrier (CTMC-COB) [33–36]. In the following sections, atomic units (a.u.) are used throughout, unless stated otherwise.

2. *Monte Carlo* simulation for electronic energy loss

To model the ion–molecule collision and estimate the electronic stopping for nucleobases and PAHs, we have performed *Monte Carlo* simulations for random trajectories of projectile ions with the help of LDA formalism developed by Lindhard et al. [37,38]. Fig. 1 displays the structure and composition of nucleobases and naphthalene (a member of PAH family) studied in this work. The validity of this model has also been studied for ion-atom [39] and ion–molecule collisions [40] which ranges from several keV to several MeV energy per atomic mass unit (amu) where collision time is shorter (10^{-16}–10^{-17} s) than the vibrational or rotational time scales (10^{-13} s or longer) [40,41]. Hence, with an assumption that the removal of electrons is faster than the nuclear motion and slower than the collision time, the simulation has been carried out for fixed orientation of the molecule as well as fixed inter-nuclear coordinates (obtained from optimized geometry of neutral molecule) and is suitable for interpretation of the present experimental results. We consider electronic stopping as the main contributor to the energetics of the collision process. The amount of energy deposited into the molecule is the energy loss of the projectile with an approximation that the recoil energy of the projectile is negligible compared to the net energy deposited in the molecule [42] under the studied projectile velocity regime. Thus the energy loss of projectile is considered to be equal to the energy deposited into the internal degrees of freedom of the target. The energy transferred leads to the excitation and ionization of the target molecules. Since numerous ionization and fragmentation channels are supposed to be active, it is practical to use a statistical approach instead of a detailed quantum–mechanical treatment of individual processes. A separately calculated electron density distribution represents the target through which the randomly generated trajectories pass. The detailed formalism of LDA is discussed elsewhere [38]. The contribution from each volume element in the path of the projectile is summed to obtain the mean energy loss over that trajectory. The deceleration as well as Coulomb deflection of the projectile ions along their trajectories is considered insignificant and hence ignored in the calculations. We calculate the mean energy loss of the projectile ion as a line integral along the trajectory [37] with the assumption as per Russek–Meli–Cocke model [43,44] that the energy loss is considered as a statistical process.

As the velocity of the projectile considered here is of the same order of magnitude as the velocity of the inner most electron of the target, we have taken the total electron density as the input for LDA model instead of restricting to only valence electron density. The total target electron density was obtained quantum mechanically using the Density Functional Theory (DFT) in conjunction with a non-local hybrid Becke three-parameter LeeYang-Parr functional (B3LYP) basis. These were computed with the help of a quantum chemistry packages GAUSSIAN09 [45]. The optimized geometry as well as the total electron density was computed using 6-311G (2d, p) basis set. For simplicity, we consider the plane of the molecule to be XY plane with longer axis of the molecule in the X-direction. The simulation was performed in two configurations of trajectories: i) From all directions randomly (to understand and compare with the experimental results), and ii) Plane-wise (to understand the behavior of electronic stopping as per structure and composition of the molecule). The *Monte Carlo* simulations of individual plane-wise interaction correlate strongly with the structure of the molecule.

3. Simulation results and discussion

For intermediate velocity projectile collision, the energy deposited into the molecule due to a light ion like proton is dominated by electronic processes; the electronic stopping power is much larger than the nuclear one. In ionmolecule collision experiments, two things are not controlled: the impact parameter and the molecular orientation. And hence the site and amount of energy deposited into the molecule cannot be controlled experimentally. Consequently the knowledge regarding amount of energy deposition can be obtained only from the degree of ionization or

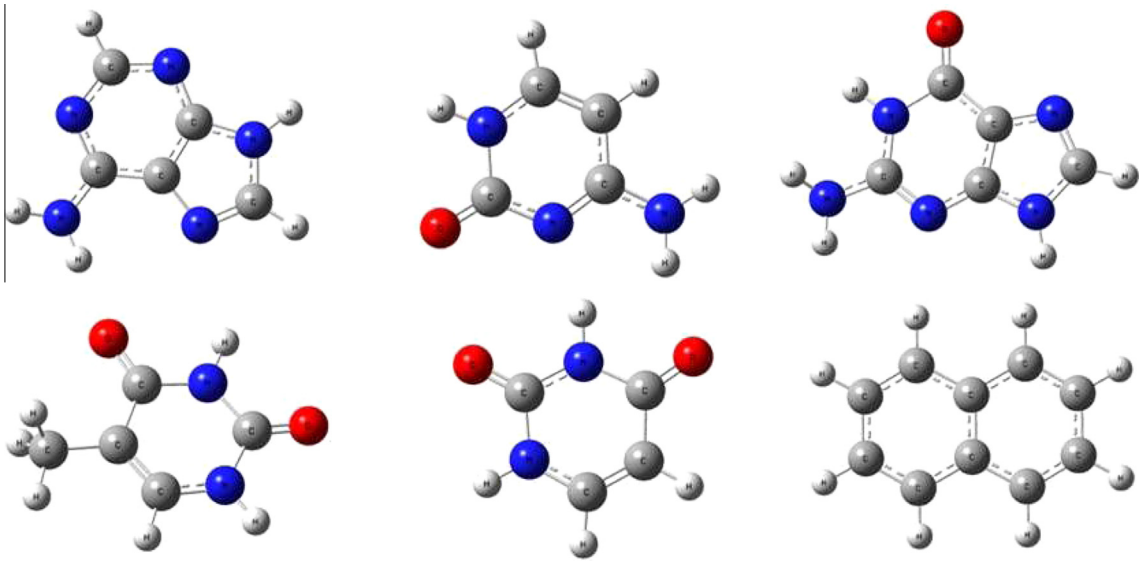

Fig. 1. Schematic picture for five nucleobase adenine, cytosine, guanine (top three left to right), thymine, uracil and one PAH: naphthalene (bottom three left to right). Color code for atoms: carbon (grey), hydrogen (white), oxygen (red), nitrogen (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)