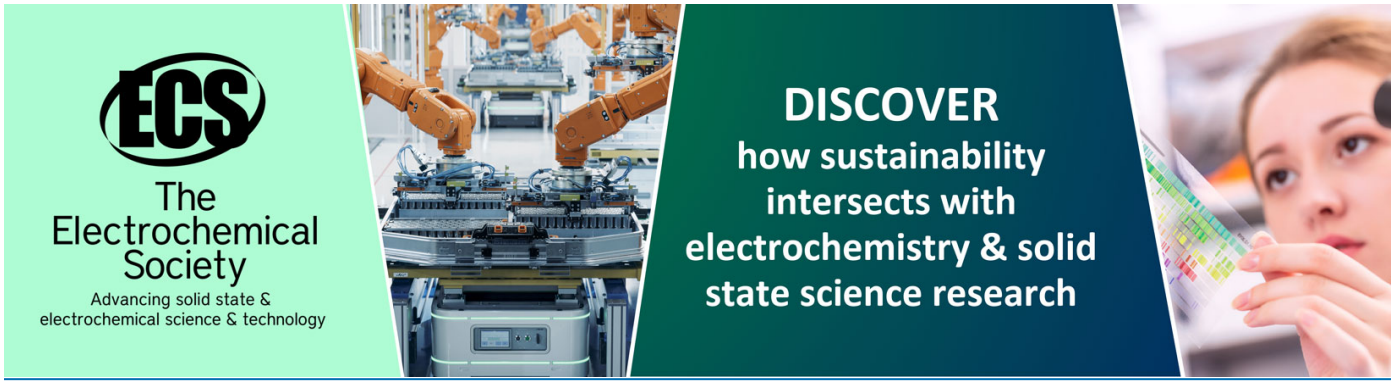
Modeling ion-molecule collision using *Monte Carlo* simulation



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Modeling ion-molecule collision using *Monte Carlo* simulation

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Abstract. *Monte Carlo* simulation is performed under local density approximation for electronic energy loss distribution by intermediate velocity protons for several examples of polycyclic aromatic hydrocarbon (PAH) molecules as well as for some of naphthalene derivatives. The energy loss distribution was found to peak in the range of 50-70 eV for all the molecules except C_{60}. Apart from this, a strong orientation effect with respect to projectile for electronic stopping magnitude is observed for all molecules except C_{60} due to its icosahedral symmetry. This work helps in estimation of the ionization and fragmentation cross sections using electronic stopping.

1. Introduction

Intermediate velocity collision experiments where the capture and ionization cross sections have competing contributions, highlight the complexity and importance of theoretical modeling for these processes. For the cases like PAH molecules, it is not practical to perform experiments on each and every member of the family to obtain such cross sections. Therefore electron capture processes are often calculated using coulomb over the barrier model to a very good agreement with experimental measurements. Similarly for ionization as well as fragmentation various approaches are followed. On the other hand the complexity in theoretical calculations is enhanced for the case of large molecules like PAHs where the potential energy surface cannot be calculated numerically to a good accuracy. Moreover in such collision processes the energy loss is not a discrete quantity and is governed by statistical processes [1].

The present work helps in estimating fragmentation cross section for ion-molecule collision from mean energy loss calculations with the help of a simple local density approximation (LDA) and *Monte Carlo* simulation. Using various thresholds and ionization potentials, these values can be converted to ionization or fragmentation cross sections. LDA is a useful approach for large systems where the statistical processes dominate. The validity of the simulation is established for a PAH molecule namely naphthalene for which the experimental fragmentation yields agree well with the simulated geometric cross section [2] and for nucleobases as well [3].

The molecules considered for the present investigation are PAHs and their derivatives interacting with protons. PAHs are a family of hydrocarbons consisting hexagon or pentagon rings of carbon (C) atoms with hydrogen (H) at periphery of the ring. The inherent stability for PAHs and aromatic character is due to the existence of delocalized electrons because of sp^2 hybridized C atoms. The studies of high energy radiation interaction with PAHs are important in interstellar physics [4] as well as on earth [5]. PAHs, their cations and their hydrogenated

derivatives are considered to be the possible carrier of diffuse interstellar bands [6, 7] and their spectroscopic observations match with the unidentified infrared (UIR) band emission at 3.3, 6.2, 7.7, and 11.3 μm from different galactic sources. The interstellar heating is also attributed to the PAHs [8]. PAHs also interact with cosmic ray radiation which consist of 99% of protons [4]. On earth PAHs are formed due to incomplete combustion of C rich compounds like fuel, coal, crude oil and they remain in human body on inhalation of polluted air or intake of improperly treated food. Then upon exposure to the solar radiation PAHs become mutagenic and carcinogenic inside human body [5, 9]. Proton therapy is a well known technique in treatment of cancer where the knowledge of energy deposition into the biomolecules inside the body is very crucial to avoid undesirable radiation effect during the treatment [10]. Hence the mean energy loss calculations are helpful in biological, medical as well as physics applications. The simulations are performed for 80 and 100 keV proton beam due to its significance in therapy known as Bragg peak energy which causes the highest dose deposition in radiation therapy [11, 12]. So far the application of LDA to PAHs (except fullerene and anthracene) has not been studied and the estimation of the fragmentation cross section from electronic stopping distribution is for the first time reported as part of this work for naphthalene. Hence this work will help in validating the future experiments at intermediate velocity collision for any ion-molecule combination.

2. Mean electronic energy loss calculation

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 with an assumption that removal of electron is faster than the nuclear motion. The projectile can transfer varied amount of its kinetic energy to the target depending on the nature of interaction whether direct ionization or electron capture or transfer ionization. The fragmentation dynamics depends upon the coulombic interaction between projectile and target, and hence on the energy transfer into the molecule. In the energy range under consideration here, the recoil energy of the projectile is negligible compared to the net energy deposited in the molecule [13]. To estimate the energy transferred to the target molecule from the projectile ion we have performed *Monte Carlo* simulations for random trajectories of projectile ions using the LDA model developed by Lindhard *et al.* [14, 15] .

2.1. Local density approximation

The LDA is a well known approach in stopping power for solid targets [14, 15]. This model has also been used for ion-atom [16] and ion-molecule collisions [17] and is applicable for a range 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) [17]. The detailed formalism of the calculation adapted here is reported in literature [14, 17]. The LDA approximates the target as a non uniform distribution of electron density and the energy loss distribution due to the interaction of projectile (considered as a point charge) is thus calculated at each volume element of the total electron density, which finally provides the mean energy loss.

2.2. Monte Carlo simulation details

The 10^6 randomly generated trajectories are made to pass through a non-uniform electron density distribution representing the target. Using LDA method, energy loss is calculated for each volume element of the electron density and the total energy loss is calculated as the sum of all these contributions. In the simulation, the deceleration of projectile ions along their trajectories as well as the coulomb deflection of these ions in the field of the target nuclei is neglected. Total electron density is considered as the input for LDA model as the magnitude of the projectile velocity is close to that of the velocity of the inner most electron of

the target molecule. The target electron density was obtained quantum mechanically using the non-local hybrid Becke three-parameter Lee-Yang-Parr functional (B3LYP) basis at 6-311G (2d, p) with Density functional theory (DFT) method using GAUSSIAN09 [18]. The simulation has been carried out for a fixed orientation of the molecule as well as for fixed inter-nuclear coordinates, thus making it suitable for interpretation of the experimental results. In the *Monte Carlo* simulations, two methods have been used in order to generate the random trajectories of the projectile: i) From all directions, to compare and understand the experimental results, and ii) Plane-wise, to understand the behavior of electronic stopping according to the elemental composition and geometry of the molecule. The first case is reported here showing the electronic stopping distribution. The geometric cross sections (inset of figure 1) are calculated by integrating the area under the curve (see figure 1) of the energy loss distribution (with first ionization potential as the lower limit of area integral) and then normalizing it with the total number of trajectories.

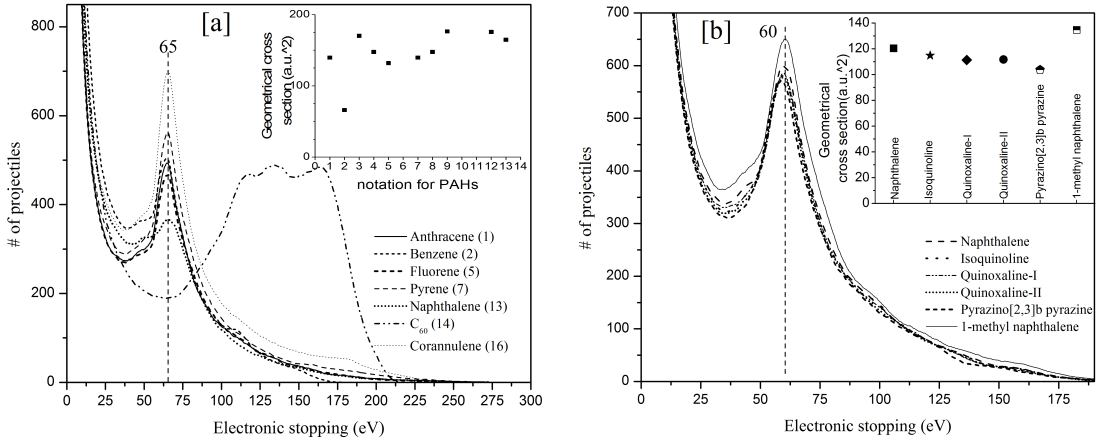

Figure 1. Mean energy loss calculation using *Monte Carlo* simulation for interaction of randomly generated proton projectiles of [a] 100 keV with PAH targets and [b] 80 keV with naphthalene derivative targets. Insets showing the geometrical cross section obtained for different targets: anthracene(1), benzene(2), benzo[c]phenanthrene(3), fluoranthene(4), fluorene(5), phenanthrene(6), pyrene(7), tetracene(8), tetrahydrochrysene(9), tetrahydropyrene(10), tetraphene(11), triphenylene(12), naphthalene(13), C_{60}(14), coronene(15), Corannulene(16) using *Monte Carlo* simulation results with proton projectile.

3. *Monte Carlo* simulation results for electronic stopping

Figure 1 shows the electronic stopping distribution curve for randomly generated 10^6 linear trajectories of the proton projectile ions interacting with PAHs as well as naphthalene derivative target. The peak of mean energy loss remains same for all the molecule except C_{60} due to the difference in symmetry and electron density distribution. However, the probability of higher energy loss decreases rapidly after a pronounced peak. This peak is a result of the trajectories which pass through the molecular volume almost perpendicular to the molecular plane. This is due to the fact that this orientation offers the largest geometrical cross section to the incoming projectile beam. But at the same time this orientation causes much less energy loss compared to the in plane collision and this is the reason of the peak position in the energy loss distribution being independent of the PAH species. The peak height is decided by the total number of C atoms in the molecule. It is also seen from simulation results (not shown here) that contour plot of electronic stopping for perpendicular impact of proton beam with respect to the plane

of molecule for planar PAHs demonstrates the structure very well and is in agreement with the distribution of electron density over the molecular plane [2].

In our previously reported work [2], the geometric cross section obtained from this simulation for proton-naphthalene system successfully reproduced the experimental fragmentation cross section. Here the geometric cross section obtained from simulation of proton-PAHs and proton-naphthalene derivative interaction using the first ionization potential as the threshold for fragmentation is shown in inset of figure 1. All the PAHs (excluding benzene) show a large (nearly 30%) variation due to size and composition. In figure 1[a], only few examples out of all molecules is shown (see the caption of figure 1[a] for nomenclature of molecules). As can be seen from inset of figure 1[a], anthracene and phenanthrene show almost same cross section. Similarly tetracene, tetrahydropyrene and tetra hydrochrysene show similar cross sections. In figure 1[b] inset, all the naphthalene and its derivatives show relatively low (about 15%) variation in the cross sections except 1-methyl naphthalene where the additional methyl group introduces excess electron density causing larger cross section.

4. Conclusions

The *Monte Carlo* simulation of intermediate velocity protons interacting with PAHs and their derivative are performed. The electronic energy loss process is found to deposit about 50-70 eV energy with highest probability. This is because the planar orientation of target offers largest cross section for the interaction. The geometric cross sections were found to be dependent on the number of carbon atoms present. Using the first ionization potential as the cut off, the geometric cross sections can be calculated. Similarly for other processes like fragmentation also the cross sections can be estimated using the known or measured threshold values.

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