

Article ID: 1007-4627(2012)03-0279-06

DFT Studies on Proton-ethylene Collisions

WANG Zhi-ping^{1, 2}, ZHANG Feng-shou², WANG Jing²

(1. School of Science, Jiangnan University, Wuxi 214122, Jiangsu, China;

2. The Key Laboratory of Beam Technology and Material Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, China)

Abstract: In the framework of the time-dependent local-density approximation (TDLDA), which applied to valence electrons, coupled non-adiabatically to molecular dynamics of ions, the microscopic mechanisms of collisions between energetic protons and ethylene are studied. Not only the amount of energy lost of the projectile, but also the electron and vibration excitations of the target are identified. In addition, the influences of the collision orientation on the energy loss of the proton and excitation dynamics of ethylene are discussed. It is found that the ionization is enhanced and more electrons are captured by the proton when the proton with the impact energy less than 250 eV moves perpendicularly to the molecular plane. A strong relation between the proton energy lost and the impact orientation is obtained when the impact energy is larger than 250 eV.

Key words: ionization of molecule; energy loss; collision orientation

CLC number: O561.5 **Document code:** A

1 Introduction

It is well known that the radiation ionization in biological tissue can induce severe damage to DNA^[1-2]. With the development of ion sources such as the electron cyclotron resonance (ECR) ion source and modern accelerators such as cooling storage ring (CSR), a lot of investigations have been devoted to studying the molecular mechanisms underlying biological radiation damage. More recently, a number of research efforts have been devoted both in experiment and theory to the action of ions on molecules with high and low energies^[3-5]. These investigations provide significant new information for understanding not only the process of charge transfer but also the processes

with high excitation, such as Coulomb explosion.

It is known that the quantum mechanical theories must face up to the difficulty of treating the full degrees of freedom of ions and electrons. In contrast, the time-dependent local-density approximation (TDLDA)^[6], for the electrons combined with classical molecular dynamics (MD) for the ionic cores, namely TDLDA-MD, provides an effective method to treat the electron and ion degrees of freedom simultaneously. It has been successfully applied to calculate the energy transfer in collisions between charged projectiles and small molecules, clusters and fullerene, and the radiolysis of liquid water^[7-15].

In this paper, the microscopic mechanisms of

Received date: 16 Dec. 2011; **Revised date:** 11 Jan. 2012

Foundation item: Fundamental Research Funds for Central Universities (JUSRP111A21); National Basic Research Program of China (973 Program) (2010CB832903); Self-determined Research Program of Jiangnan University; "Eleven-Five" Planning Issues for Education and Science of Jiangsu Province under Higher Education System 34 of 2008; "Eleven-Five" Planning Issues for Higher Education of Jiangsu Province (JS053)

Biography: WANG Zhi-ping(1981-), female (Han Nationality), Changzhou, Jiangsu, Doctor, working on material physics; E-mail: zpwang03247@163.com

irradiation of biological molecules are investigated. We employ TDLDA-MD to obtain microscopic insight into the electron and vibration excitations during collisions between energetic proton and ethylene.

2 Theory

The technicalities of the model used in this paper have been presented in detail elsewhere and for a review see Ref. [7]. Here we recall the ingredients and a few relevant formulas. The molecule is described as a system composed of valence electrons and ions. For ethylene there are 12 valence electrons and 6 ions. Valence electrons are treated by TDLDA together with an average-density self-interaction correction (ADSIC)^[16] to achieve the correct ionization potential (IP), which is crucial to describe electron emission correctly. Ions are treated as classical particles. They interact with others via their repulsive Coulomb force. The coupling between electrons and ionic cores is mediated by Goedecker-type^[17] non-local pseudo-potential. The original parameterizations employ different Gaussian widths for each material and contribution. This restrains the numerical precision in coordinate space grids. Wavefunctions and fields are represented on a 3D coordinate-space grid of dimension $96 \times 72 \times 72$ with a grid spacing of $\Delta = 0.41$ Bohr. The TDLDA equations are solved numerically by time-splitting technique^[18]. For the nonlocal part contained in Hamiltonian, we deal with it in an additional propagator and treated it with a third-order Taylor expansion of the exponential function^[19]. The equation to be solved for ion dynamics is

$$m_1 \frac{d^2 \mathbf{R}_1}{dt^2} = \mathbf{F}_1(\mathbf{R}_1, t). \quad (1)$$

A constant time step $\Delta t = 6.05 \times 10^{-4}$ fs is used for the evolution of electrons and ions. The absorbing boundary condition is employed to avoid periodic reflecting electrons^[20]. Thus the total

number of electrons $N = N(t)$ decreases in time. The number of escaped electrons $N_{\text{esc}} = N(t=0) - N(t)$ is a measure of average ionization. The root-mean-square radius of electrons is defined as

$$rms_{\text{el}}(t) = \sqrt{\int d\mathbf{r} r^2 \rho(\mathbf{r}, t) / N_{\text{el}}},$$

where $\rho(\mathbf{r}, t)$ is the electron density and N_{el} is the number of electrons.

3 Results and discussions

In our calculation, ethylene is in the xy plane with two carbon atoms on the x axis. The center of mass is at the grid origin.

We first explore the influence of collision orientation on the ionization of ethylene, as shown in Fig. 1. Two different collision orientations are considered. One is the proton moves in the plane of ethylene, which is moving along the x direction towards the center of mass of ethylene starting from the initial position $(-23 \text{ Bohr}, 0, 0)$. The other one is the proton moves perpendicularly to

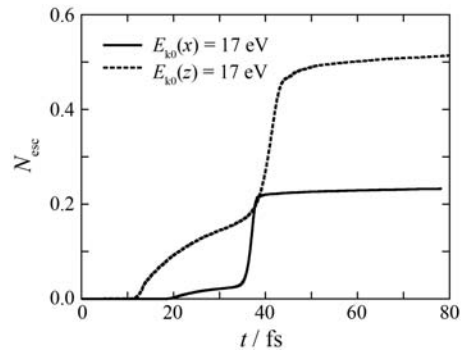


Fig. 1 The influence of collision orientation on the time evolution of ionization of the system. Solid line for proton moves along the x direction and dashed line for proton moves along the z direction. In both cases the proton moves towards the center of mass of ethylene and $E_{k0} = 17 \text{ eV}$.

the molecular plane, which is along the z direction towards the center of mass of ethylene starting from the initial position $(0, 0, 16 \text{ Bohr})$. From Fig. 1 one can see a common feature of curves, which is a slow increase of N_{esc} first, then a sudden

jump, finally reaching a saturation, where the sudden jump indicates that the proton carrying the captured electrons from the ethylene is leaving the numerical box. However, the difference of ionization between two cases is obvious. The ionization takes place earlier in the second case. This is due to the fact that it takes shorter time for proton to contact ethylene when it moves along the z direction. Moreover, it is easy to find that the total ionization is enhanced in the second case. In the first case, finally, there is a loss of about 0.22 charge units, where about 0.2 charge units are

captured by the proton, whereas in the second case, 0.51 charge units are lost, where about 0.3 charge units are captured by the proton. There are two counteracting influences. On one hand, the slower proton exposes lower frequency components to the ethylene. On the other hand, the interaction time becomes much longer leading to an enhanced reaction yield. As a consequence, in the low impact energy range ($E_{k0} \leq 250$ eV), the enhancement by increased interaction time dominates over the lower frequency components.

Fig. 2 shows the time evolution of motion of

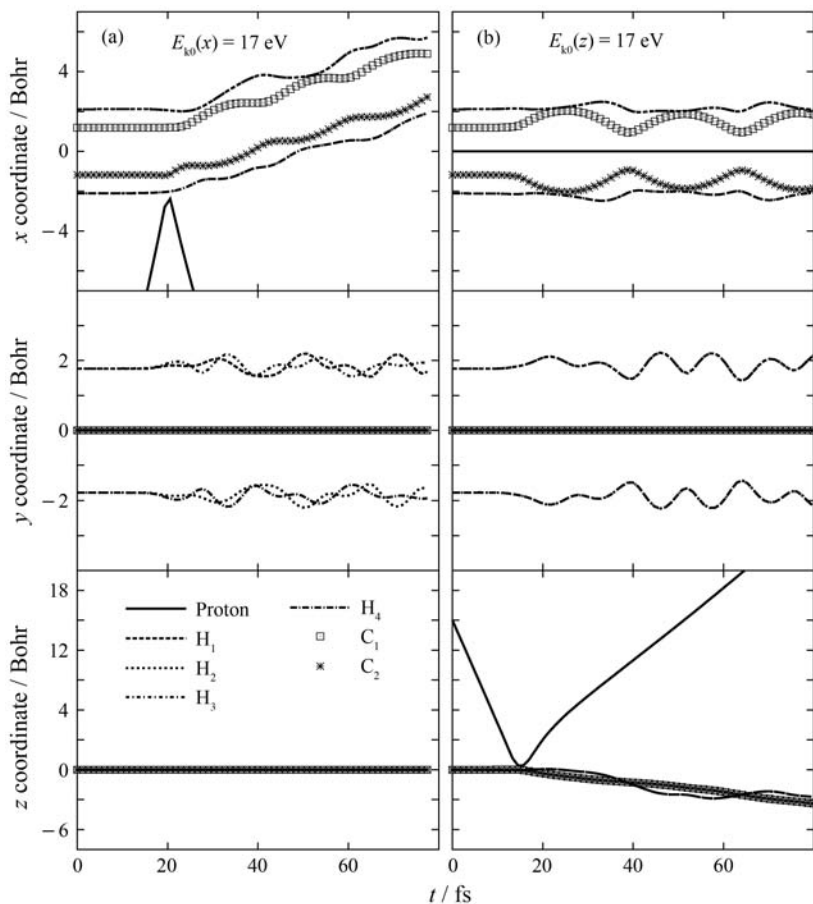


Fig. 2 The time evolution of motion of proton and ethylene for the same events shown in Fig. 1.

proton and ethylene for the same events in Fig. 1. In Fig. 3 the time dependence of the kinetic energy loss of proton and kinetic energy of ethylene are presented.

In Fig. 2, one can find that in the first case, as shown in the top panel in Fig. 2(a), the proton

is backward scattered in the ethylene plane and, thereby, about 29% of its initial kinetic energy is lost (in Fig. 3(a)). After the excitation energy is transferred, the ethylene exhibits oscillation both in x and y directions, while it is rigid in the z direction. A closer look at the top two panels in Fig. 2

(a) shows that after the closest approach, the whole molecule moves towards the positive direction along the x axis and in the x direction carbon ions move more intensively than hydrogen ions, whereas in the y direction, carbon ions are rigid and hydrogen ions move obviously.

In the second case, as shown in the bottom panel in Fig. 2(b), the proton is backward scattered on the ethylene plane. As a result, about 80% of its initial kinetic energy is lost [in Fig. 3(a)]. Because of the large excitation energy transferred [in Fig. 3(b)], the ethylene exhibits some strong oscillations in x and y directions and direct extension in the z direction. Finally, ethylene fragments in the z direction (not shown). Again, as

shown in Fig. 2(b), we can find that the carbon ions move more intensively than hydrogen ions in the x direction while the carbon ions are rigid in the y direction. Furthermore, from Figs. 3(a) and (c), it is easy to see that the kinetic energy of proton first increases before contact. We attribute this to the medium-range polarization interaction. Comparing Figs. 3(b) and (d) one can find that in the second case, ethylene gained more energy because the proton penetrates more. This is in accord with the ionization of ethylene in Fig. 1. Furthermore, the vibrational kinetic energy of ethylene in Figs. 3(b) and (d) indicates that the ethylene is oscillating for some time after the collision.

Fig. 4 shows the time evolution of the root-

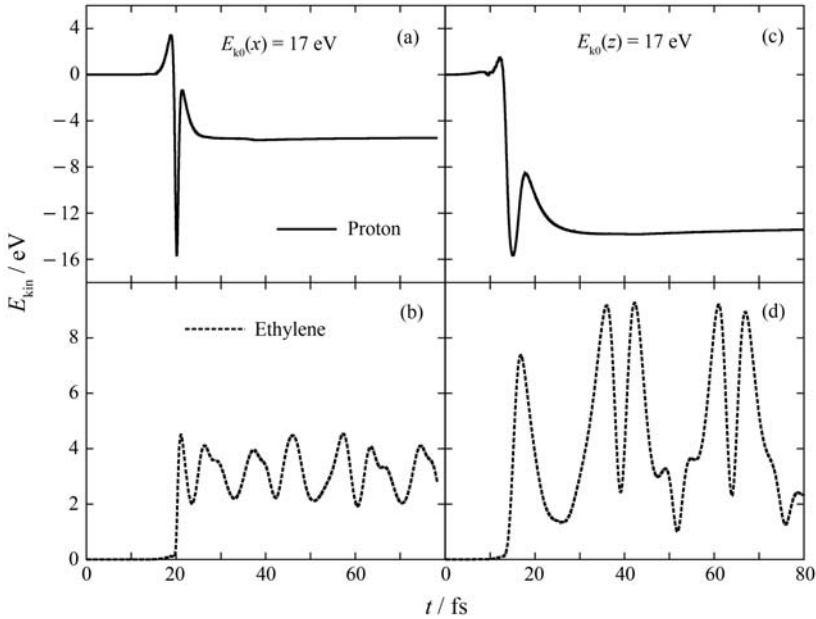


Fig. 3 The time evolution of the kinetic energy loss of proton and kinetic energy of ethylene for the same events(in Fig. 1).

mean-square radius of electrons for the same events shown in Fig. 1. Comparing the time scales in Fig. 4 and Fig. 1, we can find that, in both cases, the $rm_{s_{el}}$ starts to increase when electrons start to escape. After the proton leaves the numerical box, the $rm_{s_{el}}$ decreases quickly trying to find the new equilibrium state. After the N_{esc} is almost saturated, as the ions are moving, the $rm_{s_{el}}$ shows oscillation. However, for the case of $E_{k_0}(z) = 17$

eV, ions get more kinetic energies during the collision process, as a consequence, the $rm_{s_{el}}$ exhibits stronger oscillation than the case of $E_{k_0}(x) = 17$ eV.

In Fig. 5, the kinetic energy loss of proton as a function of impact energy E_{k_0} and collision orientation is shown. It is easy to find that when the collision orientation is along the x direction, the kinetic energy loss of proton ΔE_{kin} increases smoothly with E_{k_0} , whereas when the collision orientations

are along the y and z directions, as shown in the insert of Fig. 5, ΔE_{kin} decreases first with increasing E_{k_0} , while for $E_{k_0} \geq 250$ eV, ΔE_{kin} increases with increasing E_{k_0} . Thus, the microscopic calculations reveal some velocity-dependent excitation energies with dominating electron nature. This is in accord with the velocity-proportional electron stopping power model^[21]. Furthermore, comparing the scales of energy loss in Fig. 5, we can also find that for the same E_{k_0} , the ΔE_{kin} is much larger when the collision orientation is along the x direction.

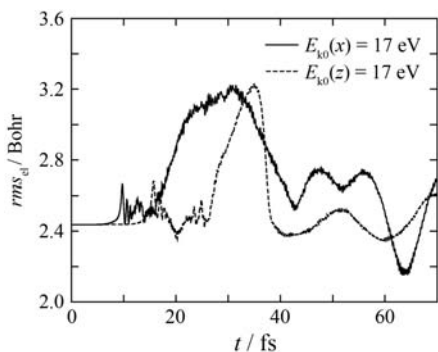


Fig. 4 The time evolution of the root-mean-square radius of electrons for the same events shown in Fig. 1.

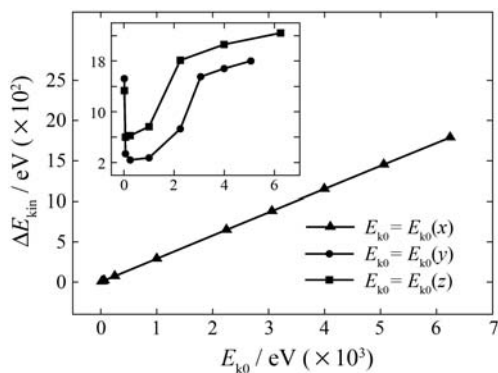


Fig. 5 The kinetic energy loss of proton as a function of impact energy E_{k_0} of proton for three different collision orientations.

4 Conclusion

In summary, in the framework of the time dependent local density approximation, which applied to valence electrons, coupled non-adiabatically to molecular dynamics of ions, we explore the elec-

tron and vibration excitations of ethylene colliding with proton. The influence of collision orientations on the collision scenario were studied in detail. It was found that for the same impact energy 17 eV, ionization is enhanced and the proton could capture more electrons when the collision orientation is along the z direction. In addition, a strong relation of the electronic and ionic excitation process is observed. Furthermore, it is found that the velocity-dependent excitation energies obtained in our microscopic calculations are consistent with the velocity-proportional electron stopping power model.

References:

- [1] SONNTAG C. The Chemical Basis for Radiation Biology. New York; Taylor and Francis in London, 1987, 302–334.
- [2] MICHAEL B D, ONEILL P D. Science, 2000, **287**: 1603.
- [3] LUNA H, MONTENEGRON E C. Phys Rev Lett, 2005, **94**: 043201.
- [4] MELO W S, SANTOS A C F, ANNA M M S, *et al.* J Phys B, 2006, **39**: 3519.
- [5] BACCHUS-MONTABONEL M C, TERGIMAN Y S, TALBI D. Phys Rev A, 2009, **79**: 012710.
- [6] DREIZLER R M, GROSS E K U. Density Functional Theory: An Approach to the Quantum Many-body Problem. Berlin: Springer, 1990, 189–223.
- [7] CALVAYRAC F, REINHARD P G, SURAUD E, *et al.* Phys Rep, 2000, **337**: 493.
- [8] REINHARD P G, SURAUD E, ULLRICH C A. Eur Phys J D, 1998, **1**: 303.
- [9] YABANA K, TAZAWA T, ABE Y, *et al.* Phys Rev A, 1998, **57**: R3165.
- [10] SAALMANN U, SCHMIDT R. Phys Rev Lett, 1998, **80**: 3213.
- [11] BAER R, SIAM N. J Chem Phys, 2004, **121**: 6341.
- [12] KUNERT T, SCHMIDT R. Phys Rev Lett, 2001, **86**: 5258.
- [13] TRUJILLO R C, DEUMENS E, OHRN Y, *et al.* Phys Rev A, 2007, **75**: 052702.
- [14] TAVERNELLI I, GAIGÉOT M P, VUILLEUMIER R, *et al.* Chem Phys Chem, 2008, **9**: 2099.
- [15] LEVINEANDAND Z, SOVEN P. Phys Rev A, 1984, **29**: 625.
- [16] LEGRAND C, SURAUD E, REINHARD P G. J Phys B,

- 2002, **35**: 1115.
- [17] GOEDECKER S, TETER M, HUTTER J. Phys Rev B, 1996, **54**: 1703.
- [18] CALVAYRAC F. Ann Phys (NY), 1997, **255**: 125.
- [19] CALVAYRAC F. Ann Phys (Paris), 1998, **23**: 1.
- [20] ULLRICH C A. J Mol Struct (THEOCHEM), 2000, **501**—**502**: 315.
- [21] ZIEGLER J F, BIRSACK J P, LITTMARK U. The Stopping and Range of Ions in Solids. New York: Pergamon Press, 1985, 121—142.

质子与乙烯分子碰撞的密度泛函理论研究

王志萍^{1, 2, 1)}, 张丰收², 王 菁²

(1. 江南大学理学院, 江苏 无锡 214122;

2. 北京师范大学核科学与技术学院, 射线束技术与材料改性教育部重点实验室, 北京 100875)

摘要: 采用含时局域密度近似与分子动力学相结合的方法研究了不同入射速度的质子与乙烯分子碰撞的动力学。计算了质子的能量损失及碰撞后乙烯分子的电子和离子的运动状态, 研究了质子的入射方向及入射动能对整个系统的碰撞动力学的影响。计算结果表明, 当入射质子的动能较小($E_{k0} < 250$ eV)时, 在相同的入射速度下, 当质子垂直于分子平面入射时, 系统的电离最大, 质子俘获的电子多; 当质子的入射动能 $E_{k0} > 250$ eV 时, 质子的能量损失与入射方向有密切的关系。

关键词: 分子电离; 能量损失; 碰撞方向

中图分类号: O571.5 **文献标志码:** A

收稿日期: 2011-12-16; 修改日期: 2012-01-11

基金项目: 中央高校基本科研业务费专项资金资助(JUSRP111A21); 国家重点基础研究发展计划项目(973 计划)(2010CB832903); 江南大学自主科研项目; 江苏省教育科学“十一五”规划课题(2008 年度高教系统 34); 江苏省高等教育学会“十一五”教育科学规划课题(JS053)

1) E-mail: zpwang03247@163.com