

Low-energy Electron Collisions with Gas-phase Thymine Molecule

Irina V. CHERNYSHOVA¹, Jenő E. KONTROS¹, Otto B. SHPENIK¹,
Jelena TAMULIENE^{2*}, Mindaugas L. BALEVICIUS³

¹ Institute of Electron Physics, Ukrainian National Academy of Sciences, 88 017 Uzhgorod, Ukraine

² Institute of Theoretical Physics and Astronomy, Vilnius University, A. Gostauto 12, LT-01108 Vilnius, Lithuania

³ Physic Faculty, Vilnius University, Sauletekio al. 9 III rumai, LT-10222 Vilnius, Lithuania

crossref <http://dx.doi.org/10.5755/j01.ms.17.3.601>

Received 01 October 2010; accepted 20 March 2011

The paper presents an investigation of the negative ion formation of the thymine (T) molecule. The formation of negative ions by electron impact of this molecule is measured. The quantum mechanical investigations are performed to calculate the electron attachment cross section, the force constants, the resulting vibrational frequencies and intensities. The absorption spectrum and their nature are investigated too. The obtained results allows us to foresee the mechanism of production of the [T-H]⁻ ion and explain the origin of some features in the experimental negative ion formation of the thymine molecule.

Keywords: low energy, electron collision, thymine, cross section.

1. INTRODUCTION

The low energy electron attachment to DNA is known as the dissociative electron attachment process that causes single and double strands breaks. These breaks are responsible for about one-third of the mutagenic damages and about two-thirds of the damages can be linked to the secondary species such as electrons and radicals formed in the interaction of the primary radiation with the irradiated materials [1]. At the present time, a lot of examinations of bond breaking initiated by electron impact on the gas phase constituents of DNA have been performed to understand the above dissociative electron attachment process. Although the considerable progress has been made to identify a number of resonances that are important in the disruption of DNA by slow electrons, the identity of the observed resonances is not always clear. Moreover, comparisons between attachment and transmission measurements on the nucleobases show only a partial correspondence, indicating that the strongest resonance features in the total cross section are not necessarily responsible for the strongest features in dissociative-attachment cross section [2, 3]. On the other hand, the energy positions of low energy resonances presented in the electron scattering are different. As an example, many resonances observed in spectrum measurement by S. Denifl et al. are not present in spectrum of M. A. Huels. Tonzani and Green found resonances at 2.4 eV, 5.5 eV and 7.9 eV for thymine, while Winstead et al. prove that the above resonances is 0.3 eV, 1.9 eV and 5.7 eV [2, 4]. Moreover, disagreement between interpretation of the results obtained Aflatooni et al. assigned the anion states to occupation of the lowest antibonding π_1^* orbitals of thymine, while Burrow and et al. proposed that H atoms released from the N site in thymine are produced by coupling between the temporary anion states associated with π_1^* and σ^* orbitals [5, 6]. Of course, the above

disagreements have been present because temporary anions can form through several possible mechanisms: valence or dipole-bound shape resonances, vibrational Feshbach resonances, core-excited resonances built on low-lying excited states.

In the present work, we discuss the experimental results on the formation of negative ions for low-energy (0 eV–6 eV) electrons and electron attachment to the DNA base thymine molecule. The quantum chemistry investigation of neutral thymine molecule and their anion are performed to shed some light on which orbital an electron could locate. On the other hand, our interpretation guided on experimental and theoretical results help us explain one of the possible mechanisms of electron attachment to thymine.

2. DETAILS OF INVESTIGATIONS

The negative ion formation for low-energy (0 eV–6 eV) electron scattering and electron attachment to the DNA base thymine molecule in the gas-phase were carried out using a gas-filled cell. The controlled-energy electron beam ($\Delta E_{1/2} = 0.15$ eV) was formed by using a hypocycloidal electron monochromator [7]. The reservoir with thymine heated to 390 K was employed. The above temperature was considerably below the parent molecule decomposition temperature of about 590 K. Negative ions were extracted from the interaction region by a low voltage (~ 1.5 V) applied to the ion collector. The electron energy scale was calibrated using the position of the maximum of the first derivative of the electron beam current in the initial region of the voltage-to-current characteristic.

The structural origin of the thymine molecule has been studied by using the generalized gradient approximation for the exchange-correlation potential in the density functional theory (DFT) as it is described by Becke's three-parameter hybrid functional, using the non-local correlation provided by Lee, Yang, and Parr [8–10]. The DFT method is commonly referred to as B3LYP, that is a representative standard DFT method. The cc-pVTZ basis

*Corresponding author. Tel.: +370-5-2193259; fax.: +370-5-2125361.
E-mail address: Jelena.Tamulienė@tfai.vu.lt (J. Tamulienė)

set has been used as well [11]. It is Dunning's correlation consistent triple-zeta basis set that has had redundant functions removed, but includes polarization functions and have been rotated in order to increase the computational efficiency.

The structure of the investigated thymine molecule has been optimized globally without any symmetry constraint by using Berny geometry optimization procedure applying the above approach [12]. The force constants, the resulting vibrational frequencies and intensities are also computed applying the above approach. The analysis of the most intensive frequencies allowed us to foresee the most probable dissipation (fragmentation) of thymine. Additionally the negative ion formation cross-section of the thymine molecule has been calculated using the binary-encounter-Bethe (BEB) model [13]. Applying the above approach, the electron-induced cross-section was obtained as the sum of the cross-sections for each individual molecular orbital. The electron occupation number was evaluated from Mulliken population analysis [14]. The electron binding energy, the orbital kinetic energy were calculated for the ground state of the geometrically optimized molecule at the above described level using Gaussian and GAMESS program packets [15–16]. The experimentally measured negative ion formation cross-section for electron scattering as a function of electron energy for thymine was normalized to cross-section calculated using the above approach. The optical spectrum of the thymine molecule was obtained by the singly-excited CI (CIS) method that is the simplest way to treat the excited states [17].

3. RESULTS

The experimentally obtained negative ion formation cross-section of the thymine molecules is presented in Fig. 1. This cross-section was normalized to cross-section calculated using B3LYP/cc-pVTZ approach at the energy 5 eV.

It is necessary to mention that in the calculated cross-section curve a distinct resonant-like peak is not observed. Usually, the above distinct resonant-like peaks are attributed to the formation of short-lived negative-ion state(resonance) when the approaching electron is captured temporarily by the molecule into a vacant energy level and

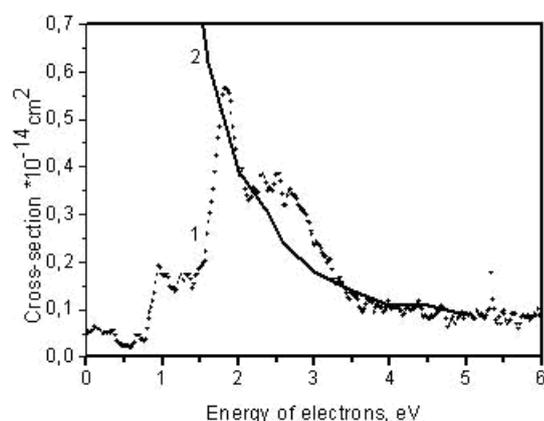


Fig. 1. The negative ion formation cross-section of thymine molecule obtained experimentally (1) and calculated (2)

then the extra electron may leave the parent molecule in the vibration level of the ground electronic state or may decompose into negative and neutral fragments [13]. However, in the experimental negative ion formation cross-section of the thymine molecule some features are appeared (Fig. 1). Such features were observed by Aflatooni and et al. [5]. The observed peaks are broad that allows to predict the production $[T-H]^-$ from thymine that proceeds through loss of H [6].

It is very well known that the wave functions play an important role in the electron scattering processes. Hence, we intend to discuss nature of the occupied and virtual orbitals that are presented in Fig. 2 and Table 1. It is possible to see that in Fig. 2 presented orbitals are antibonding. It implies that the molecule could be destructed without any temporary state, i. e. the excitation of this molecule could lead to the production of the negative ion formation.

Table 1. The most important orbitals for excitations of the thymine molecule and their nature

Excitation	Transitions	Nature
I	HOMO-2 \rightarrow LUMO	$\sigma \rightarrow \pi^*$
II	HOMO \rightarrow LUMO	$\pi \rightarrow \pi^*$
III	HOMO-3 \rightarrow LUMO+1	$\sigma \rightarrow \pi^*$
IV	HOMO \rightarrow LUMO+1	$\pi \rightarrow \pi^*$
V	HOMO-1 \rightarrow LUMO+1	$\pi \rightarrow \pi^*$
VI	HOMO \rightarrow LUMO+2	$\pi \rightarrow \sigma^*$
VII	HOMO-1 \rightarrow LUMO+1	$\pi \rightarrow \pi^*$
VIII	HOMO-3 \rightarrow LUMO	$\sigma \rightarrow \pi^*$
IX	HOMO-2 \rightarrow LUMO+1	$\sigma \rightarrow \pi^*$
X	HOMO \rightarrow LUMO+2	$\pi \rightarrow \sigma^*$

Hence, to explain production of the $[T-H]^-$ ion from thymine the excitation spectrum was calculated. The spectrum is presented in Fig. 3. It is possible to see that the excitation from ground to II, IV, IV and VII excited states are allowed while the excitation to III, V, and IV investigated state is forbidden. The investigations of molecular orbital coefficients of the most important molecular orbital allow us recognize the nature of excitation. The results obtained are presented in Table 1. It is possible to see that the forbidden excitations correspond to $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ excitations. These excitations are important for the destruction of the thymine molecule because the excited molecule dissipate their energy due to vibrations and rotations to reach ground state and, as a consequence, to decompose into negative and neutral fragments. However, excitation energy does not correspond to any resonances observed in the negative ion formation cross-section. Therefore transitions between excited states were investigated. It was found several transition energies that are equal to the energies of the above features (Table 2). The above transitions between excited states are partly or fully forbidden and indicate that the excitation energy should be absorbed or dissipated through vibrations and rotations.

Based on the analysis of the normal modes of the thymine molecule it is possible to foresee that during the vibrations and rotations the thymine molecule could be deprotonated, i. e. one of the bond with H atom should be destructed.

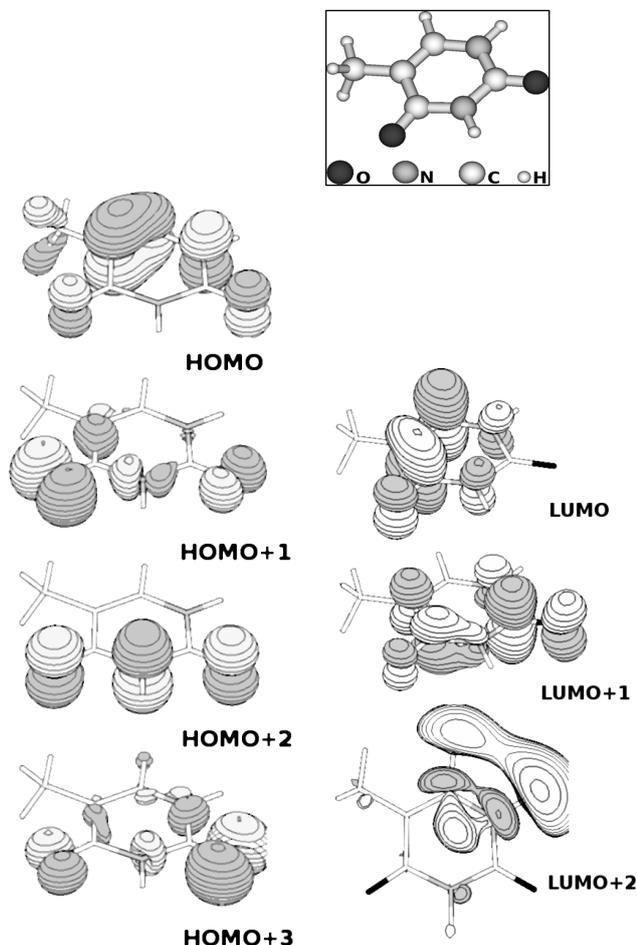


Fig. 2. Views of the thymine molecule (on bottom) and their highest occupied (on left) and the lowest valence (on right) orbitals

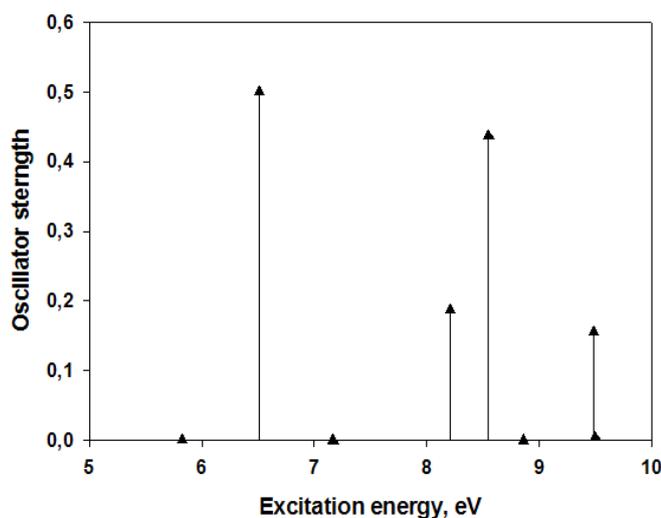


Fig. 3. Excitation spectrum of the thymine molecule obtained by CIS RHF/cc-pVTZ approach

Most probably, that N-H bond could be destructed to form $[T-H]^-$ ion, because in all normal modes the vibrations or rotations of the H atoms bonded with N atoms are presented.

Hence, basing on the results of investigations it is possible to explain the observed peaks of the resonance energies in the negative ion formation cross-section of the thymine molecule and the formation of the anions in the following way:

1. The impact electron excites the thymine molecule;

2. The two possible schemes could be realised: (i) the excited thymine molecule dissipates its energy due to vibrations and rotations and, as a consequence, the $[T-H]^-$ ion is formed; (ii) the other electron excites the thymine molecule (for example, from I to III excited state) again and this excitation leads to formation of the $[T-H]^-$ ion.

Table 2. Most important transitions between excited states for the electron-thymine scattering

Transitions	Energy, eV
I \rightarrow III	1.32
I \rightarrow VII	3.63
I \rightarrow VIII	3.65
I \rightarrow XI	4.40
II \rightarrow IV	1.71
II \rightarrow IX	3.75
II \rightarrow X	3.90
III \rightarrow VI	1.69
IV \rightarrow V	0.34
V \rightarrow VI	0.31
V \rightarrow IX	1.70
V \rightarrow X	1.86
IX \rightarrow X	0.16

4. CONCLUSIONS

We present investigation results of the thymine molecule negative ion formation cross-section. The measured cross-section is normalized to obtain theoretically one. This combined work demonstrates the following:

1. The resonances in the negative ion formation cross-section of the thymine molecule are obtained due to the thymine molecule excitations.

2. Interaction of low-energy electrons with the thymine molecule leads to the formation of $[T-H]^-$ anion. Most probable that the above anion is formed due to N-H bonds breaking.

According to the results of our investigations the first features could be identified as mixed π^*/σ^* shape resonances, while the last one could be π^* shape resonance.

In summary, it is necessary to mention that our results fit very well with the previously obtained results on the electron impact excitation of thymine molecule. Results of our investigations indicate that free electron attachment to thymine yields major fragment $[T-H]^-$ anion and no parent anions effectively. It is obtained that the above anion is produced through loss of the H atom from the N sites takes

place by π^*/σ^* mixing and produce a broad peak at the energy of the resonances also [6].

Acknowledgments

The work was supported, in part, by the Lithuania-Ukraine projects M/78-2009 (ICh, JK) and by Research Council of Lithuania TAP-55/2010, TAP-37/2010 (JT) as well as COST MP 0802 activity.

REFERENCES

1. **Denifl, S., Ptasinka, S., Cingel, M., Matejcik, S., Scheier P., Mark, T. D.** Electron Attachment to the DNA Bases Thymine and Cytosine *Chemical Physics Letters* 377 2003: pp. 74–80.
2. **Winstead, C., McKoy, V.** Resonant Interactions of Slow Electrons with DNA Constituents *Radiation Physics and Chemistry* 77 2008: pp. 1258–1264.
3. **Sanche, L.** Low Energy Electron-driven Damage in Biomolecules *European Physical Journal D* 35 2005: pp. 367–390.
4. **Tonzani, S., Green Ch. H.** Low-energy Electron Scattering from DNA and RNA Bases: Shape Resonances and Radiation Damage *Journal of Chemical Physics* 124 2006: pp. 054312 (1)–054312 (11).
5. **Aflatooni, K., Gallup, G. A., Burrow, P. D.** Electron Attachment Energies of the DNA Bases *Journal of Chemical Physics* A 102 1998: pp. 6205–6207.
6. **Burrow, P., Gallup, G. A., Scheer, A. M., Denifl, G., Ptasinka, S., Mark, T., Scheier, P.** Vibrational Feshbach Resonances in Uracil and Thymine *Journal of Chemical Physics* 124 2006: pp. 124310(1)–124310(7).
7. **Romanyk, N. I., Shpenik, O. B., Mandy, I. A., Papp, F. F., Chernyshova, I.V.** Hypocycloidal Electron Monochromator with a Nonuniform Electric Field and Its Optimization *Technical Physics* 38 1993: pp. 599–603.
8. **Becke, A. D.** Density-functional Thermochemistry. III. The Role of Exact Exchange *Journal of Chemical Physics* 98 1993: pp. 5648–5653.
9. **Lee, C., Yang, W., Parr, R. G.** Development of the Colle-Salvetti Correlation-energy Formula into a Functional of the Electron Density *Physical Review B* 37 1998: pp. 785–89.
10. **Miehlich, B., Savin, A., Stoll, H., Preuss, H.** Results Obtained with the Correlation-energy Density Functionals of Becke and Lee, Yang and Parr *Chemical Physics Letters* 157 1989: pp. 200–206.
11. **Wilson, A. K., van Mourik, T., Dunning Jr., T. H.** Gaussian Basis Sets for Use in Correlated Molecular Calculations. VI. Sextuple Zeta Correlation Consistent Basis Sets for Boron through Neon *Journal of Molecular Structure (Theochem)* 388 1996: pp. 339–49.
12. **Li, X., Frisch, M. J.** Energy-represented DIIS within a Hybrid Geometry Optimization Method *Journal of Chemical Theory and Computation* 2 2006: pp. 835–39.
13. **Szmytkowski, C., Domaracka, A., Mozejko, P., Ptasinska-Denga, E.** Electron Collisions with Ethylene Oxide Molecules *Journal of Physics B: Atomic, Molecular and Optical Physics* 41 2008: pp. 065204 (1)–065204 (6).
14. **Mulliken, R. S.** Electronic Population Analysis on LCAO-MO Molecular Wave Functions *Journal of Chemical Physics* 23 1955: pp. 1833–1840.
15. Gaussian 03, Revision C.02, **Frisch, M. J., Trucks, G. W., Schlegel, H. B., and et al.** Gaussian, Inc., Wallingford CT, 2004.
16. Advances in Electronic Structure Theory: GAMESS a Decade Later **Gordon, M. S., Schmidt, M. W.** pp. 1167–1189, in "Theory and Applications of Computational Chemistry: the First Forty Years" C. E. Dykstra, G. Frenking, K. S. Kim, G. E. Scuseria (editors). Elsevier, Amsterdam, 2005.
17. **Foresman, J. B., Head-Gordon, M., Pople, J. A., Frisch, M. J.** Toward a Systematic Molecular Orbital Theory for Excited States *Journal of Physical Chemistry* 96 1992: pp. 135–149.