Commun. Comput. Chem.
doi: 10.4208/cicc.2016.v4.n3.1

Vol.4, No.3, pp.73-77
Dec 2016

COMMUNICATION

Underestimation of Charge-Transfer Emission Energy Calculated by State-Specific Polarization Continuum Model

Jian Luo[a,b], Songqiu Yang[a]*

[a]*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, China.*

[b]*University of the Chinese Academy of Sciences, Beijing 10049, China.*

Received 1 Dec 2016; Accepted (in revised version) 25 Dec 2016

ABSTRACT Charge-transfer (CT) emission energies of adenine-thymine dinucleotide are calculated by two commonly used polarized continuum models (PCM): linear-response PCM (LR-PCM) and state-specific PCM (SS-PCM). Time-dependent functional theory is used. The SS-PCM method is found to underestimate the CT emission energy relative to the LR-PCM method. The underestimation degree is more significant as the amount of transferred charges is larger. As a result, the SS-PCM method should be used with great caution when dealing with electronic transitions with significant CT characters.

AMS subject classifications: 82B21, 82C21,92C45

Keywords: TDDFT, DNA, excited state, theory method.

In the photodynamics of DNA, Charge-transfer (CT) states are easily formed between two stacked bases and play an essential role in the photophysical and photochemical properties of DNA [1-3]. Time-resolved spectroscopy detects the evolutions of CT states and measures their lifetimes. Ab initio calculations can give deep insights into the nature of CT states, such as the amount of transferred charges and their energy profiles [4]. The reliability of the theoretical method is of primary importance when discussing the theoretical results. A simple and common criterion is to compare the calculated electronic excitation and emission energies with the experimental results. Because CT states are dark states and cannot be excited by UV light, their excitation energies cannot be measured by spectroscopy techniques [5]. On the

---

* Corresponding author *E-mail address*: sqyang@dicp.ac.cn

other hand, the emissions of CT states are highly distinguishable in fluorescence spectra [3]. Therefore, the reliability of theoretical methods can be evaluated by comparing the calculated emission energies of CT states with experimental results.

Time-dependent density functional theory (TD-DFT) is commonly used in the excited-state calculations of DNA due to the large amount of atoms of DNA. Combined with linear-response polarized continuum model (LR-PCM) [6] or state-specific PCM (SS-PCM) [7], TDDFT is able to calculate the CT emission energies of DNA in aqueous solution. Generally, the geometry optimization of CT states is performed using LR-PCM due to the unavailable SS-PCM in excited-state optimizations in Gaussian 09 program [8]. Then, the minimum CT geometry is used to calculate the emission energy using SS-PCM because it is believed to be more accurate than LR-PCM owing to considering the dynamical effects [9, 10]. However, many previous studies using this combination method to calculate the CT emission energies of adenine-thymine (A-T) DNA systems find that the calculated values are significantly lower than experiment [9, 11]. Therefore, in order to provide a guideline for the future ab initio calculations on aqueous systems, it is necessary to evaluate the reliability of using SS-PCM when dealing with CT states.

In our recently published paper, we discuss the CT emission energy of T-A dinucleotide [12]. Nine water explicit molecules are included in the calculation model to consider the intermolecular hydrogen bonding interactions. The SS-PCM is found to severely underestimate the CT emission energy while LR-PCM gives reasonable results. As a result, the LR-PCM result can be used as a standard.

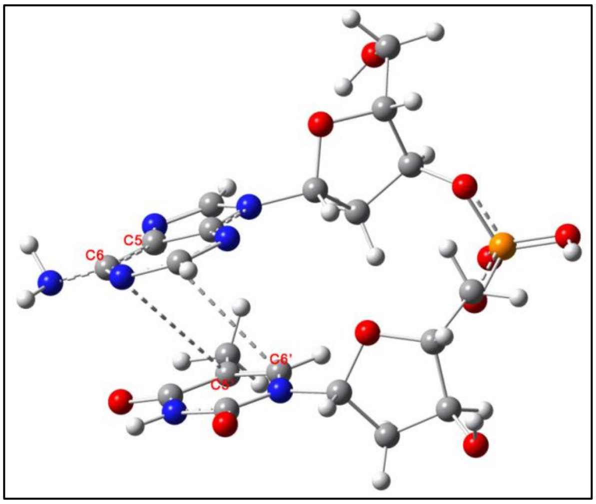

Fig. 1: Chemical structure of A-T dinucleotide.

In this communication, we give a further study on the discrepancy of SS-PCM dealing with excited states with CT characters of A-T dinucleotide (**Fig. 1**). Various A-T dinucleotide conformers with different interbase distances are discussed. We find that the underestimation of emission energies by the SS-PCM method is dependent with the amount of transferred charges in the excited-state transitions.

The M052X density functional was the primary functional because it performed well when dealing with CT states [9, 11, 12]. In all calculations, the 6-31G(d) basis set was used. The equilibrium CT geometry of A-T dinucleotide was optimized by LR-PCM/TD-M052X/6-31G(d) method. Then, after fixing the C5-C6′ and C6-C5′ bonds at a same length, the CT geometry of A-T dinucleotide was optimized at the same calculation level. Emission energies were calculated by LR-PCM and SS-PCM in equilibrium regime, respectively. The sum of atomic charges of A and T in the excited and ground states were calculated according to the Mulliken population analysis. Then the amount of transferred charges from A to T was calculated.

The equilibrium CT geometry of A-T dinucleotide by the LR-PCM/TD-M052X/6-31G(d) method is shown in **Fig. 2**, as well as the C5-C6′ and C6-C5′ bond distance. From the Mulliken population analysis, the amount of the transferred charges from A to T in the CT transition is 0.27 a.u. The emission energies of the CT state are 3.33 and 2.97 eV calculated by LR-PCM and SS-PCM, respectively. It is clear that SS-PCM underestimates 0.36 eV of the CT emission energy compared to LR-PCM.

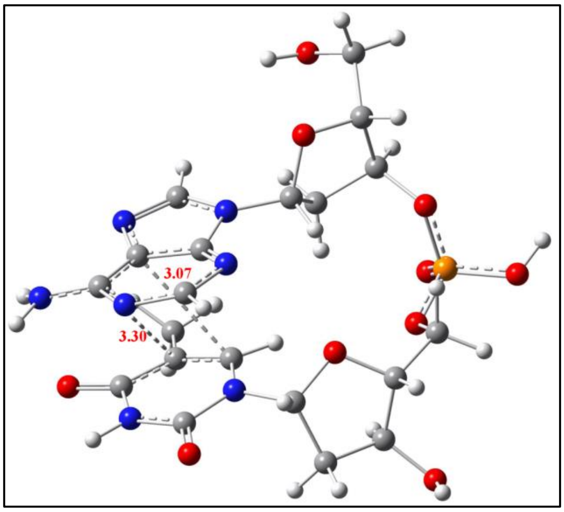

Fig. 2: The equilibrium charge-transfer geometry of A-T dinucleotide optimized by the LR-PCM/TD-M052X/6-31g(d) method. The bond distances are in unit Å.

In order to give a quantitative insight into the relationship between the underestimation of SS-PCM on the CT emission energy and the amount of transferred charges, a series of locally equilibrium CT geometries of A-T dinucleotide are optimized by fixing the interbase distance at different lengths. As shown in **Table 1**, as the interbase distance decreases, the amount of transferred charges from A to T is decreased, as well as the transition energies. In all cases, the SS-PCM method underestimates the CT transition energy relative to the LR-PCM method. And the underestimation degree is more severe when the amount of the transferred charges in the CT transition is large. When the amount of transferred charges is reduced to only 0.05 a.u, the calculated transition energies by LR-PCM and SS-PCM methods are nearly same. Note that in the equilibrium CT geometry, the underestimation of the emission energy by SS-PCM is 0.36 eV where the amount of the transferred charge is 0.27 a.u. This is in a good agreement with the tendency shown in **Table 1.**

In conclusion, we study the underestimation of the CT transition energy by the SS-PCM method relative to the LR-PCM method. As the amount of the transferred charges in electronic transitions increases, the transition energy difference between the SS-PCM and LR-PCM is increased. The discrepancy of the SS-PCM is possibly due to the way obtaining the optimized geometry, which uses the LR-PCM method. The two PCM methods use different ways to deal with the solvent response to electronic transitions [10]. Given that the SS-PCM is unavailable in the optimization process [8], it must take great caution to use SS-PCM to calculate the transition energies with significant CT characters.

Table 1 Properties of the locally optimized charge-transfer geometry of A-T dinucleotide by fixing the C5-C6′ and C6-C5′ bonds at different lengths by the LR-PCM/TD-M052X/6-31G(d) method: the amount of transferred charges (ΔQ, in a.u.) from adenine to thymine, the calculated emission energy (in eV) by LR-PCM and SS-PCM, and the energy difference (ΔE, in eV) between the two PCM methods.

	3.6Å	3.5 Å	3.0 Å	2.9 Å	2.4 Å	2.3 Å
ΔQ /a.u.	0.38	0.37	0.21	0.19	0.09	0.05
LR-PCM/eV	3.91	3.81	3.19	2.99	2.27	1.51
SS-PCM/eV	2.91	2.98	2.96	2.84	2.23	1.50
ΔE/eV	1.00	0.83	0.23	0.15	0.04	0.01

ACKNOWLEDGMENT

We are grateful to the National Natural Science Foundation of China (Grant No: 21303198).

REFERENCES

[1] L. Martinez-Fernandez, Y. Zhang, K. de La Harpe, A.A. Beckstead, B. Kohler, R. Improta, Photoinduced long-lived charge transfer excited states in AT-DNA strands, Phys. Chem. Chem. Phys., 18 (2016) 21241-21245.

[2] H. Yin, Y. Ma, J. Mu, C. Liu, M. Rohlfing, Charge-Transfer Excited States in Aqueous DNA: Insights from Many-Body Green's Function Theory, Phys. Rev. Lett., 112 (2014) 228301-228305.

[3] W.-M. Kwok, C. Ma, D.L. Phillips, "Bright" and "Dark" Excited States of an Alternating AT Oligomer Characterized by Femtosecond Broadband Spectroscopy, J. Phys. Chem. B, 113 (2009) 11527-11534.

[4] I. Conti, A. Nenov, S. Hoefinger, S.F. Altavilla, I. Rivalta, E. Dumont, G. Orlandi, M. Garavelli, Excited state evolution of DNA stacked adenines resolved at the CASPT2//CASSCF/Amber level: from the bright to the excimer state and back, Phys. Chem. Chem. Phys., 17 (2015) 7291-7302.

[5] A.W. Lange, J.M. Herbert, Both Intra- and Interstrand Charge-Transfer Excited States in Aqueous B-DNA Are Present at Energies Comparable To, or Just Above, the (1)pi pi* Excitonic Bright States, J. Am. Chem. Soc., 131 (2009) 3913-3922.

[6] M. Cossi, V. Barone, Time-dependent density functional theory for molecules in liquid solutions, J. Chem. Phys., 115 (2001) 4708-4717.

[7] R. Improta, G. Scalmani, M.J. Frisch, V. Barone, Toward effective and reliable fluorescence energies in solution by a new state specific polarizable continuum model time dependent density functional theory approach, J. Chem. Phys., 127 (2007) 074504-074509.

[8] M.J.T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.;, M.A.C. Robb, J. R.; Scalmani, G.; Barone, V.; Mennucci,, G.A.N. B.; Petersson, H.;et. al., Gaussian 09, revision D.01; Gaussian Inc. : Wallingford, CT,, DOI 10.1021/jp001362w(2009).

[9] R. Improta, V. Barone, Interplay between "Neutral" and "Charge-Transfer" Excimers Rules the Excited State Decay in Adenine-Rich Polynucleotides, Angew. Chem., Int. Ed., 50 (2011) 12016-12019.

[10] S. Corni, R. Cammi, B. Mennucci, J. Tomasi, Electronic excitation energies of molecules in solution within continuum solvation models: Investigating the discrepancy between state-specific and linear-response methods, J. Chem. Phys., 123 (2005).

[11] A. Banyasz, T. Gustavsson, D. Onidas, P. Changenet-Barret, D. Markovitsi, R. Improta, Multi-Pathway Excited State Relaxation of Adenine Oligomers in Aqueous Solution: A Joint Theoretical and Experimental Study, Chem-Eur. J., 19 (2013) 3762-3774.

[12] J. Luo, Y. Liu, S. Yang, Role of base arrangements and intermolecular hydrogen bonding in charge-transfer states of thymine-adenine dinucleotide in aqueous solution, J. Photoch. Photobio. A, 337 (2017) 1-5.