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Comment on "Density Functional Theory Study of 1,2-dioxetanone Decomposition in Condensed Phase" [J. Comput. Chem. DOI 10.1002/jcc.22997]

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The chemiluminescence mechanism of 1,2-dioxetanone is still not fully understood. Experiments point to an inefficient chemiluminescent process and larger triplet quantum yields than singlet. Although the general aspects of the decomposition reaction have been established from accurate theoretical methods,[1,2,3] these studies cannot completely rationalize the low efficiency and triplet-singlet ratio. Recently, a density functional theory (DFT) and time-dependent TD-DFT study has proposed a novel mechanism which could explain the larger quantum yield of the phosphorescence v.s. the fluorescence emission.[4] In that mechanism, the decomposition reaction, see Fig. 1, takes place via a basically concerted mechanism, characterized by a closed-shell singlet configuration of the 1,2-dioxetanone. The lowest-lying triplet state, T_1,[5] is populated via two inter-system crossing (ISCs) points along the ground state (S_0) potential energy surface (PES), see Fig. 1. On the other hand, the lowest-lying singlet excited state (S_1) has much higher energy than S_0 and T_1 states, and can only be reached via a high-energy triplet surface (T_2). The high energy of the S_1 state has then been used as an explanation for the preference for emission from the triplet rather than the singlet excited state.

[INSERT FIGURE 1]

While the results of Ref. [4] could possible provide a qualitative explanation of the observed S-T emission ratio, is comes with two major concerns which will need to be explained in order to give any credit to the proposed new mechanism. First, the energy difference between the S_1 and T_1 states is unexpectedly large during the entire reaction path; always larger than 14 kcal/mol.[4] As these excited states are expected to be of biradical character when the O-O bond breaks, with one unpaired electron on each oxygen, this splitting would indicate an extremely strong coupling between the spins on two rather distant atomic centers. In comparison, for the more congested methylene biradical, where the spin-coupled electrons are located on the same atom, the S-T energy splitting is just 11 kcal/mol.[6]

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Secondly, the results of the DFT study are in qualitative disagreement with the results from previous theoretical studies on the chemiluminescence process of the molecule in vacuo carried out by two independent and complementary high-level *ab initio* multiconfigurational methods; the complete active space second-order perturbation theory (CASPT2)[1] and two-electron reduced-density matrix (2RDM)[2,3] methods, respectively. Both these methods give a uniform qualitative and quantitative description of the reaction. The decomposition is a two-step biradical mechanism. First O-O bond cleavage takes place, producing a biradical intermediate, followed by breaking of the C-C bond, see Fig. 2. In the vicinity of the transition state (TS) related to the O-O cleavage, the ground state becomes degenerate with some low-lying singlet and triplet excited states, which features n_O to σ^* excitations. Subsequently, the molecule enters into a region of biradical character, where the two lowest-lying singlet states and the triplet state remain close in energy within 5 kcal/mol. Finally, the system reaches the second TS, related to the C-C bond breaking, from where carbon dioxide (CO_2) is formed in the ground state and formaldehyde either in the ground state (thermal reaction) or in the excited S_1 or T_1 states (chemiluminescence).

[INSERT FIGURE 2]

Hence, the issues of (a) a suspiciously large exchange stabilization of the T_1 state over the S_1 state and (b) that the presented TD-DFT results are in severe conflict with two independent and complementary state-of-the-art *ab initio* methods with respect to the characteristics of the reaction path and the relative energies of the low-lying singlet and triplet stats, leads us to revisit the results reported by da Silva and da Silva.[4] We will here be using the same levels of theory as reported in Refs. [1] and [4], i.e., CASSCF(16 electrons, 13 orbitals)/ANO-RCC-VDZP in vacuo and MPWB1K/aug-cc-pVDZ in benzene, respectively. All calculations were performed at the geometries along the intrinsic reaction coordinate (IRC) path as reported by da Silva and da Silva.[4] The CASSCF calculations were carried

out with the MOLCAS-7 software[7] and the DFT computations with GAUSSIAN-03.[8] (See Refs. [1] and [4] for the computational details).

First, we analyze the electronic structure along the DFT path using the CASSCF method. Despite the change in reaction coordinate, as compared to the original CASSCF study, the electronic structure at the TS (IRC 0.0) has an open-shell character similar to the scenario found in the step-wise mechanism computed with the MS-CASPT2//CASSCF approach, and in contrast with the originally reported MPWB1K results. The S_1 and T_1 states feature n_O to σ^* excitations.

Second, the discrepancy between DFT and CASSCF results can be resolved by a careful analysis of the DFT results. It turns out that the closed-shell singlet reported in Ref. [4], is not a stable solution along a large part of the reaction coordinate. Instead, it is possible to find an open-shell singlet which is lower in energy (approx. 16 kcal/mol at IRC 0.0), see Fig. 1. This solution corresponds to a biradical configuration in which the spin densities are mainly localized in the oxygen atoms, similar to the results from CASSCF. Subsequent TD-DFT energy computations on top of the open-shell ground state wave function provide a new scenario for the S_1 PES with energies close to the corresponding triplet state, as can be seen in Fig. 1.

The present contribution is not aimed to evaluate the performance of different computational approaches, but rather to point out the dangers of an unreflected use of DFT for complex reactions. Although the findings reported by da Silva and da Silva seemed to offer an explanation of chemiluminescence of 1,2-dioxetanone, the results were based on an incorrect ground-state wave function, which in turn led to large errors in the calculation of the first singlet excited state. In addition to its execution, the design of the study also deserves criticism. The choice of DFT functional (MPWB1K) were made by comparisons to the observed activation barrier for the decomposition

reaction. However, most functionals designed to give accurate barriers have a large amount of Hartree-Fock exchange (44 % in the present case), which can make them inappropriate for the description of degeneracies or singlet-triplet splittings. From a methodological perspective it is also questionable to make a fit to a single data point (barrier height), especially if it is not guaranteed that the right reaction mechanism has been located.

Taking into account the presence of degeneracies (conical intersections, CIs) along the CASSCF/CASPT2 and 2RDM paths reported for the 1,2-dioxetanone decomposition reaction,[1,2,3] and the known deficiencies of DFT to describe CIs,[9] it would be challenging to apply single-reference techniques to properly characterize these crossing regions of the PESs. We believe that improvements of the theoretical description of the mechanism must be pursued in the context of accurate *ab initio* non-adiabatic nuclear dynamics.

To conclude, the reported characteristics in Ref. [4] of the 1,2-dioxetanone dissociation as a concerted reaction with a single TS is not supported by *ab initio* nor DFT theory. Furthermore, at the TS of the reaction da Silva and da Silva failed to correctly find and assign the S_0 and S_1 states. Hence, the suggested mechanism of the T-S ratio of the emission is not corroborated by any *ab initio* or DFT results and can at best be considered an unsupported hypothesis.
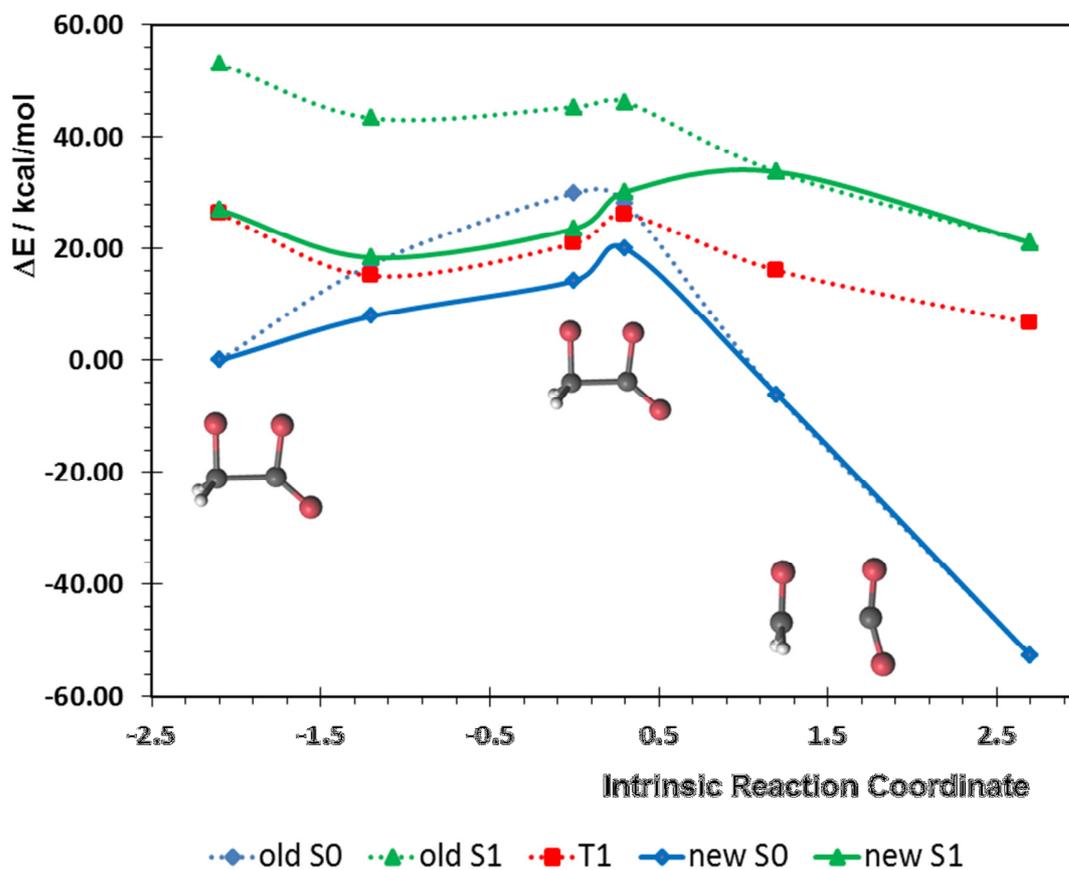
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Figure 1. Potential energy surfaces of the lowest-lying singlet and triplet states of the 1,2-dioxetanone molecule computed using MPWB1K/aug-cc-pVDZ along the decomposition reaction path. Results from the original DFT study (Ref. [4]) are shown with dotted lines while results from the present study are shown with solid lines. Note that the reaction coordinate is different from the reaction coordinates in Fig. 2.
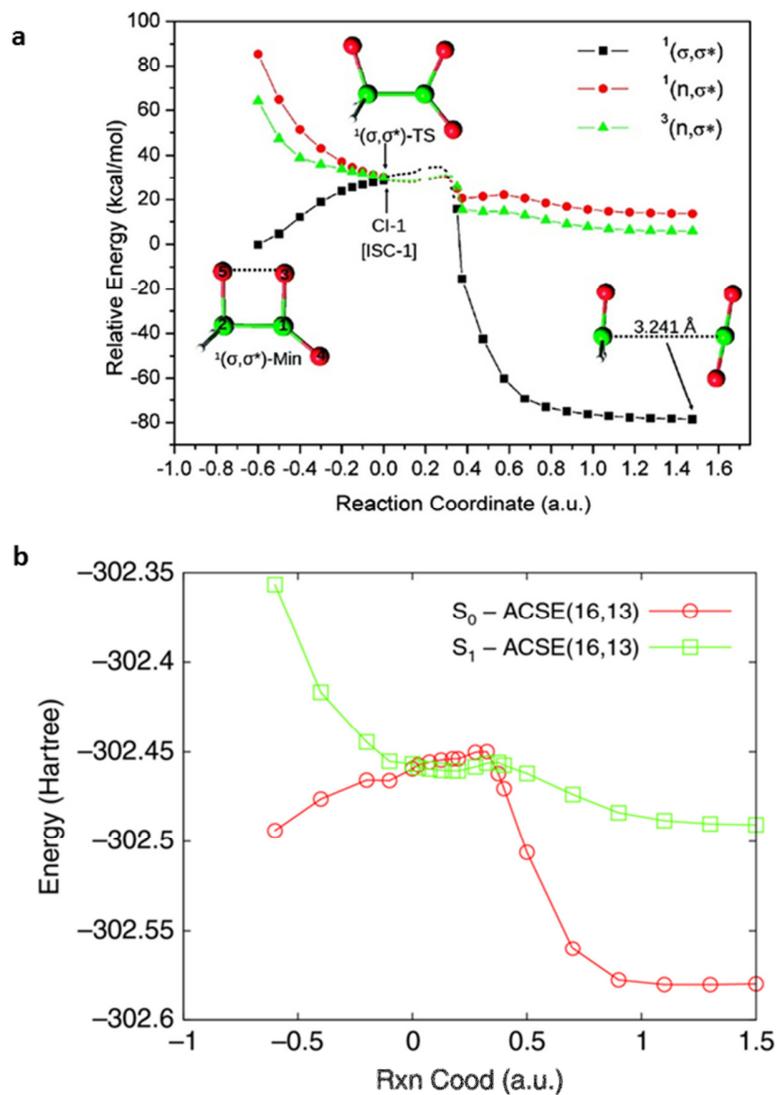
Figure 2. Potential energy surfaces of the lowest-lying singlet and triplet states of the 1,2-dioxetanone molecule computed at the MS-CASPT2//SA-CASSCF (a) and 2RDM (b) levels of theory along the decomposition reaction path. Illustrations adapted from Refs. [1] and [3], respectively.

REFERENCES

[1] F. Liu, Y. Liu, L. de Vico, R. Lindh, *J. Am. Chem. Soc.* **2009**, *131*, 6181.

[2] L. Greenman, D. A. Mazziotti, *J. Chem. Phys.* **2010**, *133*, 164110.

[3] L. Greenman, D. A. Mazziotti, *J. Chem. Phys.* **2011**, *134*, 174110.

[4] L. P. da Silva, J. C. G. E. da Silva, *J. Comp. Chem.* **2012**, DOI 10.1002/jcc.22997.

[5] The lowest-lying triplet state in organic spectroscopy and photochemistry is denoted as T_1, see for instances N. J. Turro in "Modern Molecular Photochemistry". We will henceforth use this notation for the state which da Silva and da Silva denotes the T_0 state. This also means, in accordance with the standards, that the states denoted T_1 by da Silva and da Silva will be denoted T_2.

[6] H. F. Schaefer III, *Science* **1986**, *231*, 1100.

[7] F. Aquilante, L. de Vico, N. Ferré, G. Ghigo, P.-Å. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, R. Lindh, *J. Comput. Chem.* **2010**, *31*, 224.

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03 (Revision E.01); Gaussian: Wallingford CT, **2004**.

[9] B. G. Levine, C. Ko, J. Quenneville, T. J. Martínez, *Mol. Phys.* **2006**, *104*, 1039.