Response to a "Comment on excitations in photo-active molecules from quantum Monte Carlo"

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Citation

Filippi, C., & Buda, F. (2005). Response to a "Comment on excitations in photo-active molecules from quantum Monte Carlo". *Journal Of Chemical Physics*, *122*(8), 087102. doi:10.1063/1.1844292

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Citation: J. Chem. Phys. **122**, 087102 (2005); doi: 10.1063/1.1844292
View online: https://doi.org/10.1063/1.1844292
View Table of Contents: http://aip.scitation.org/toc/jcp/122/8
Published by the American Institute of Physics

THE JOURNAL OF CHEMICAL PHYSICS **122**, 087102 (2005)

Response to "Comment on 'Excitations in photoactive molecules from quantum Monte Carlo' " [J. Chem. Phys. 122, 087101 (2005)]

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(Received 18 October 2004; accepted 9 November 2004; published online 14 February 2005)

[DOI: 10.1063/1.1844292]

The preceding comment[1] concerns whether our findings[2] on the generally poor performance of the restricted open-shell Kohn-Sham (ROKS) method in describing excited state potential energy surfaces (PES) are relevant to excited-state molecular dynamics simulations of the isomerization path of formaldimine.

Using both ROKS and the complete active space self-consistent field approach, we constructed an isomerization path of formaldimine by optimizing the structure in the excited state at different constrained torsional angles.[2] The molecular structures obtained by the two techniques are significantly different (our geometrical data are plotted in Fig. 1 of the Comment) and the ROKS energetics along the ROKS path are at variance with highly correlated quantum chemical and quantum Monte Carlo calculations (see Figs. 2 and 3 in Ref. 2).

The authors of the Comment argue that the geometrical configuration obtained within ROKS at a constrained torsional angle of 0° is not explored in a molecular dynamics at finite temperature since its ground state energy is 1 eV higher than that of the ground-state minimum. However, we are *not* interested in the molecular dynamics in the ground state but in the *excited* state. The excited state energy of the contested configuration is *lower* than the Franck–Condon (FC) energy and is accessible from the FC region. Therefore, this configuration can well be explored in an excited-state molecular dynamics at finite temperatures.

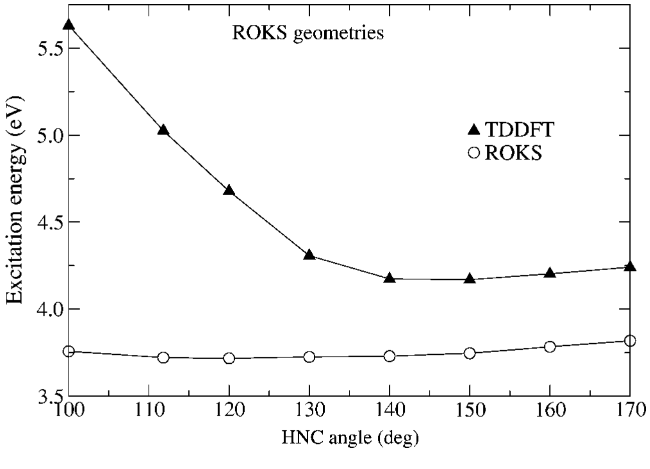

FIG. 1. ROKS and TDDFT excitation energies in eV as a function of HNC angle at a torsional angle of 0°. The excited state geometries are optimized within ROKS with respect to all other degrees of freedom.

Moreover, the excited state PES around this configuration is incorrectly described by ROKS as shown in Fig. 1, where the geometry of formaldimine is optimized within ROKS for different values of the HNC angle at a torsional angle of 0°. ROKS is quite insensitive to changes in the value of the HNC angle, with a minimum which is very difficult to locate between 110° and 140°. On the other hand, time-dependent density functional theory (TDDFT) has a clear minimum at about 140° and yields energy variations of more than 1 eV on the same range of HNC angles. Therefore, by tuning the HNC angle, while the ROKS energy remains unchanged, we can induce either the disappearance or the enhancement of the barrier in the TDDFT curve of Fig. 2 in our paper.[2] Note that all the geometries of Fig. 1 are pyramidalized: the use of a nonpyramidalized structure at 0 torsional angle[2] is contested in the comment, but pyramiladization only yields energy changes smaller than 0.1 eV, without affecting the overall picture (see *Notes added in proof* in our paper).

Therefore, since regions of the excited state PES which are potentially accessible during a molecular dynamics at finite temperature are not correctly described by ROKS, the claim of the authors of the comment that a dynamics at finite temperatures within ROKS is correct cannot be demonstrated with the only use of ROKS geometries and without computing the real excited state PES with the use of highly correlated quantum chemical methods. In conclusion, ROKS is a computationally cheaper method to perform excited state molecular dynamics but its predictions need always to be validated via highly correlated quantum chemical methods.

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[1] N. L. Doltsinis and K. Fink, J. Chem. Phys. **122**, 087101 (2005), previous paper.

[2] F. Schautz, F. Buda, and C. Filippi, J. Chem. Phys. **121**, 5836 (2004).