

SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

The STSM applicant submits this report for approval to the STSM coordinator

Action number: 41694

STSM title: Study of excited states for the dynamic of malonaldehyde.

STSM start and end date: 15/09/2018 to 15/11/2018

Grantee name: Dr Tarek Ayari

PURPOSE OF THE STSM/

The major purpose of this STSM is to establish long term collaboration between group of Nadja Doslic at the Ruder Boskovic Institute (IRB) and the group of Majdi Hochlaf at the University Paris-Est Marne-La-Vallée (UPEM) through sharing their expertise. Indeed, the group at UPEM has well recognised experience with very accurate multireference electronic structure calculations for ground and excited electronic states. Over the years they performed ab-initio studies for different sizes and types of molecules using a variety of electronic structure methods among them the recently implemented explicitly correlated multi Reference Configuration Interaction (MRCI-F12) and multi-state second order perturbation theory (MS-CASPT2) methods using the MOLPRO code. The group at IRB is expert in on-the-fly dynamics of electronically excited molecular systems.

Our common project deals with the application of these particular methods to treat the intramolecular dynamics of malonaldehyde (MA) in the S_1 state, via the evaluation of the barriers to H-transfer S_1 state. Benchmarks on well-studied, experimentally and theoretically, the H-transfer in the S_0 state are performed. This result is needed in order to validate the quality of the electronic structure method that will be used to compute the tunnelling splitting using the instanton approach.

So, the goal of this study is to assess the applicability of very high level electronic structure methods for the calculation of the portions of the malonaldehyde potential energy surface S_1 state relevant for the intramolecular tunneling effect.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The first part for this collaboration is the photodynamics of MA through the accurate description of the H-atom transfer dynamics in the excited electronic state.

Note that numerous efforts have been devoted to the computation of tunneling induced splittings in the ground state of MA. In contrast, there is no published work on the H-transfer in the first excited state of MA.

Several tests were been performed. This includes the verification of the results obtained by two basis sets (the aug-cc-pVDZ and aug-cc-pVTZ basis sets) and with two different active spaces ([10,10] and [12,12] where the number in the brackets indicate the number of electrons and molecular orbitals that were taken into account). These tests were started without a threshold value for the computations done by the explicitly correlated Multi Reference Configuration Interaction (MRCI-F12) and the multi-state second order perturbation theory (MS-CASPT2) levels for theory. Subsequently, calculations with threshold values of 0.005 and 0.01 were performed. The adequate threshold was chosen to remedy convergence problems and to reduce the calculation time.

Table: MRCI-F12 vertical excitation energies for the MA with different basis sets and active spaces. Threshold : coefficient value under which electronic configurations are discarded in the MRCI calculation. Configurations : Total number of uncontracted configurations in the MRCI calculation. ΔE : Vertical excitation energy between the S_0 and S_1 state.

	Method	Basis	Active space	Threshold	Configurations	ΔE MRCI (eV)	Time (days)	Disk used
Test 1	MRCI-F12	avdz	(10,10)	0.005	1.6×10^9	4.297	2 days	27 GB
Test 2	MRCI-F12	avtz	(10,10)	0.005	1.0×10^{10}	4.096	3 days 4 hours	60 GB
Test 3	MRCI-F12	avdz	(10,10)	0.01	8.5×10^8	4.298	1 day 3 hours	18 GB
Test 4	MRCI-F12	avtz	(10,10)	0.01	4.2×10^9	4.101	2 days 5 hours	39 GB
Test 5	MRCI-F12	avdz	(12,12)	0.01	1.3×10^9	4.096	3 days 4 hours	29 GB
Test 6	MRCI-F12	avtz	(12,12)	0.01	8.5×10^9	4.105	7 days 6 hours	67 B

After the selection of the most suitable method, we started with the evaluation of the barrier to H-transfer in the S_0 and S_1 states of MA. This requires the optimizations (in C_1 point group) of the minimum energy structure in the S_0 and S_1 states, as well as the optimization of their transition states connecting these minima. The vertical excitation energies for these structures were calculated later using the MRCI method in the goal of the check the barriers energy values between each two states for S_0 and S_1 .

DESCRIPTION OF THE MAIN RESULTS OBTAINED

After our benchmarks treating the excited state of MA, it is appeared that the computations of the electronic excited states are challenging. For instance, we found that:

- the use of the costly explicitly correlated Multi Reference Configuration Interaction (MRCI-F12) method is needed to correctly describe the S_1 potential.
- the multi-state second order perturbation theory (MS-CASPT2) method, which is used for on-the-fly instanton dynamics, may be used with caution. Indeed, appropriate basis set and active space should be used to describe the S_0 and S_1 states (minimum and transition state) and to calculate their potential energy surfaces.

Through these ab-initio studies, we succeeded to identify the optimized structures for the ground state S_0 of malonaldehyde in its minimum and its transition state TS using the explicitly correlated Multi Reference Configuration Interaction (MRCI-F12) and the multi-state second order perturbation theory (MS-CASPT2) methods in conjunction with the aug-cc-pVDZ basis set. The same procedure was used for the first excited state S_1 for malonaldehyde. These computations were done with different active spaces ([10,10] and [12,12]).

In this way, many old works using ab initio methods about MA and they were focused to compute the barriers of S_0 states and the tunnelling splittings. In some of these models, the potential was obtained that gave barrier heights in the range of 6–10 kcal/mol and the calculated tunnelling splittings varied from roughly 60 cm^{-1} to values close to experiment. Even a fairly recent 3 degree of freedom model for the H-atom transfer and an adiabatic treatment of the remaining 18 degrees of freedom reported by Sewel *et al.* obtained a tunnelling splitting of 21.8 cm^{-1} . However, with a saddle point barrier height that is roughly 2.5 times the accurate value of 4.1 kcal/mol, using high-level ab-initio calculations. Recent theoretical work has been done in the full 21dimensional vibrational space using relatively low level *ab-initio* calculations with MP2/6-31G(*d*, *p*). This PES has a barrier of 3.61 kcal/mol and was used in recent full dimensional treatment. The calculated H-atom splitting was 30.7 cm^{-1} . A more accurate *ab-initio* treatment was done the result that for the best estimate of the barrier height of 3.8 kcal/mol, the tunneling splittings were calculated to be 21–22 cm^{-1} .

In this moment we don't have our potential energy barriers within the S_0 and S_1 states done with the two active spaces [10,10] and [12,12] because the calculations are still running right now.

These data should allow checking validity of the outcomes of the instanton dynamical computations that are running at IRB, especially the tunnelling splittings in the S_1 state of MA.

FUTURE COLLABORATIONS (if applicable)

This collaboration Ruder Boskovic Institute (Zagreb, Croatia) and University Paris-Est Marne-La-Vallée (Paris, France) is aimed to continue and to be developed in the future. It will be extended to other some small and medium sized organic molecular systems. This should include the characterization with different theoretical methods and many basis sets of the optimised geometries structures as well as the potential energies curves to obtain reliable results for the molecular dynamics of these systems.

In this context, we started during this STSM to check the feasibility of the study of the dynamics for the first chiral molecule detected in the interstellar medium, methyloxirane (R-methyloxirane and S-methyloxirane) [1]. The goal of this study is to check, for the first time, on the valence-Rydberg character of the S_1 and S_2 electronic excited states of the methyloxirane and then on the use of these results for the nonadiabatic dynamic study of this system. This work in progress, where we are establishing the electronic structure methodology for the description of the potential energy surfaces of the S_0 , S_1 and S_2 states of methyloxirane. The outcomes of this project should help into the proposition of plausible mechanism for the formation of chiral molecules in the astrophysical media.

[1] Manuel Hodecker, Malgorzata Biczysko, Andreas Dreuw, and Vincenzo Barone, J. Chem. Theory Comput. 2016, 12, 2820–2833.