# Work Plan

This work will be executed in collaboration with the:
**"Laboratoire Modélisation et Simulation Multi Echelle",**
**Université Paris-Est, MSME UMR 8208 CNRS,**
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and in particular with the **"Theoretical Chemistry"** team lead by Prof. Majdi Hochlaf.

## Background:

Since the pioneering measurements of Wilson and coworkers malonaldehyde (MA) has been the subject of intense experimental and theoretical research [1].

## Preliminary work:

In our current study we examine the photodynamics of MA from a new perspective. Our goal is to understand why is the photodynamics of MA so different from that of the closely related acetylacetone. We already characterized key molecular geometries such as minima, transition states and conical intersections using the approximate coupled cluster singles and doubles (CC2) and Multi-state second order perturbation theory (MS-CASPT2) methods.
We also performed surface hopping nonadiabatic molecular dynamics simulations.

## Goal:

A particularly interesting aspect of the photodynamics of MA is the description of the H-atom transfer dynamics in the excited electronic states.
It is well known that much effort has 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-After our preliminary study of the excited state of MA, it is clear that the computation in the excited electronic states is a very difficult problem. Therefore, the goal of this study is to assess the applicability of very high level electronic structure methods for the calculation of the relevant portion of the MA potential energy surface.

## Planed research:

The study will begin by testing by the Explicitly Correlated Multi Reference Configuration Interaction (MRCI-F12) method and the most appropriate basis set and active space to optimize $S_0$ and $S_1$ states (minimum and transition state) and to calculate their potential energy surface.

Several tests will be performed. This includes the verification of the results obtained by two basis sets: aug-cc-pvdz and aug-cc-pvtz and those obtained with two different active spaces. We plan to perform [10,10] and [12,12] calculations where the brackets indicate the number electrons and molecular orbitals that will be taken into account. Testings will start without a threshold value. Subsequently, calculations with threshold values of 0.005 and 0.01 will be performed. The adequate threshold will be chosen to remedy convergence problems and to reduce the calculation time. After the selection of the most suitable method, we will start with the evaluation of the barrier to H-transfer in the $S_1$ state of MA. This requires the optimization of the minimum energy structure in the $S_0$ and $S_1$ states, as well as the optimization of their minimums in $C_{2v}$ symmetry.

[1] S. L. Baughcum, R. W. Duerst, W. F. Rowe, Z. Smith, E. B. Wilson, *J. Am. Chem. Soc.* **1981**, *103*, 6296.