

## SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: 42155 (CM1405)

STSM title: SAPT in reactive collisions: the case of SH<sub>2</sub><sup>+</sup> system

STSM start and end date: 21/10/2018 to 09/11/2018

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### PURPOSE OF THE STSM:

The project was focused on the interactions and dynamics of SH<sup>+</sup> + H -> S<sup>+</sup> + H<sub>2</sub> reactive system.

### DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

In this project we performed the pilot calculations of most challenging parts of the potential energy surface of SH<sub>2</sub><sup>+</sup> system by exploiting the open-shell symmetry adapted perturbation theory (SAPT) [1-2] and RCCSD(T) calculations. Since the present fit of the potential energy surface for SH<sub>2</sub><sup>+</sup> system was based on MRCI calculations [5] which is not size consistent, we decided to carefully test its long-range behavior for planned calculations at low kinetic energies. While for the quarter state it was possible to use CCSD(T) calculations, to obtain the doublet state interaction we used recently developed spin-flip SAPT [6] which directly calculates the difference between multiplicities resulting from adding two nonzero spins of monomers. With such approach we can obtain both quartet and doublet surface of the SH<sup>+</sup>+H interaction in a fine grid at R which is distance between center of SH<sup>+</sup> cation and H incoming atom and some selected r which is inter-nuclear distance and theta, is a Jacobi angle.

### DESCRIPTION OF THE MAIN RESULTS OBTAINED

We compared SAPT and CCSD(T) results with existing fit values obtained from MRCI data as shown in Figure 1. and Figure 2. The comparison of fit values from MRCI calculations seems not

re-produce the shape of CCSD(T) calculations especially at low interaction region and SAPT do good at large distance. In principle from SAPT it is possible to extract the data for accurate van der Waals coefficients even for strongly stretched bond of  $\text{SH}^+$  molecule, which might be of key importance for studies of the dynamics of cold chemistry. To take into account this issue we have decided to implement the CCSD(T) and SAPT methods for all the possible geometries to obtain a global PES for dynamic calculations. 3D calculations on this side are quite challenging and our works in this side is still undergoing. We found big differences between fitted MRCI potential and SAPT+RCCSD(T) combined approach which should be later addressed. The spin exchange seems to agree quite well with MRCI fit for  $\text{SH}^+ + \text{H}$  interactions for 90 degrees Jacobi angle as shown in the figures, but quite spectacularly disagrees for linear configuration S-H-H, which might be due to a bond formation on a singlet surface.

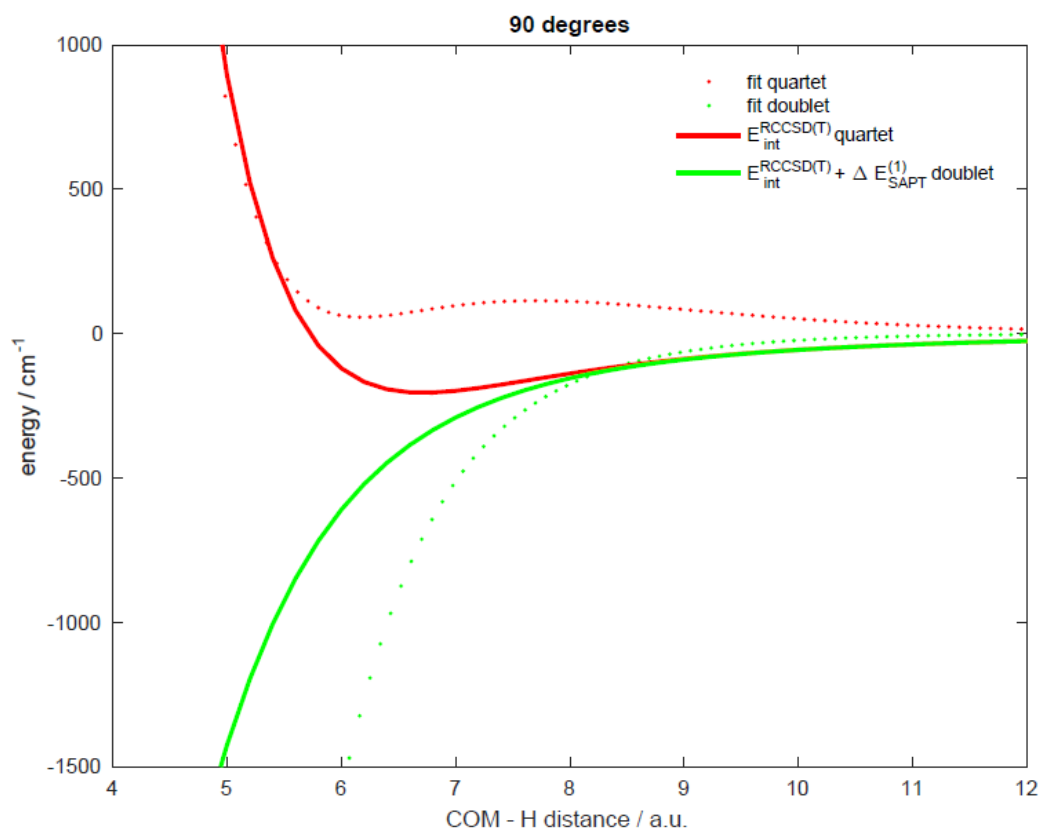


Figure 1.:  $R$ -dependent potential energy curves for quartet and doublet state of the  $\text{SH}^+ + \text{H}$  interaction at fixed equilibrium internuclear distance ( $r=1.37$  angstrom) and at 90 degrees.

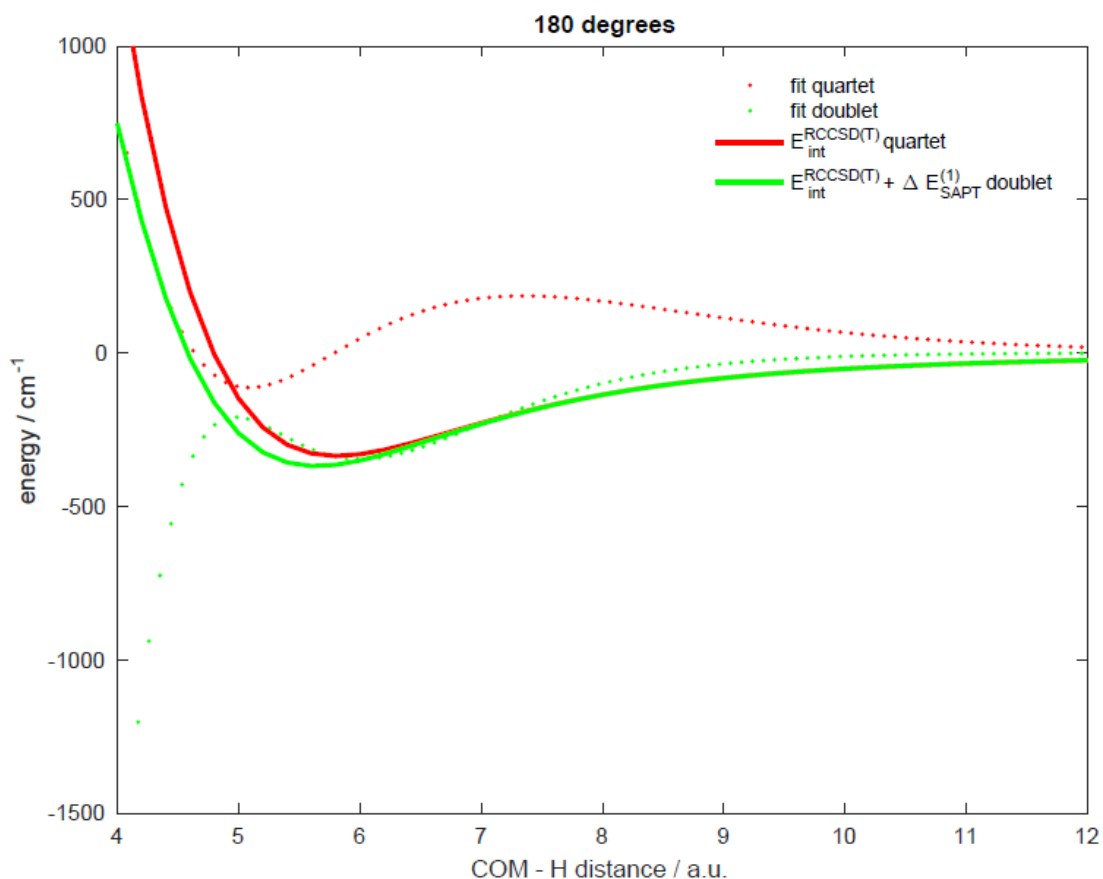


Figure 2.: Same as Fig.1 but for a coolinear geometry (theta=180 degrees).

#### FUTURE COLLABORATIONS (if applicable)

This research will be continued and comparisons with OH<sub>2</sub><sup>+</sup> potential (which is better studied than SH<sub>2</sub><sup>+</sup>) would be very helpful in diagnostics of SAPT+RCCSD(T) approach. After having the global PES, we plan to perform the dynamical calculations of the SH<sup>+</sup>+H collision in detail for the exchange and destruction product channels for a cold regime which is quite important for astro chemical tolls. State-to-state reaction and inelastic rate constant will be calculated in a cold regime and these data should contribute to the SH<sup>+</sup> detection in space. For all the dynamic calculation we will implement an accurate wave packet method developed by Roncero and coworkers [3,4].

[1] Nagy Z. et al., 2013, The chemistry of ions in the Orion Bar I. – CH<sup>+</sup>, SH<sup>+</sup>, and CF<sup>+</sup>, *Astronomy and Astrophysics* 550, A96

[2] Zuchowski P. S. et al., 2008, Symmetry-adapted perturbation theory utilising density functional description of monomers for high-spin open-shell complexes. *The Journal of Chemical Physics* 129, 084101

[3] Carrasco-Gomez S., Roncero O., 2006, Coordinate Transformation Methods to Calculate State-to-State Reaction Probabilities with Wave Packet Treatments, *The Journal of Chemical Physics* 125, 054102.

- [4] Bulut N., Lique F., Roncero O., 2015, Exchange and Inelastic  $\text{OH}^+\text{+H}$  Collisions on the Doublet and Quartet Electronic States, *The Journal Physical Chemistry A* 119, 12082-12089.
- [5] Alexandre Zanchet, Marcelino Agundez. Victor J. Herrero, Alfredo Aguado, and Octavio Roncero, *The Astronomical Journal*, 146:125 (7pp), 2013.
- [6] Konrad Patkowski, Piotr S.Zuchowski, and Daniel G. A. Smith, *The Journal of Chemical Physics*, 148, 164110 (2018).