

## Report on the outcomes of a Short-Term Scientific Mission<sup>1</sup>

Action number: CA20129

Grantee name: Dário Barreiro-Lage

### Details of the STSM

Title: **Unravelling the Molecular Dynamics of Excited CO<sub>2</sub> Ices**

Start and end date: 04/05/2025 to 16/05/2025

### Description of the work carried out during the STSM

During my STSM at Professor Jónsson's group within the COST Action *Unraveling the Molecular Dynamics of Excited CO<sub>2</sub> Ices*, I aimed to (1) learn and implement molecular dynamics (MD) simulations in excited states, and (2) apply them to study the dynamics of Rydberg states in CO<sub>2</sub> dimers using our methodology based on GPAW with Direct Optimization and SIC corrections.

In the first week, I focused on understanding the group's framework for MD in excited states by discussing with group members (notably Dr. Gianluca Levi) and reviewing key literature. We performed initial calculations on CO<sub>2</sub> dimers using our established methodology. However, we encountered issues: the excited states obtained were significantly affected by delocalization errors typical of DFT, particularly for Rydberg states. The PBE/SIC approach, while promising, still inherited poor initial guesses from delocalized PBE excited-state solutions, producing intrusive or spurious states.

Additionally, our approach to using complex orbitals in ground-state (GS) calculations—intended to access degenerate HOMO/HOMO-1 orbitals for selective excitation—led to undesired stabilization of triplet states due to spin asymmetry. These challenges prompted a strategic pivot: rather than proceed directly to dimers, we refocused on the CO<sub>2</sub> monomer. This allowed us to fine-tune our methodology and aim for correct, localized excited-state solutions without compromising symmetry. We also explored two parallel implementations of our methodology: one using finite differences (FD) and the other using a linear combination of atomic orbitals (LCAO). FD is more accurate for describing diffuse Rydberg states but is computationally more expensive. To assess the LCAO approach's feasibility, we compared the FD results with calculations using increasingly diffuse atomic basis sets—specifically aug-cc-pVDZ and d-aug-cc-pVDZ. As shown in the accompanying figure 1, d-aug-cc-pVDZ closely reproduces FD results, validating its use as a cost-effective alternative for excited-state Rydberg calculations.

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<sup>1</sup> This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

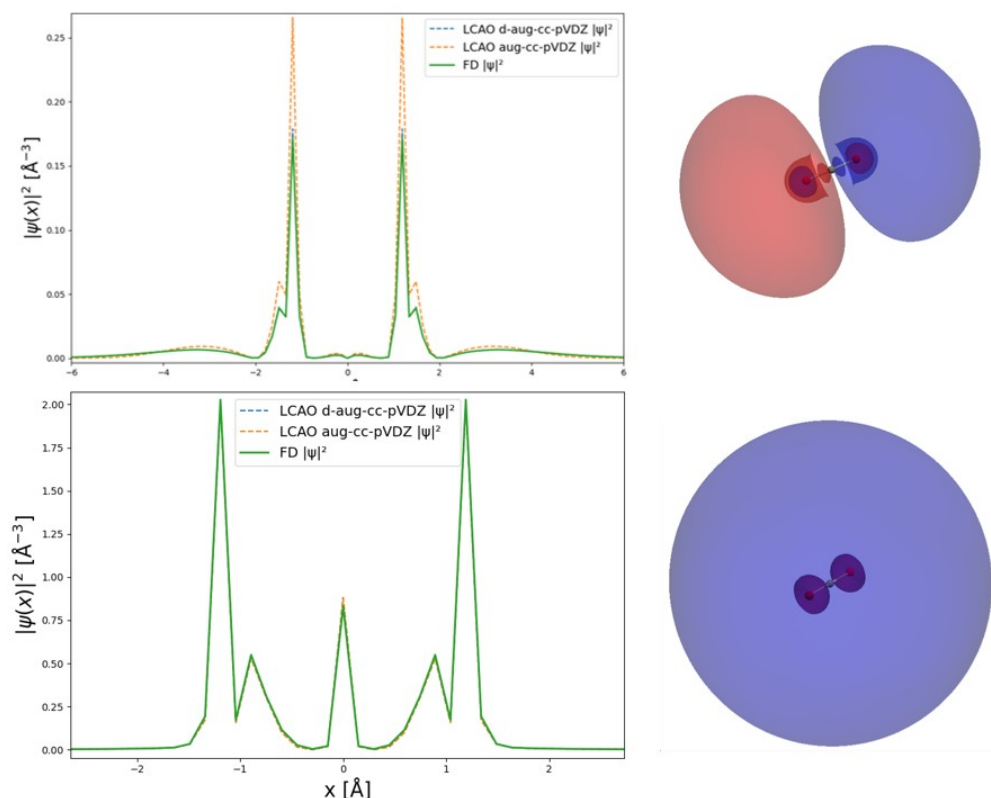


Figure 1

In the second week, we developed a reliable protocol for the CO<sub>2</sub> monomer. Using Direct Optimization and LCAO mode in GPAW, we generated dissociation curves (CO + O) for the ground state and low-lying singlet excited states (notably the 3s Rydberg and  $\pi^*$  states). These were then compared to benchmark diabatic potential energy curves computed from EOM-CCSD and MRCI dynamics in Triana et al.<sup>1</sup> (Figure 2). Our results exhibit excellent agreement, validating our approach as both accurate and computationally efficient.

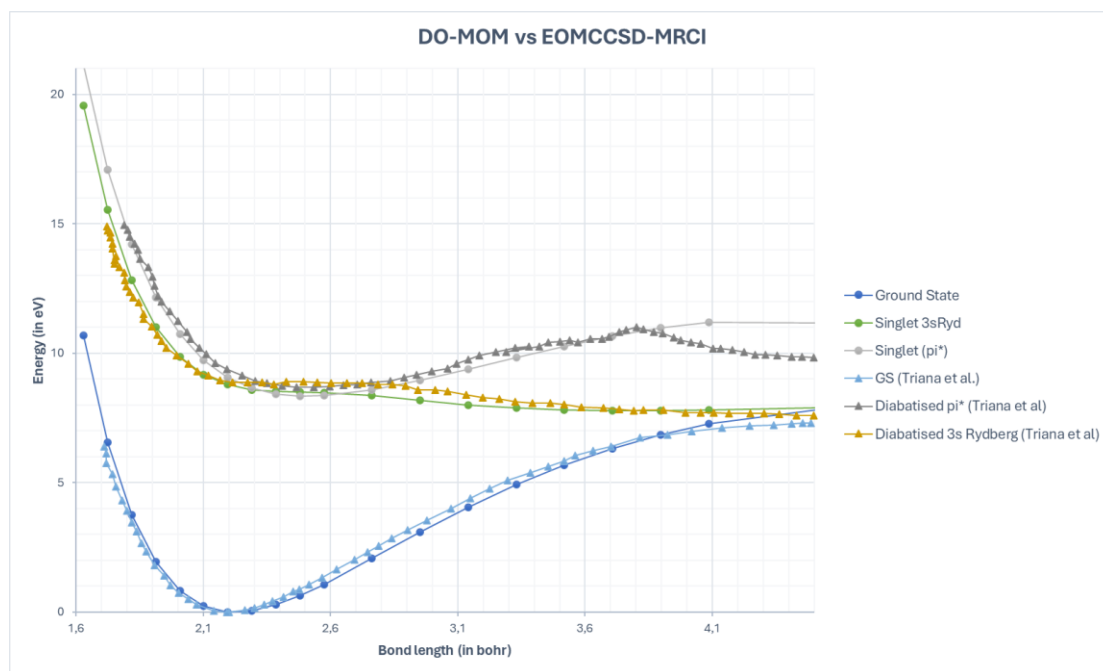


Figure 2

### **Description of the STSM main achievements and planned follow-up activities**

While the original plan included performing full MD simulations on excited CO<sub>2</sub> dimers, this STSM provided a critical step toward that goal by refining and validating our underlying excited-state electronic structure methodology. We identified and addressed key limitations in our workflow—specifically those arising from poor initial state guesses and spin contamination in complex orbital calculations. Shifting our focus to the CO<sub>2</sub> monomer allowed us to isolate and correct these issues.

A major achievement was obtaining accurate dissociation curves for excited states using PBE DO-MOM and the Direct Optimization method. As shown in the attached figure, these curves closely match those from high-level ab initio methods used in Triana et al. This breakthrough confirms the potential of our approach for broader application in excited-state dynamics, especially in systems where traditional methods are too costly.

This work not only strengthens the foundation for future excited-state MD simulations but also contributes a validated, cost-effective methodology for accessing diabatic surfaces. A manuscript documenting these results is in preparation, and further collaborative work with Prof. Jónsson's group is planned. Specifically, we aim to implement excited-state MD on the validated DO-MOM surfaces and explore energy transfer and dissociation dynamics in CO<sub>2</sub> clusters relevant to astrochemical environments.

1. Triana, J. F.; Peláez, D.; Hochlaf, M.; Sanz-Vicario, J. L. "Ultrafast CO<sub>2</sub> Photodissociation in the Energy Region of the Lowest Rydberg Series." *Phys. Chem. Chem. Phys.* 2022, 24 (22), 14072–14084