

## Mid-term review meeting

# DFT-based theoretical modelling of the catalytic activity of deposited clusters.

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Supervised by Prof. László Nyulászi and Prof. Tibor Höltzl

ESR6

Budapest, April 22<sup>nd</sup> of 2022

# Experience

Master of Science, MSc (Synthesis, Catalysis and Molecular Design), URV.

Chemist with experience in:

- Computational Photochemistry
- Atomic and molecular structure

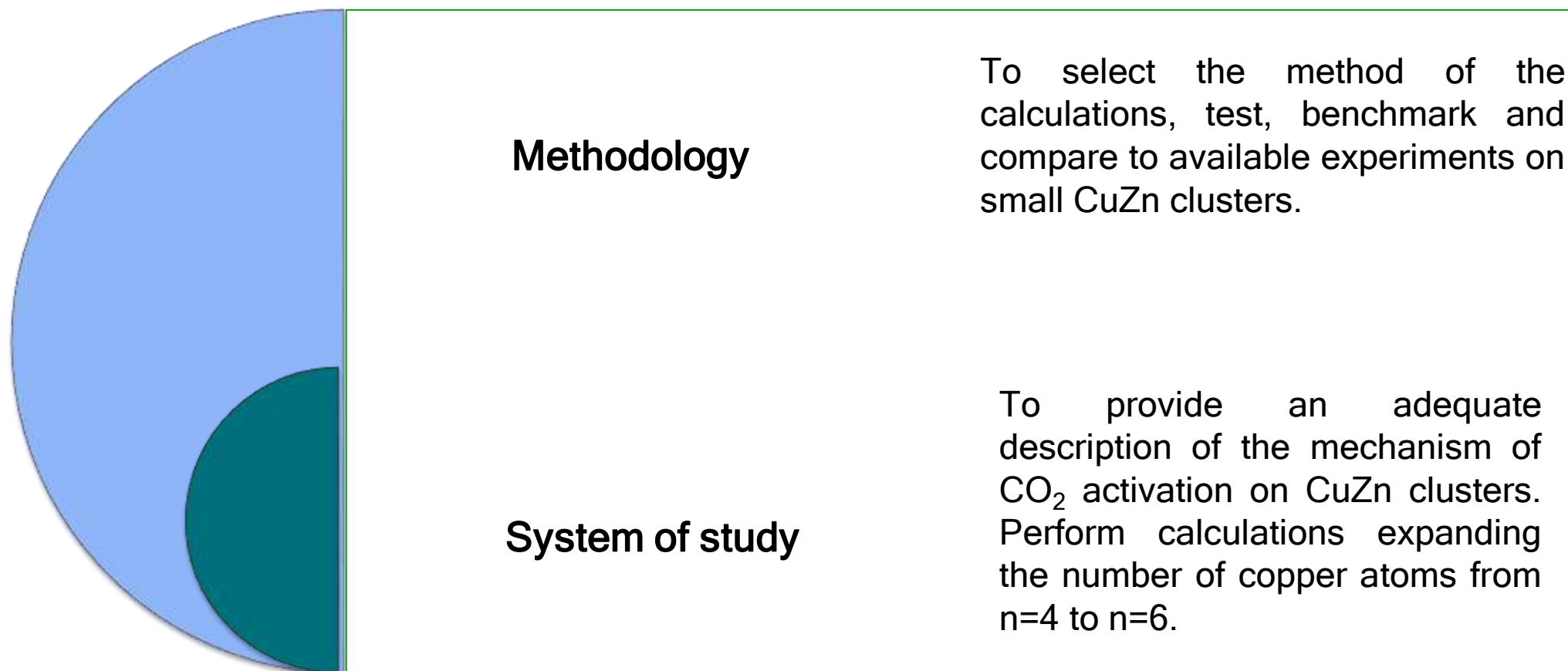


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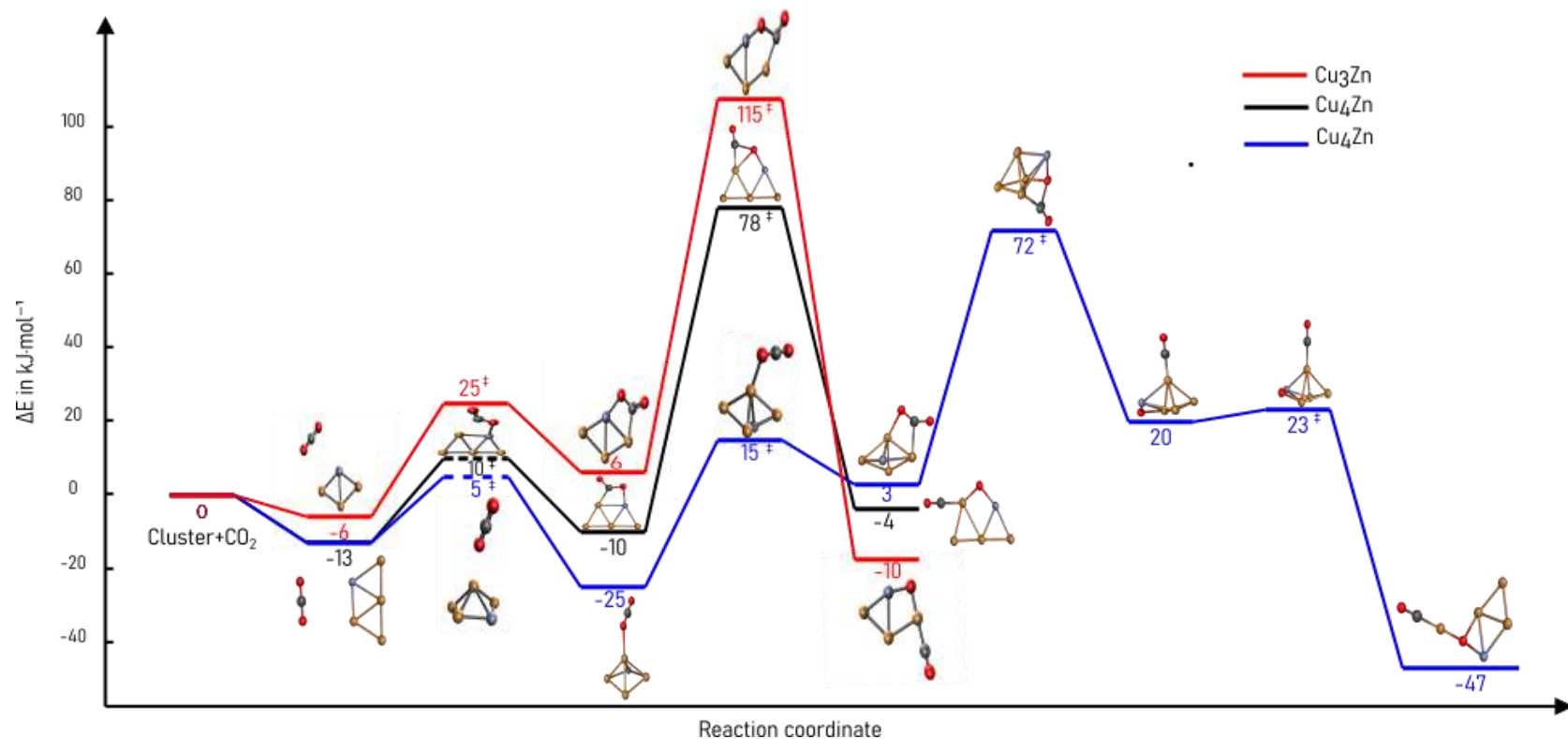
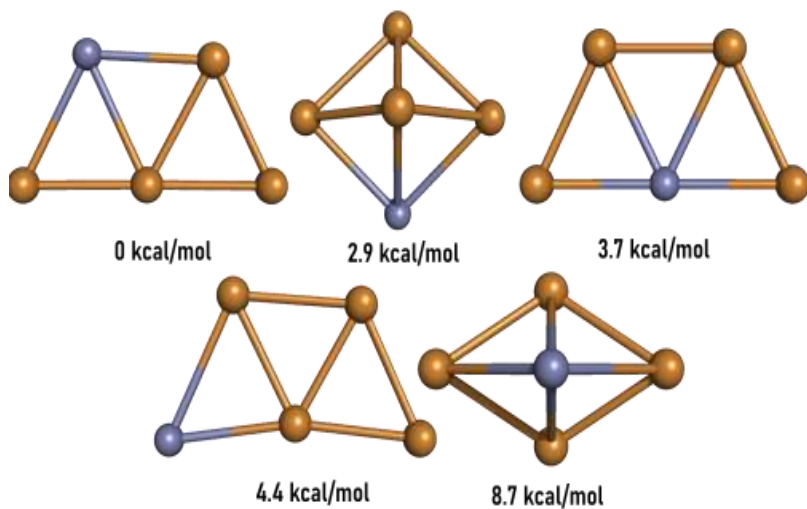


# Objectives (as part of WP3 and WP4)

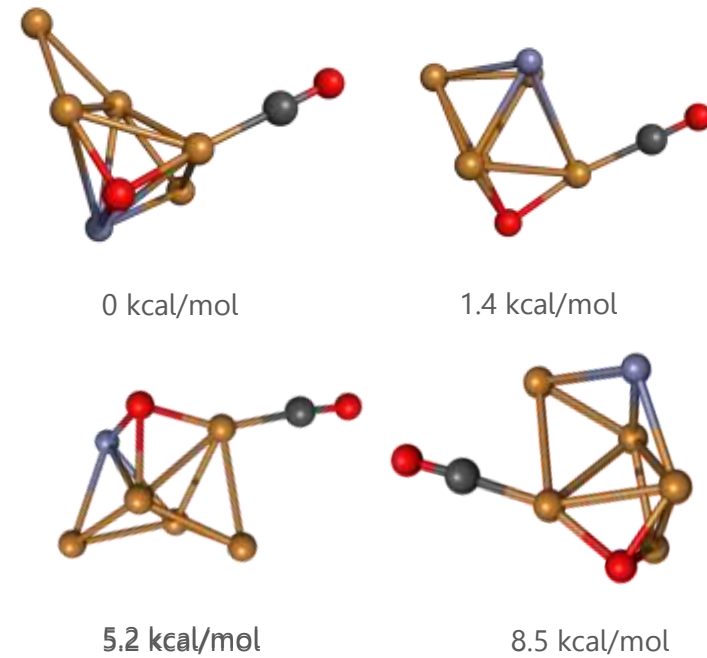
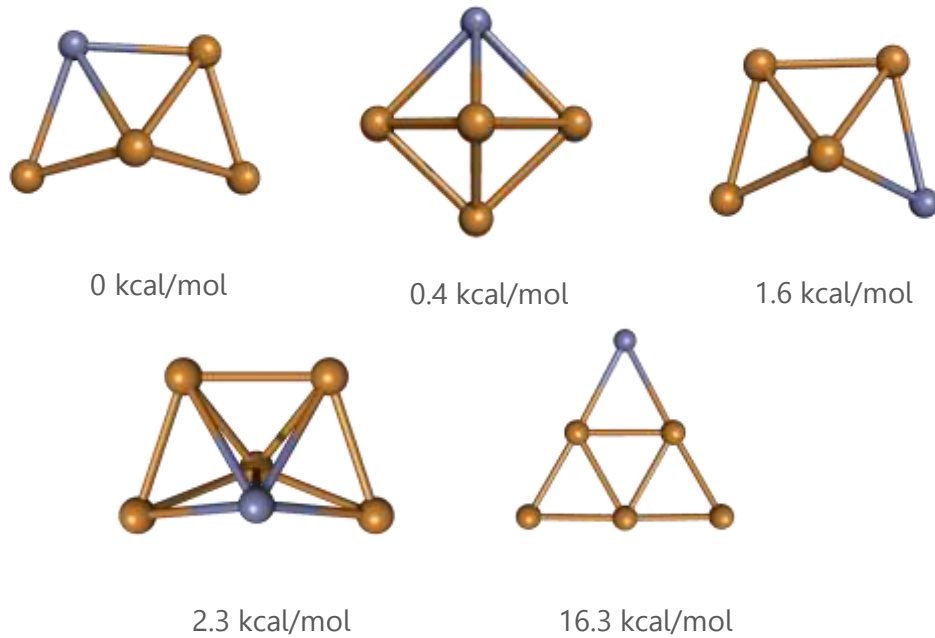
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# Results Cu<sub>4</sub>Zn



# Results Cu<sub>5</sub>Zn



# Training

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Objective	Action
Research skills	Courses: modern computational chemistry and inorganic chemistry. Seminars organized by the George Oláh doctoral school: open science practices and publishing scientific results.
Language, writing and communication	Hungarian course and poster presentation.
Teaching	General chemistry laboratory and general chemistry calculations.

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# Outreaching

Poster presentation in the workshop **Cutting-Edge Homogeneous Catalysis (CEHC-2)** (29-31 March 2022) and at the **First Catchy School** (19-21 April 2022)

**DFT-based investigation of structure and CO<sub>2</sub> adsorption on Cu<sub>x</sub>Zn clusters**  
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**INTRODUCTION**

A promising approach to the atmospheric control of carbon dioxide (CO<sub>2</sub>) into the atmosphere is the catalytic conversion of this greenhouse gas into valuable compounds. For example, the syngas (mixture of CO/CO<sub>2</sub>/H<sub>2</sub>) has been converted to methanol using heterogeneous copper catalysts.<sup>1-3</sup> Copper, as well as other copper clusters like Cu<sub>x</sub> (x is a first-row transition metal atom) have proven to be promising candidates for CO<sub>2</sub> reduction.<sup>3-6</sup>

The goal of this work is to continue the comprehensive investigation of the size-dependent CO<sub>2</sub> activation on Cu-Zn clusters.

**METHODOLOGY**

The Cu<sub>x</sub>Zn structures were optimized<sup>7-9</sup> and the frequency calculations on the optimized geometries were carried using the TPSSh/def2-TZVP method.

CO<sub>2</sub> adsorption in different binding modes was systematically investigated on the most stable Cu<sub>x</sub>Zn metal cluster structure. Intermediates and products were located, and the CO<sub>2</sub> activation pathway was explored.

**RESULTS**

**Table 1** Natural atomic charges, Wiberg bond indices and dissociation barriers for the cluster-CO<sub>2</sub> structures

Structure	CO <sub>2</sub> charge [a.u.]	Zn charge [a.u.]	β-Zn bond index	Cu-C bond index	Cu-Zn bond index	(Sociating C-O bond index	CO <sub>2</sub> dissociation barrier [kJ/mol]
Cu <sub>2</sub> Zn-CO <sub>2</sub>	-0.80	0.96	0.18	0.44	0.63	1.23	111.4
Cu <sub>3</sub> Zn-CO <sub>2</sub>	-0.88	0.74	0.18	0.29	0.22	1.43	91.881

**CONCLUSIONS AND PERSPECTIVES**

In the present contribution, we have determined computationally the lowest energy (most stable) structures for the Cu<sub>x</sub>Zn cluster and the different binding modes of CO<sub>2</sub> on the metal cluster. Furthermore, two reaction paths for CO<sub>2</sub> activation were explored and the dissociation barriers were compared with the one previously obtained for Cu<sub>2</sub>Zn.<sup>14</sup> The reaction barrier significantly decreased with larger clusters, indicating that cluster size impacts catalytic activity. Currently, this study is being expanded to include the Cu<sub>x</sub>Zn cluster size.

**ACKNOWLEDGEMENTS**

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**REFERENCES**

1. Li, H. et al. *Science* **2016**, 353, 1181-1185.  
 2. Li, H. et al. *Science* **2016**, 353, 1181-1185.  
 3. Li, H. et al. *Science* **2016**, 353, 1181-1185.  
 4. Li, H. et al. *Science* **2016**, 353, 1181-1185.  
 5. Li, H. et al. *Science* **2016**, 353, 1181-1185.

# Secondments

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Project title	Date
RU for training on IR vibrational spectroscopy of cluster-molecule complexes.	October-November 2022
KUL for TPD measurements to study deposited cluster reactivity.	March-April 2023
VITO for modelling of catalysts under realistic reaction conditions.	March-April 2024

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**Thank you for your attention**