

## Theoretical modeling of cluster@MOF catalysts for CO<sub>2</sub> conversion reaction

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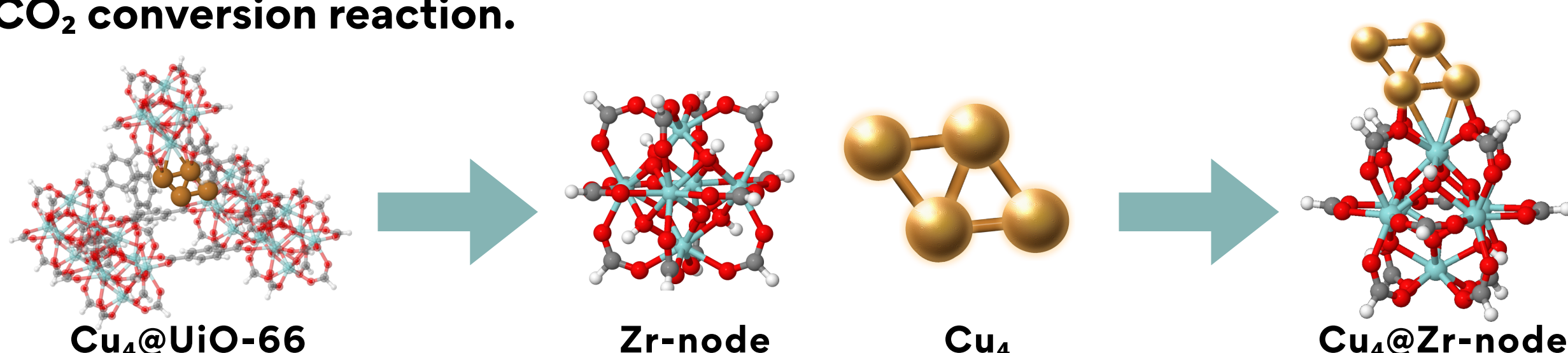


### INTRODUCTION & AIM

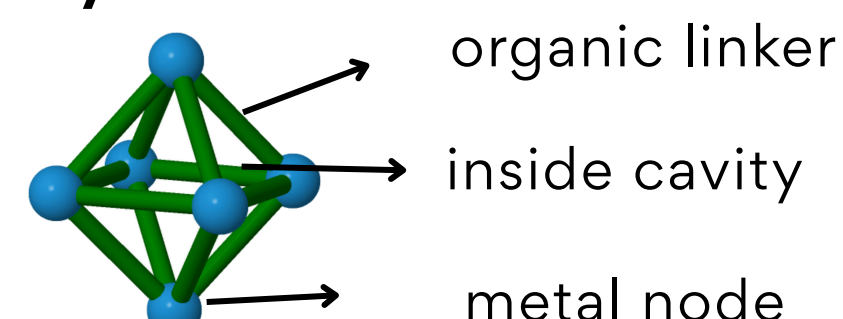
Catalytic conversion of CO<sub>2</sub>:  
• reduction of greenhouse gas,  
• production of value-added chemicals,  
• reducing dependence on fossil fuels.

Small size-selected subnanometer copper clusters on metal oxide support are highly efficient for CO<sub>2</sub> conversion into value-added products [1-2].

**AIM:** Design a new UiO-66-based MOF as a host to small Cu<sub>4</sub> clusters for CO<sub>2</sub> conversion reaction.



#### Catalytic sites in MOF



### METHOD

- Full optimization of Cu<sub>4</sub> binding was first done within pyramid MOF UiO-66 cavity.
- Reaction model system: Zr-based node with Cu<sub>4</sub> cluster.

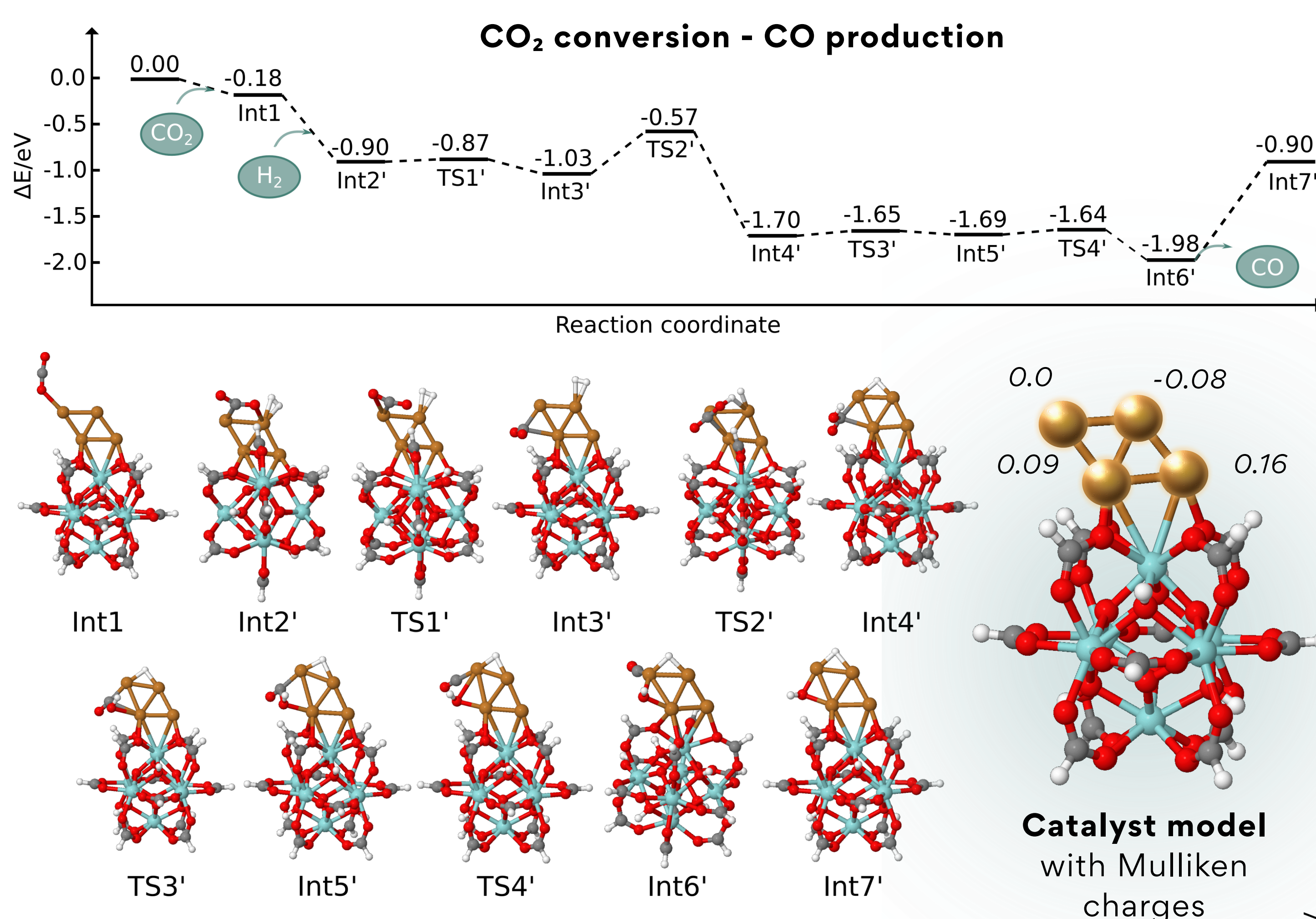
- Density functional theory (DFT) within Gaussian 16 software package.
- Functional **PBE**; basis set **LANL2DZ**; relativistic effective core potential (ECP) for Cu and Zr atoms; dispersion correction **GD3**.

$$\text{Dispersion corrected energy: } E^{DFT-D} = E^{DFT} + E^{D3}$$

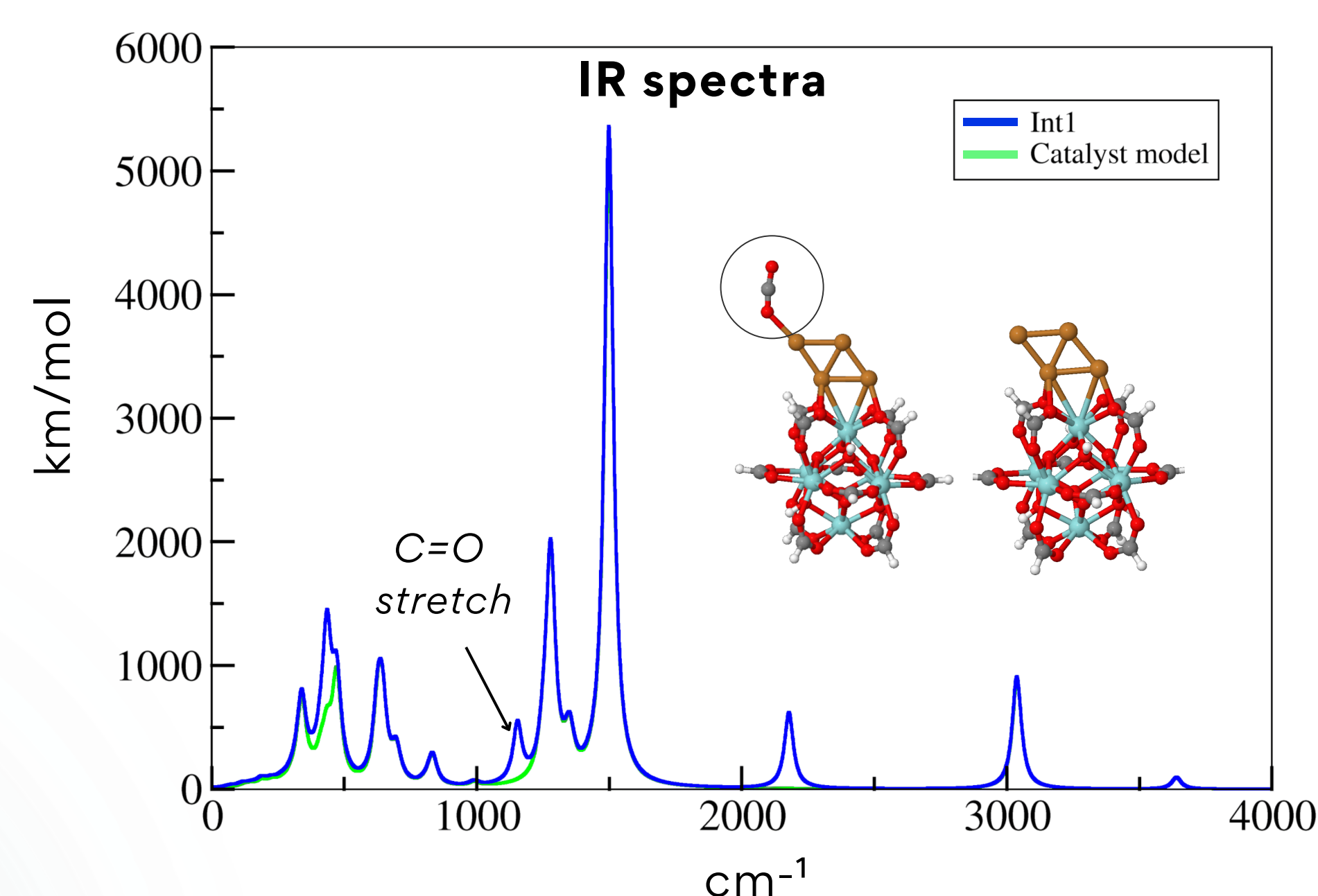
$$\text{Dispersion correction term: } E^{D3} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{damp,n}^{D3}(R_{AB})$$

- Neutral singlet ground state.
- Energy profile calculation:  $\Delta E = E_{DFT}^C - E_{DFT}^A - E_{DFT}^B$

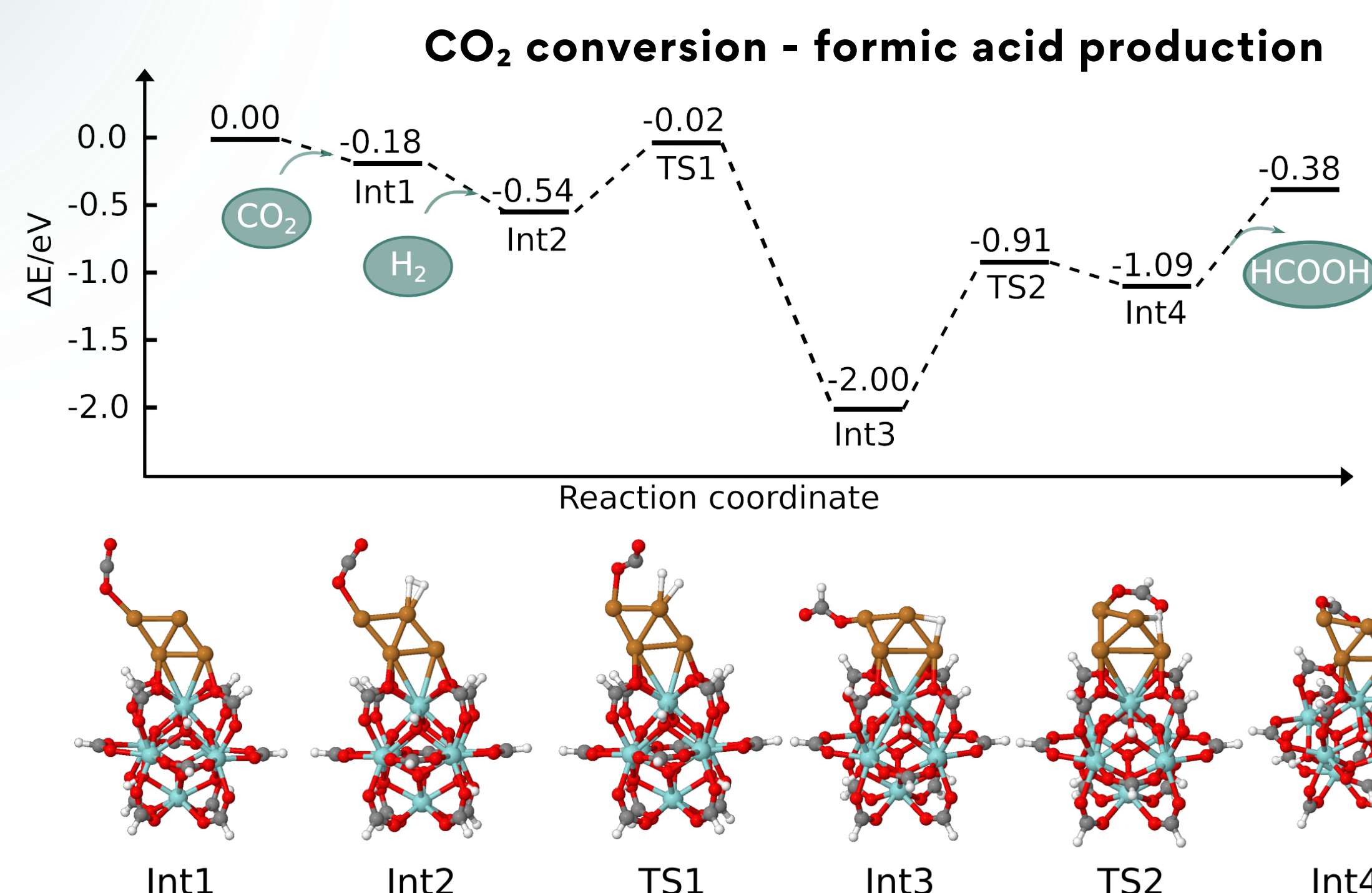
### RESULTS & DISCUSSION



Activation of CO<sub>2</sub> and formation of the **formate species** (Int3) proceed over the transition state with barrier of 0.52 eV, while the formation of the **carboxyl species** (Int4') requires 0.46 eV. Separation of the HCOOH is endothermic by 0.71 eV, and the separation of the CO by 1.08 eV.



CO<sub>2</sub> binds to the least coordinated Cu atom of the copper tetramer. This is exothermic by 0.18 eV (Int1). Next, the binding of the H<sub>2</sub> molecule to the neighbouring Cu atom proceeds to form the Int2 or Int2'. The latter is more stable by 0.36 eV.



### CONCLUSION

- The **rate-limiting step for CO** production is carboxyl species formation (-COOH), requiring 0.46 eV.
- The **rate-limiting step for HCOOH** production is 1.09 eV and corresponds to -HCOOH formation.
- Charge transfer cluster-support: 0.17.
- Three atoms actively participate in the carboxylic route and two in the formate one. Preliminary calculations on -H<sub>2</sub>COOH formation revealed the barrier of 0.75 eV.
- Future: thermochemical analysis; methanol reaction route.

### REFERENCES

- [1] A. Halder, C. Lenardi, J. Timoshenko, A. Mravak, B. Yang, L. K. Kolipaka, C. Piazzoni, S. Seifert, V. Bonačić-Koutecký, A. I. Frenkel, P. Milani, S. Vajda, *ACS Catal.* 2021, **11**, 6210-6224.
- [2] A. Mravak, S. Vajda, V. Bonačić-Koutecký, *J. Phys Chem. C* 2022, **126**, 18306-18312.