Elucidating elementary steps of CO_2 hydrogenation over copper clusters with IR spectroscopy

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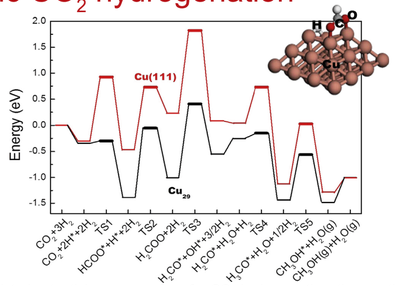
Introduction: catalytic CO_2 hydrogenation

Several novel catalysts have been proposed for CO_2 hydrogenation forming carbohydrates such as methane and methanol.

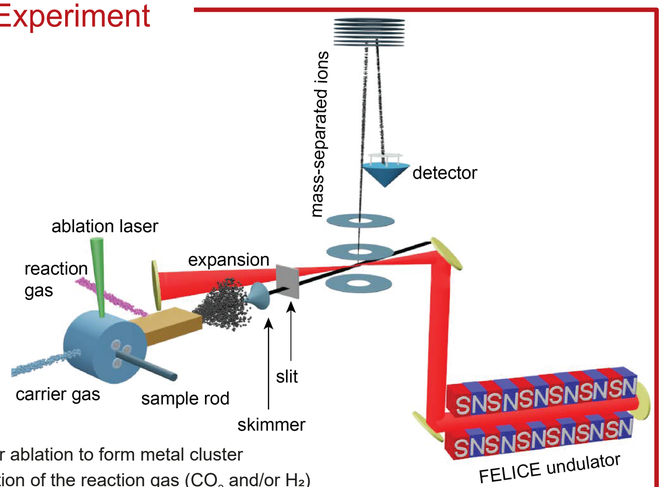
In this project we aim to unravel the catalytic mechanism at the molecular scale using clusters of various elemental compositions and sizes.

As a first step, we characterize cationic copper through IR multiple photon spectroscopy.

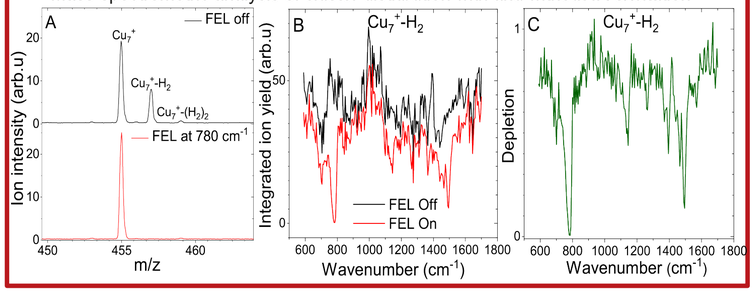


Calculated potential energy surface for CO_2 hydrogenation; the reaction barrier over a cluster is substantially lower than over a Cu-111 surface

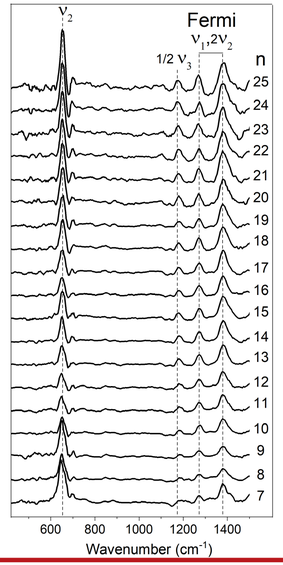
Experiment

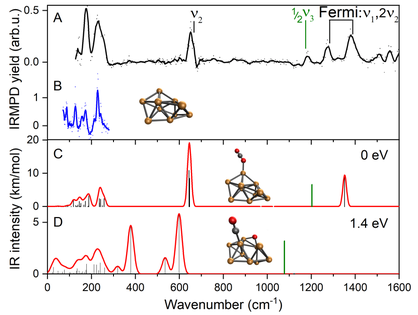


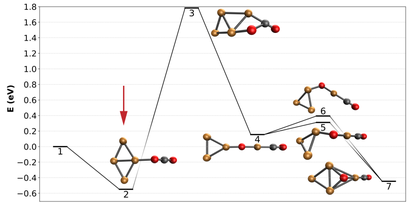
- Laser ablation to form metal cluster
- Addition of the reaction gas (CO_2 and/or H_2)
- Expansion into vacuum, molecular beam formation
- Mass-spectrometric analysis of cluster distribution with and without IR excitation



CO_2 adsorption on Cu_n^+







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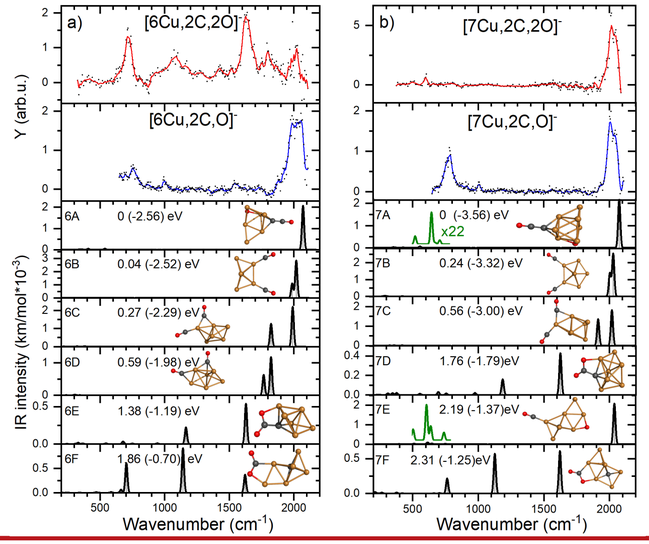
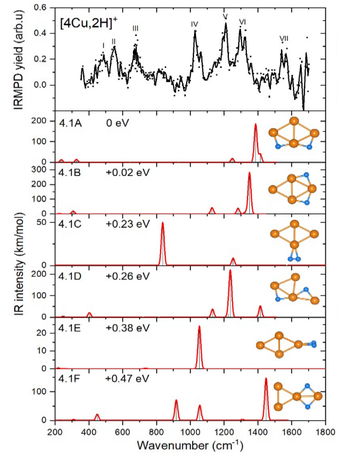
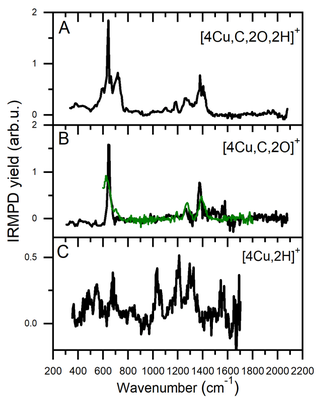
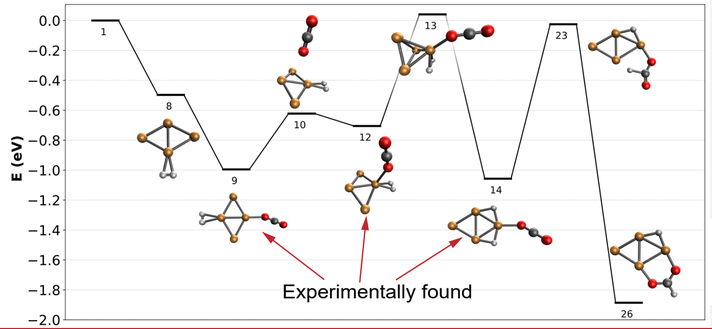


CO_2 adsorption on $[nCu,2H]^+$







Conclusions

IR spectroscopy of $Cu_n^{+/-}$ clusters with

CO_2:
Physisorption on Cu_n^+ and $[nCu,2H]^+$
Size dependent activation and dissociation over CCu_n^-

H_2:
Competition between molecular and dissociative adsorption on Cu_n^+

References

Liu, Yang, White, *Surf. Sci. Rep.* 68 233 (**2013**)
Lushchikova et al., *J. Phys. Chem. Lett* 10 2151 (**2019**)
Lushchikova et al., *J. Phys. Chem. A* 125 2836 (**2021**)