Probing for mode specificity in the chemisorption of CO_2 on H-Cu(111)

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Introduction

CO_2 concentration in the atmosphere is rising at an alarming rate. One solution to this problem is to close the carbon cycle by capturing CO_2 and then converting it into green fuels. As an initial step in the CO_2 conversion, many people are studying the interaction of CO_2 with hydrogen on copper surfaces for formate ($HCOO^-$) formation. Recently, Nakamura *et al*. reported formate synthesis via an Eley-Riedel mechanism in which 'hot' CO_2 molecules in a molecular beam react with H atoms pre-adsorbed on either Cu(111) or Cu(100) to form $HCOO^-$ adsorbates[1]. To expand the studies of Nakamura, in our lab, we plan to prepare the CO_2 molecules in a specific rovibrational state before colliding with a hydrogen covered Cu(111) surface. This would allow us to understand which vibrational mode enhances the formate formation reaction most efficiently on the surface. Another plan is to study the stereodynamics of the gas/surface interaction by aligning the CO_2 molecules in the laboratory frame through infrared pumping with a polarized laser. Our aim is therefore to perform state-specific reactivity measurements with steric control for formate synthesis on a copper catalyst. Surface bound formate is detected by reflection absorption infrared spectroscopy (RAIRS).

State-specific reactivity measurement

- Nakamura *et al*. showed that vibrational energy enhances the formate formation on a Cu surface more efficiently than the translational energy, but they used thermal method to excite all the vibrational modes of CO_2 molecules simultaneously.
- In our lab, we can use laser to excite the incident CO_2 molecules to specific rovibrational states (ν_3, R(0) and $\nu_3 + 2\nu_2$, R(0)) to study the mode specificity of this reaction.
- The following scheme highlights the steps that will be taken to carry out the proposed experiment.

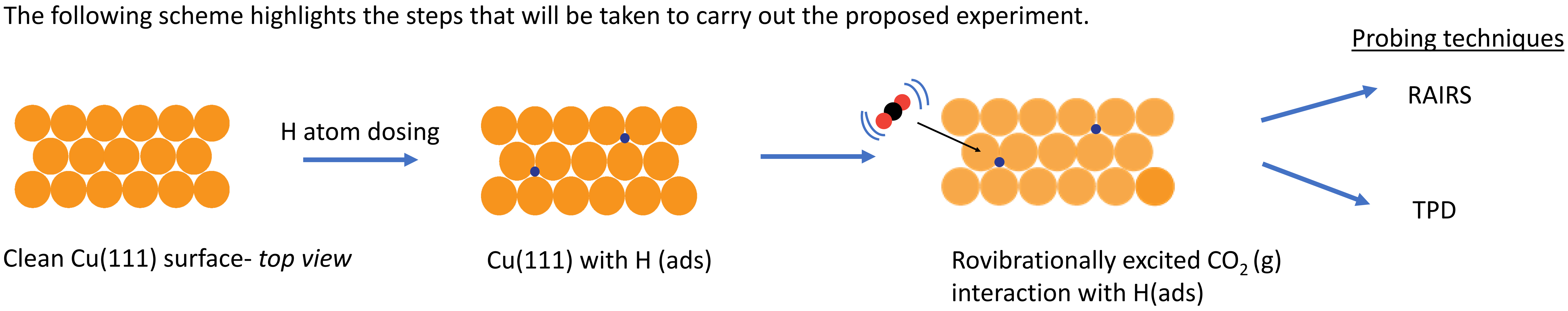

Figure 1: Schematic of the Eley-Riedel reaction for formate formation on Cu(111) with excited CO_2 molecules.

Steric effects of the reaction

- To perform stereodynamics study of CO_2 interaction on the hydrogen covered Cu(111) surface, we plan to use a linearly polarized laser beam to align the angular momentum of the incident rovibrationally excited CO_2 molecules.
- Exciting the CO_2 molecules with a laser polarised perpendicular to the surface prepares the molecules in a 'cartwheel' motion meanwhile, using a laser polarised parallel to the surface causes the CO_2 molecules to arrive on the surface in a 'helicopter' motion.
- The alignment effect on the formate formation reaction can be measured by using RAIRS, TPD and Auger (carbon content on the surface).

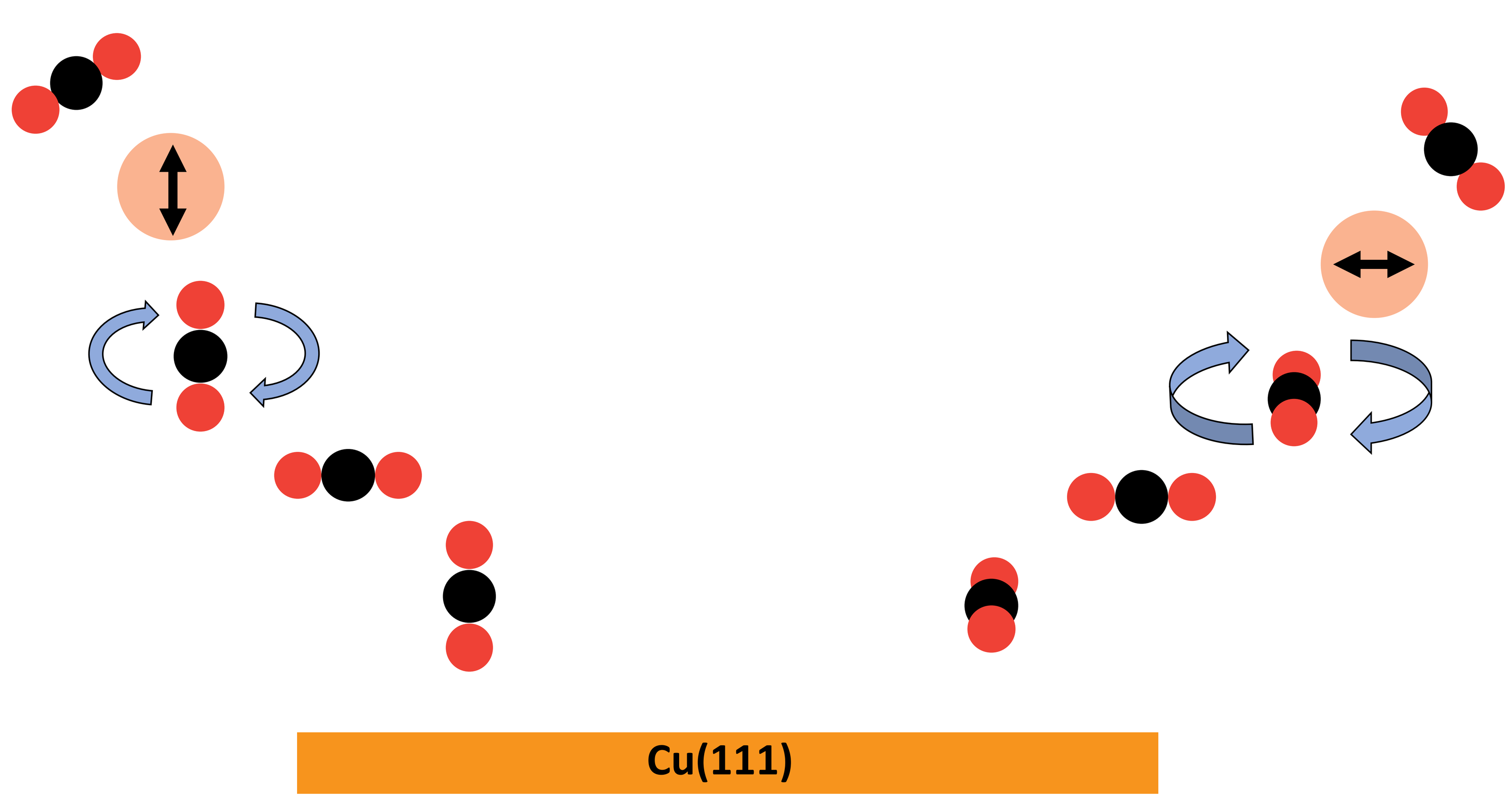

Figure 2: Alignment of the CO_2 molecules approaching the Cu(111) surface after interacting with a laser (pink circle with double headed arrow) polarised perpendicular to the surface (left) and a laser polarised parallel to the surface (right).

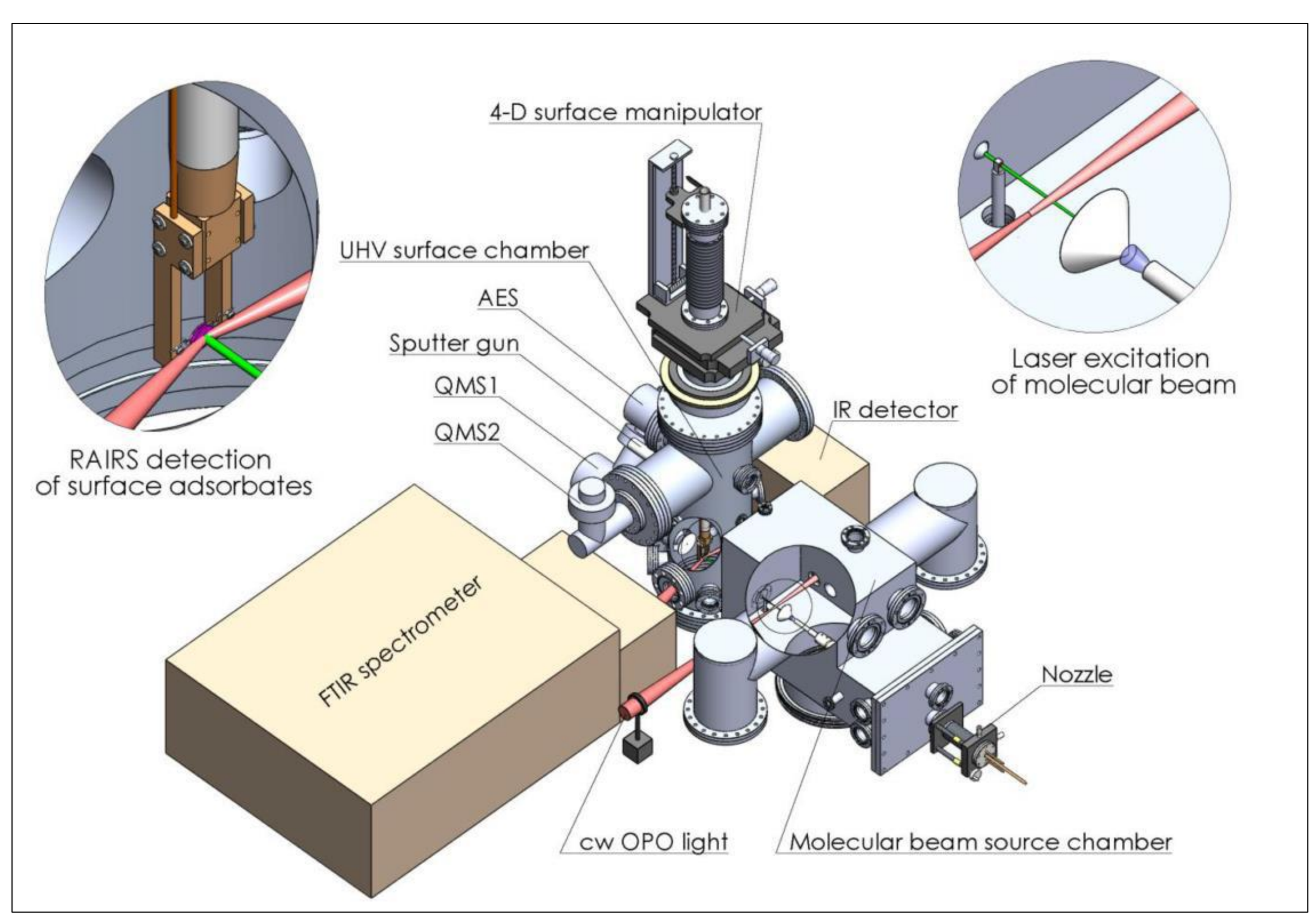

Figure 3: A model of the apparatus with the laser used for gas/surface interactions study. Taken from [2].

Reference

1. J. Quan, F. Muttaqien, T. Kondo, T. Kozarashi, T. Mogi, T. Imabayashi, Y. Hamamoto, K. Inagaki, I. Hamada, Y. Morikawa and J. Nakamura, Nat. Chem., 11, 722-729 (2019).
2. L. Chen, Vibrationally Bond-Selective Chemisorption of Methane Isotopologues of Pt(111) studied by Reflection Absorption Infrared Spectroscopy, Ph.D. thesis, École Polytechnique Fédérale de Lausanne ,Lausanne, 2012.