



A Modeling Tentative of Operation of Gas Sensor through Atomic Scale Insights

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◆ Gas sensing based on metal oxide sensing layer

Measure of conductivity

Variations come from **electronic transfers** caused by **reactions** occurring at the surface of the sensing layer due to the target gas

&

Transformation of those charge transfer processes **into measurable changes** in electrical resistance of the sensing layer



To push forward sensor development: nanostructuration, doping ...
Answers provided during this meeting!

Molecules adsorption on the surface of the sensing layer

Charges transfers btw surface species and Oxide

Concentration of adsorbed or formed specie on the surface, T influence

Other route: Fundamental Understanding

Atomic scale characterization of the of phenomena occurring at the nanoscale at the surface of the sensing layer

In situ and advanced characterizations

Theoretical concerns (DFT calculations)

- **Challenge:** Be able to predict and depict phenomena occurring at the surface of sensing layer
 - **Provide a predictive simulation of the sensor operation**
- Key points to consider:
 - Molecular level descriptions of atomistic and molecular surface reactions associated charge transfers of each formed surface species

→ Atomic scale precision

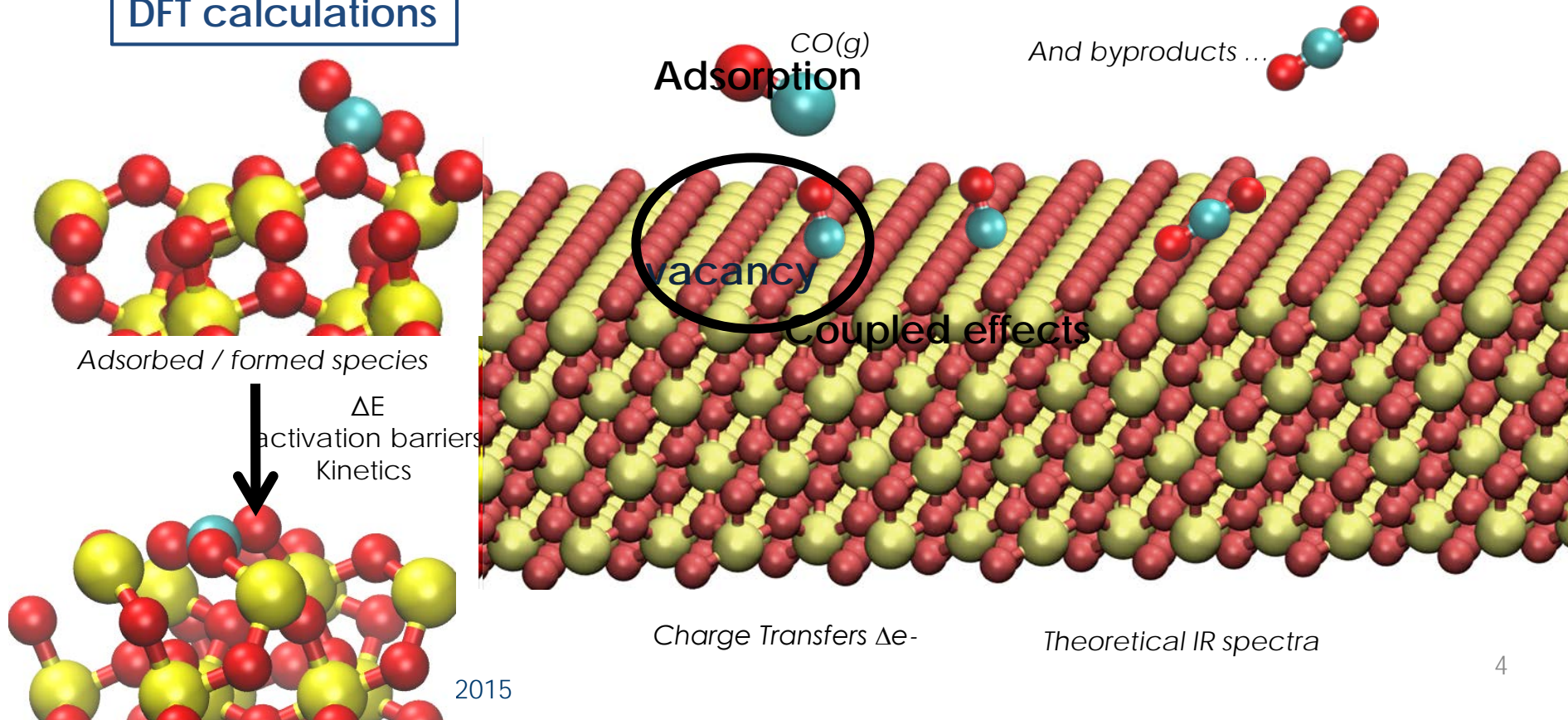
- Understanding of the macroscopic gas sensor behavior as a function of the microscopic aspects of the sensing layer

→ Mesoscopic scale

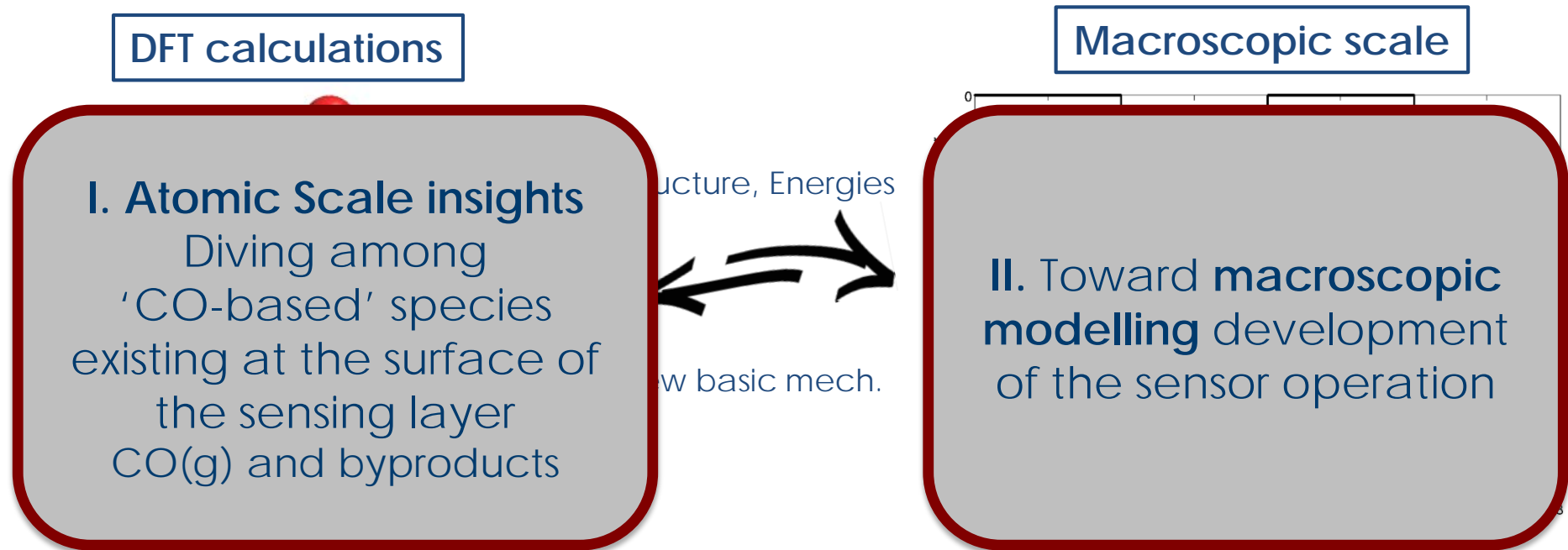
Multi-levels approach

- Applications
 - SnO₂ based sensor as a sensing layer
 - For CO(g) detection
- Overall methodology: Multi-levels strategy

DFT calculations



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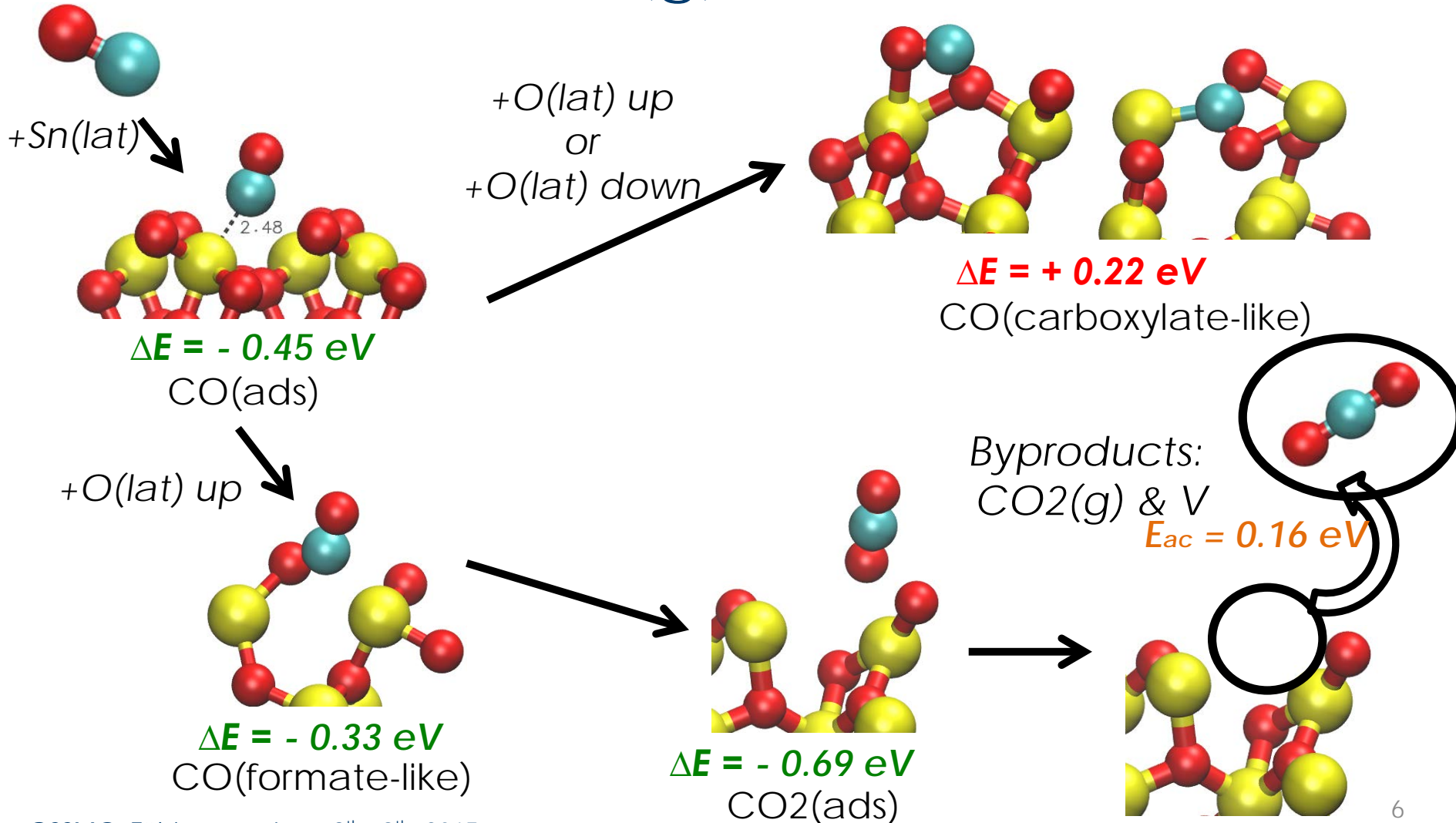


J.M. Ducéré, A. Hémercyck, ... P. Ménini, ...
 J. Comput. Chem. Vol 33, 247, (2012)

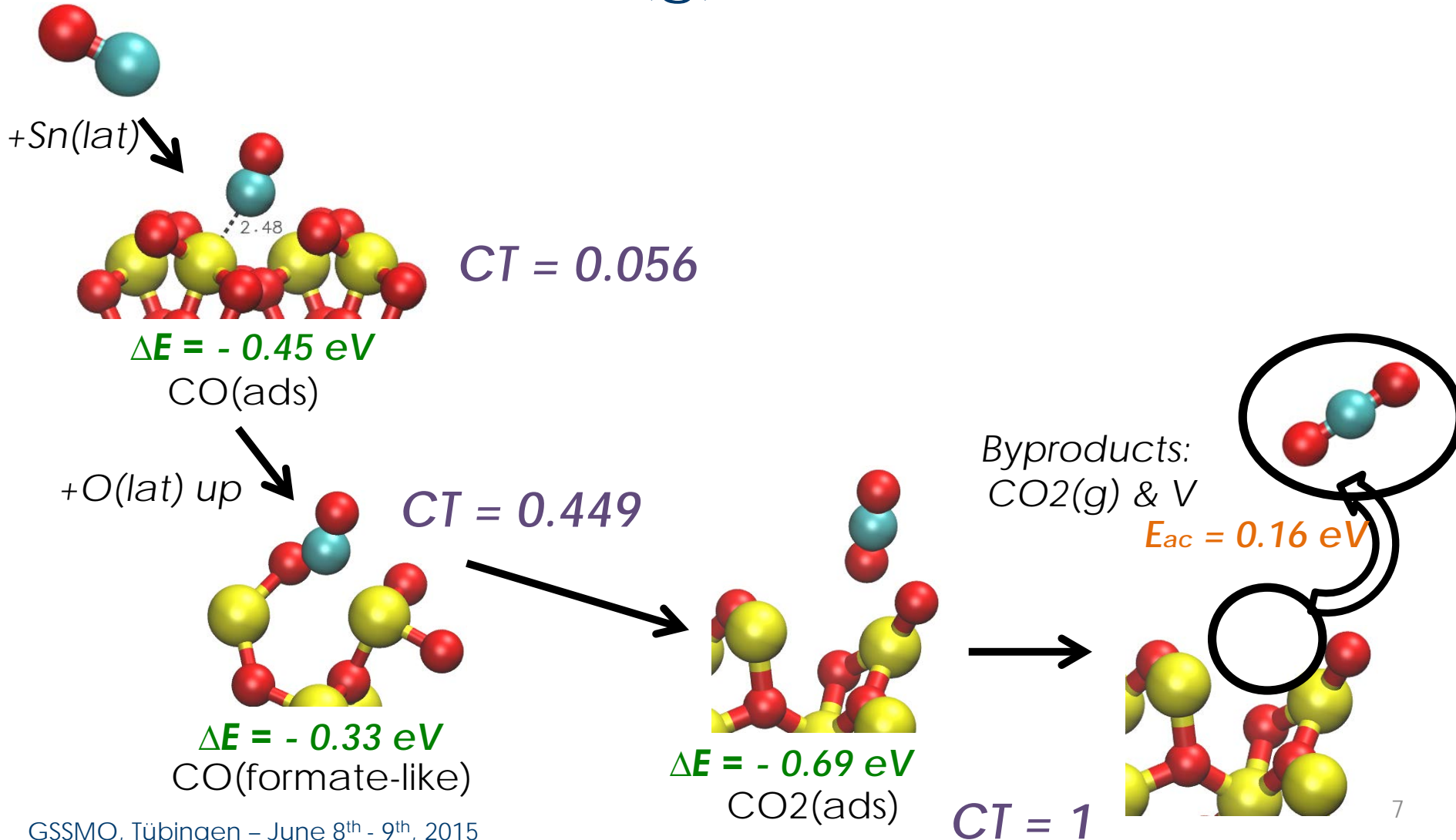
Software development & simulations

Sensor detection : Gas composition, T, P

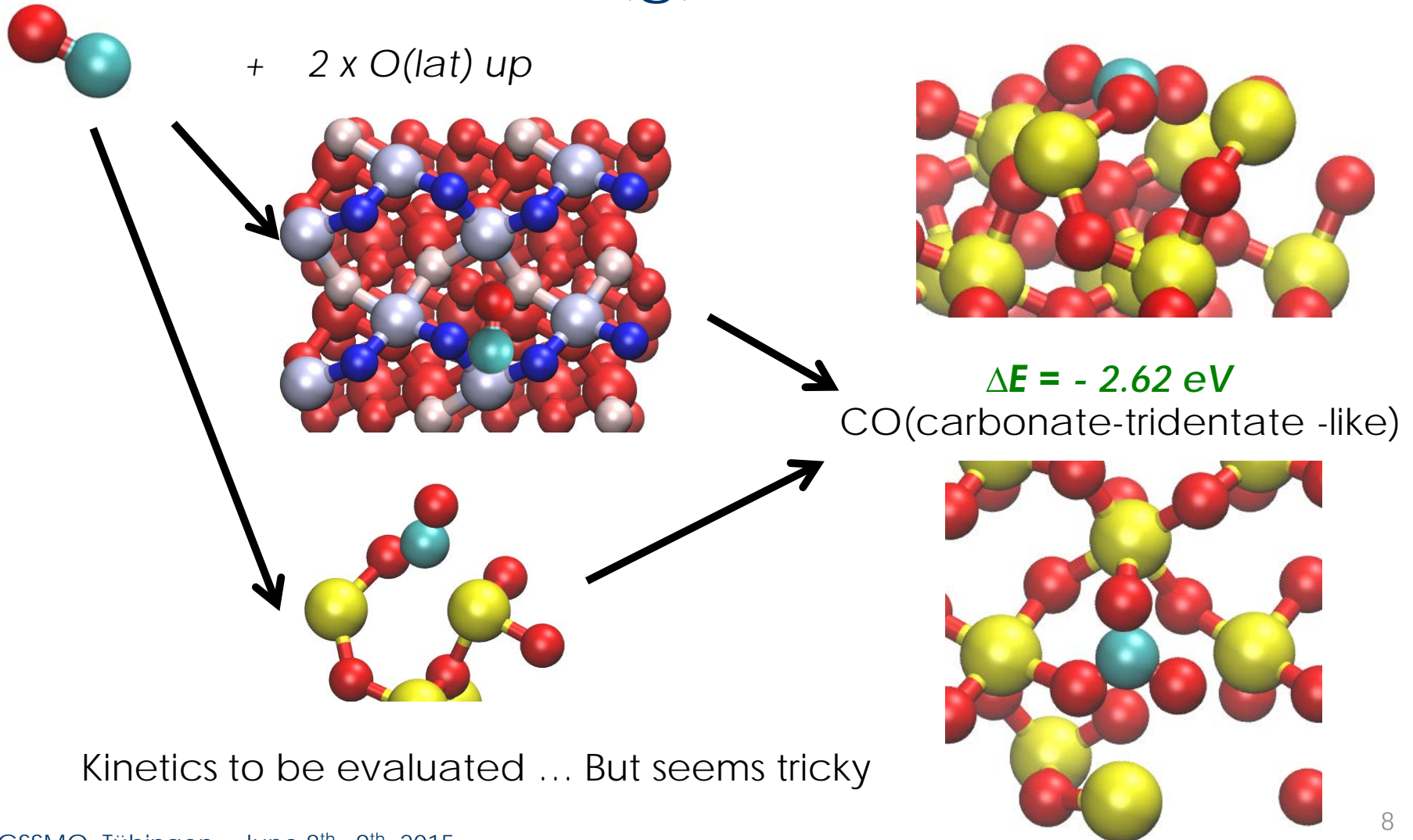
■ Detection of CO(g) on SnO₂ surface



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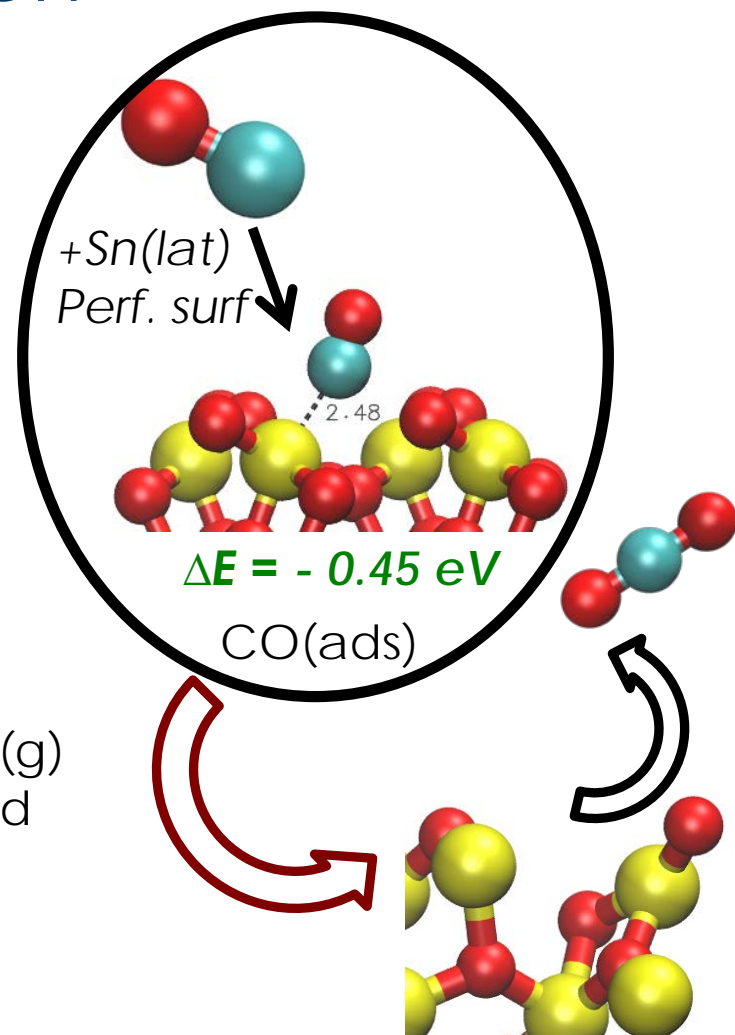
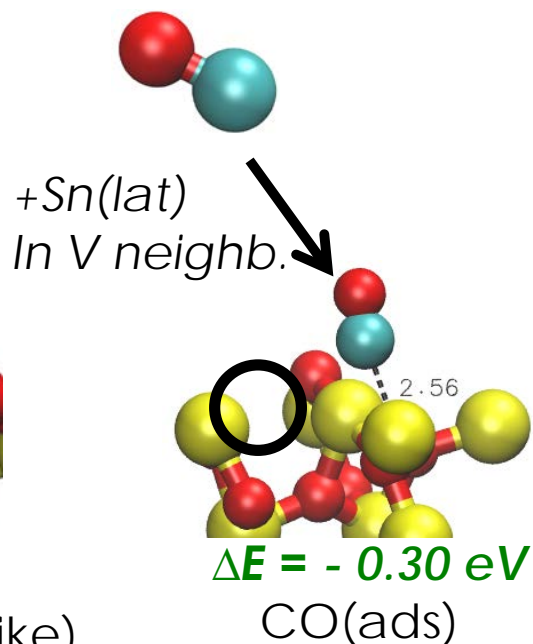
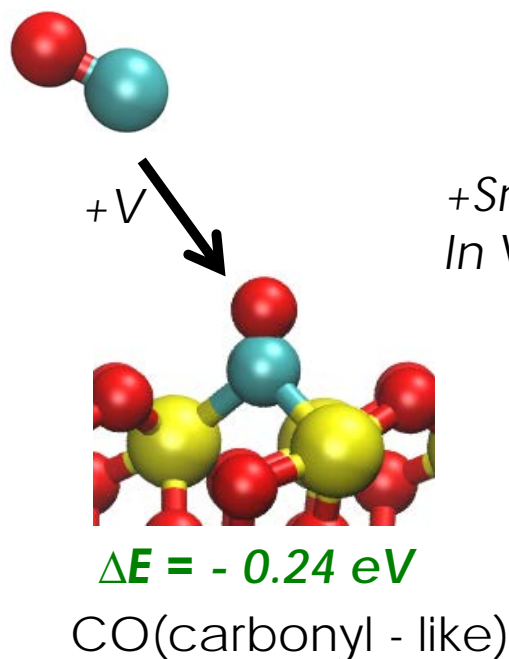


- Detection of CO(g) on SnO₂ surface



Atomic Scale Insights

- CO(g) on Vacancy as a surface reduction by CO oxidation

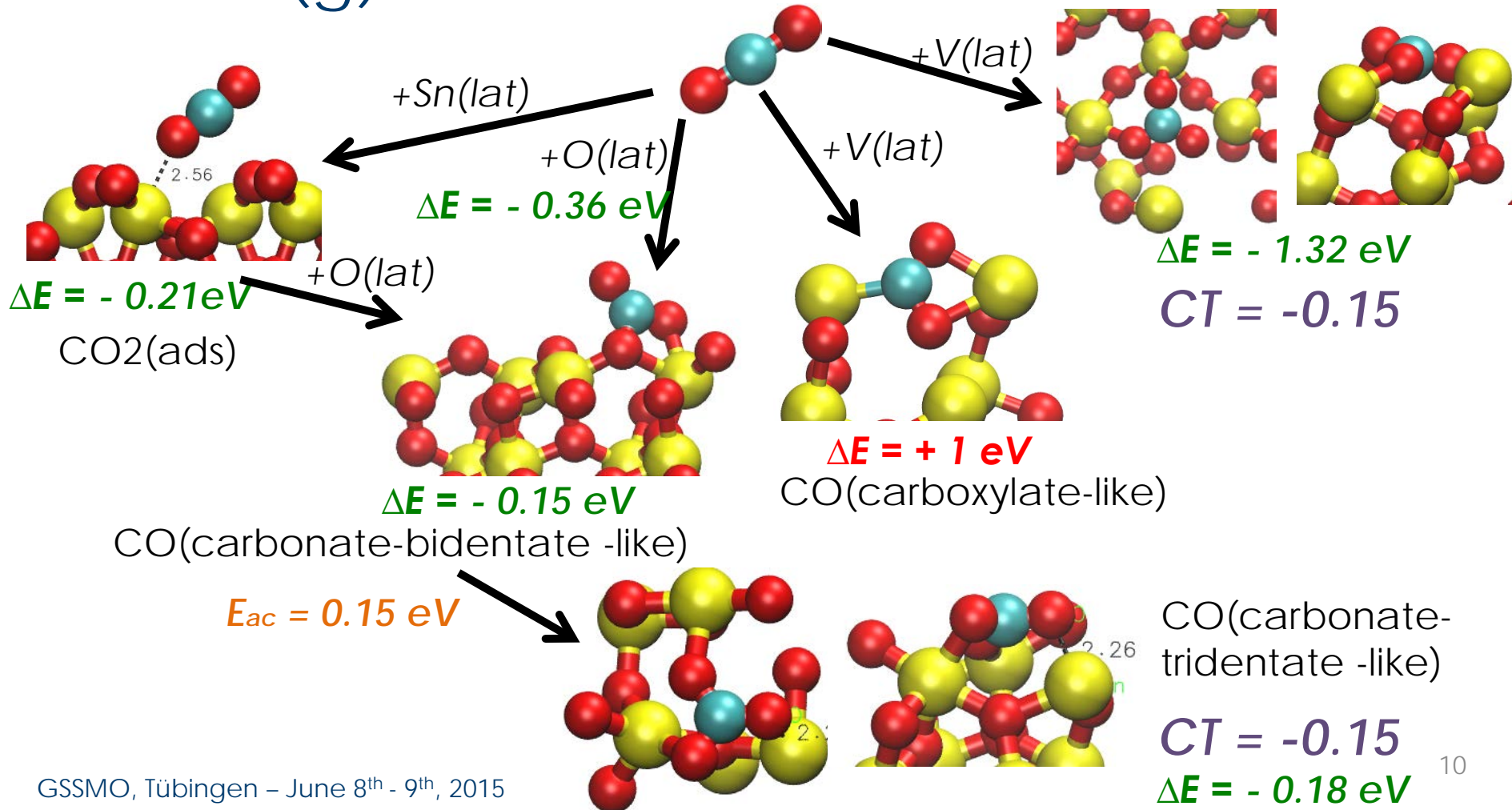


Due to kinetics and low adsorption energy: CO(g) diffuses back and forth on the SnO₂ surface and adsorbs on Sn(lat) on « perfect lattice »

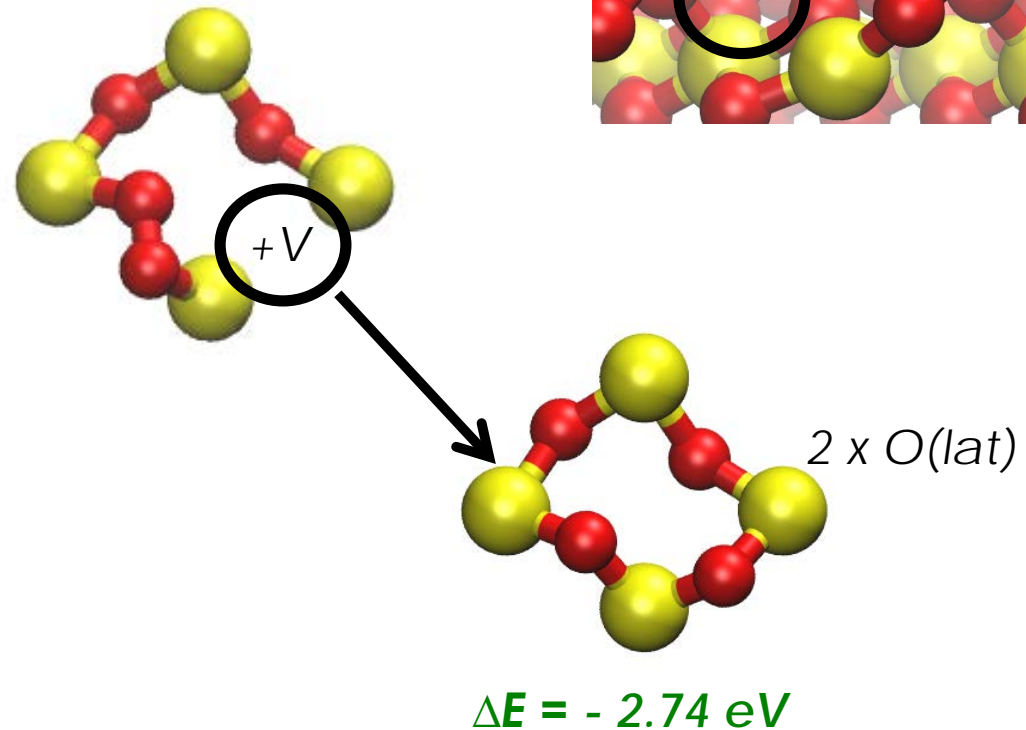
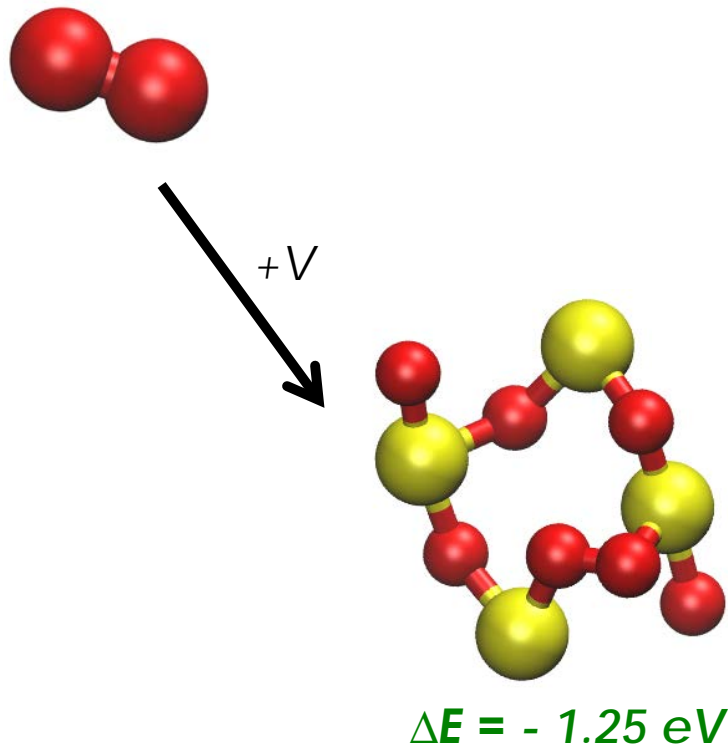
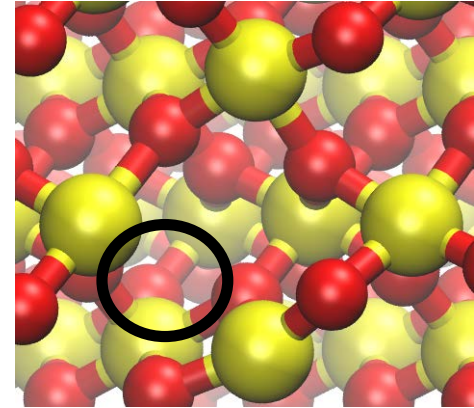
→ CO₂ desorption + V formation favored

Atomic Scale Insights

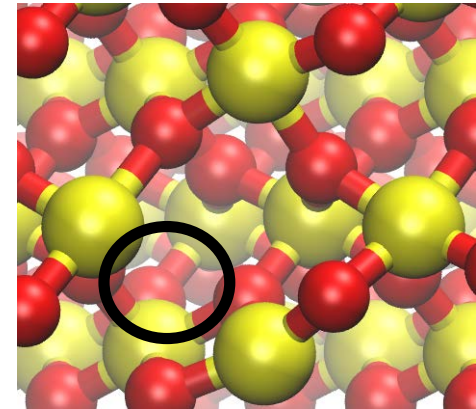
- Reaction of CO₂(g) as byproduct of CO(g) oxidation – surface reduction



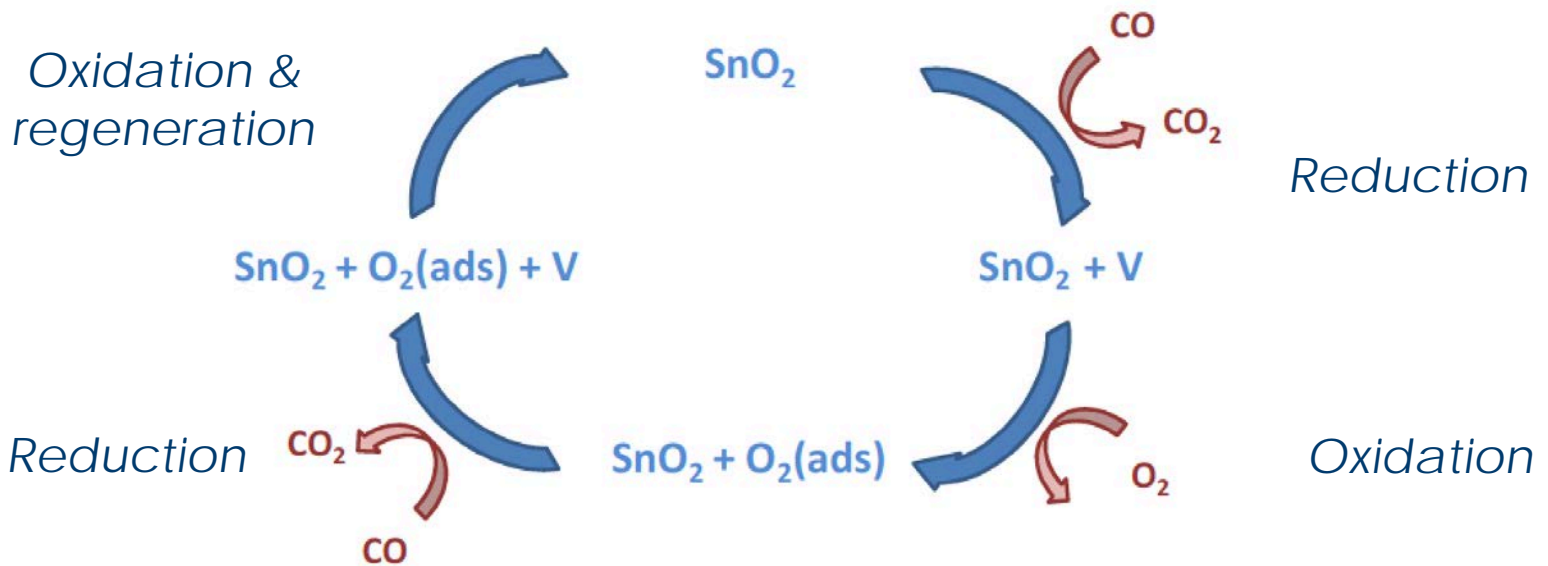
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- To pursue sensing: An oxygen source is needed



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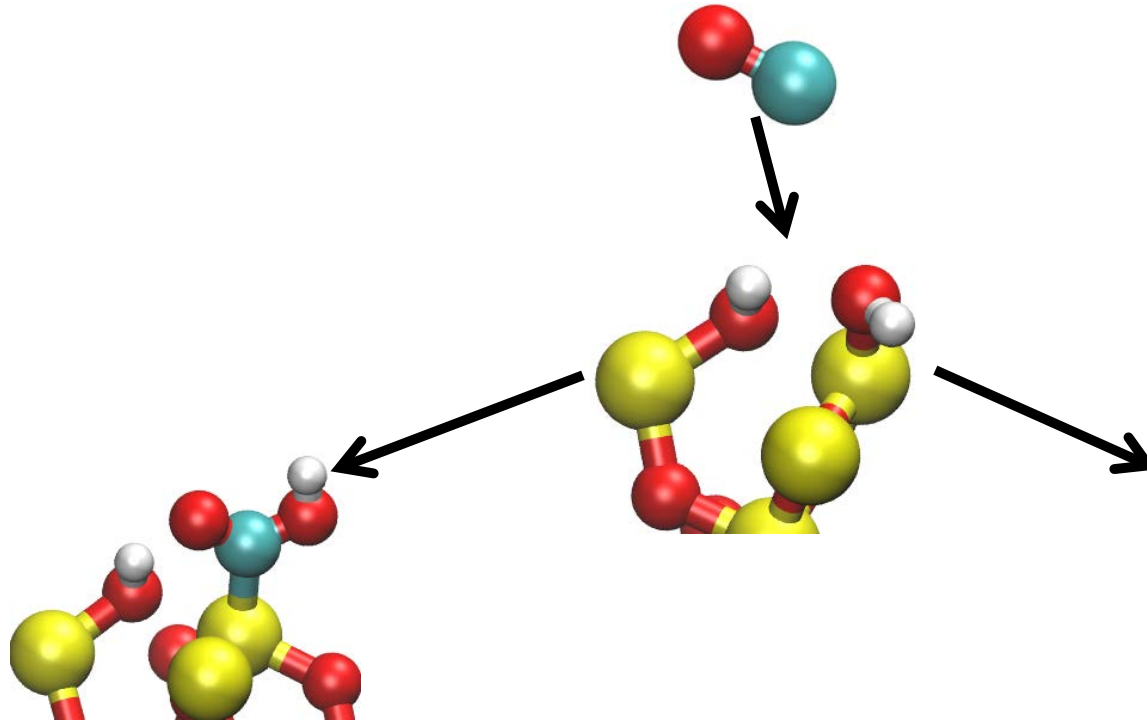
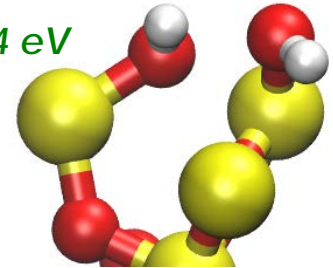


➤ **Catalytic Cycle of reduction / oxidation**
of the SnO₂ surface facing CO(g)



- Effect of Humidity (1 adsorbed H₂O)

$$\Delta E = -0.4 \text{ eV} / \text{H}_2\text{O}$$



$$\Delta E = -0.34 \text{ eV} \quad CT = -0.214$$

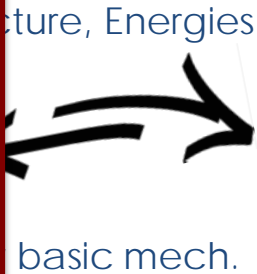
$$CT = 0.047 \quad \Delta E = -1.42 \text{ eV}$$

- CO adsorption in presence of humidity leads to stable structure
 - Water is troublesome for CO detection

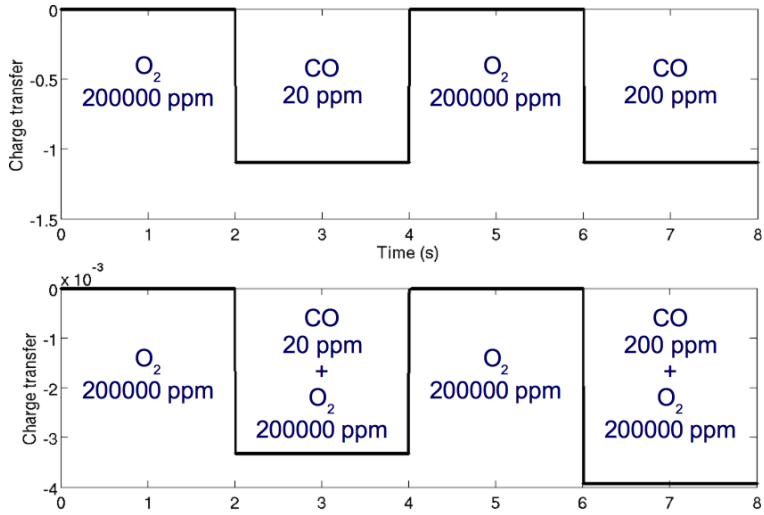
- Summary of DFT results: CO(g) detection on SnO₂(101) surface
- CO(g)
 - CO oxidation → Vacancies formation associated to high Charge Transfers → O depletion
 - Tricky to form carbonate from CO(g), no carbonyl, no carboxylate
 - Operation under O-environment → surface regeneration
 - **a catalytic cycle: oxidation/reduction**
- CO₂(g) (byproduct)
 - Reacts in defects such as Vacancies
 - Form carbonate species
- Carbonates appear as 'pollutants' because very stable
- Competition btw O₂(g) and CO₂(g) adsorption
- Water decreases CO(g) detection

- Applications
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 - For CO(g) detection
- Overall methodology: Multi-levels strategy

II. Toward **macroscopic modelling** development of the sensor operation



Macroscopic scale



Software development & simulations

Sensor detection : Gas composition, T, P

Toward a macroscopic modeling from atomic scale considerations

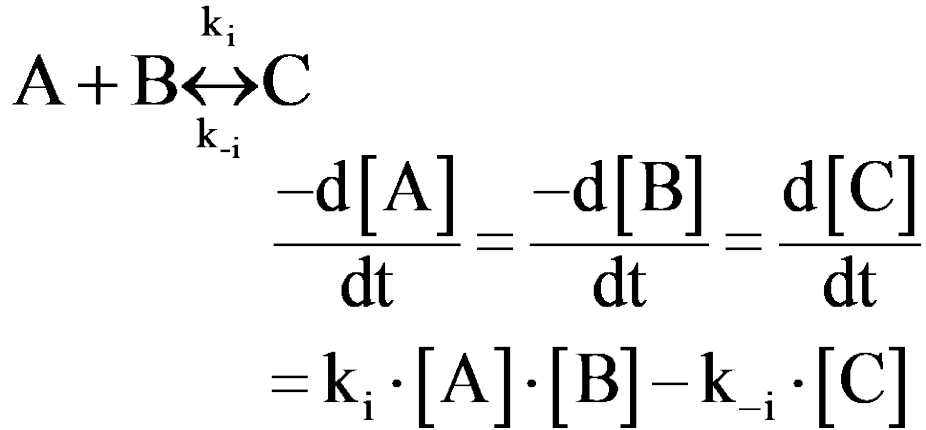
Measure of conductivity

Variations come from electronic transfers caused by reactions (adsorption, products) occurring at the surface of the sensing layer (SnO_2)

- Sensor electric response: controlled by surface chemical reaction
 - Link between Chemistry and 'electrical response'
- **SPECIFICATIONS**
 - **CT** depend on adsorbed / formed specie on the surface
 - Each specie must be followed
 - Depend on **concentration** of specie
 - Depend on kinetics of reaction (rate)
 - Depend on **Temperature and pressure** operation

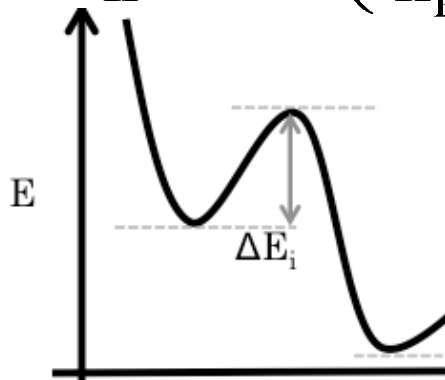
Macroscopic code developed under atomic scale considerations
 → Mixing all DFT events / Interplay of the different reactions

- Kinetic Rates Theory



- Rate constants are kinetics of the reactions (DFT activation barrier)

$$k_i = \frac{k_B T}{h} \times \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$



- ◆ Macroscopic 1D model of atomic reactions according to chemical kinetics
- ◆ Temporal evolution
Kinetic part

- ◆ Charge transfers
Measurable signal

- CT a Specie concentration

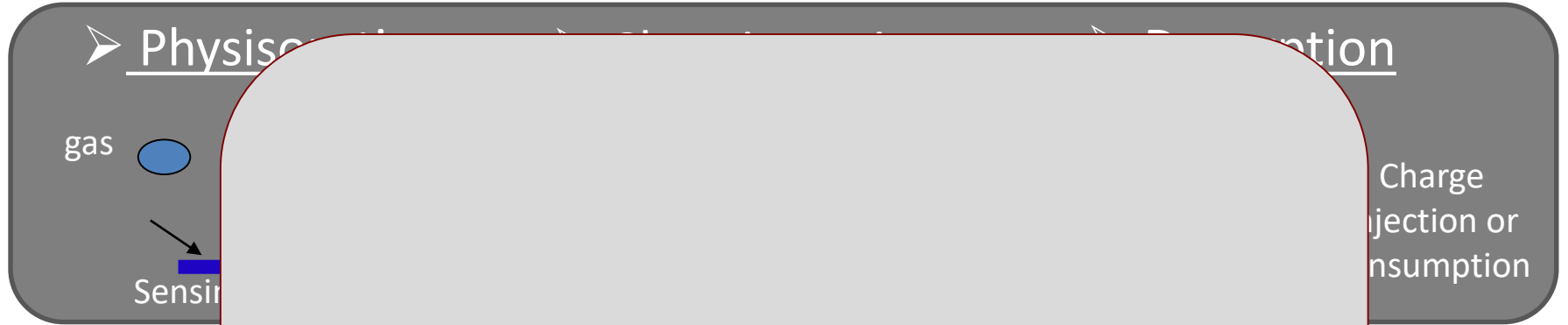
$$\frac{d(\text{CT})}{dt} = \sum_i \text{CT}_i \frac{d[i]}{dt}$$

- Detection Operation
Gas Flux: Maxwell-Boltzmann Statistics

$$C = \frac{P_{\text{gas}} S}{\sqrt{M_{\text{gas}} T_{\text{gas}}}}$$

Toward a macroscopic modeling from atomic scale considerations

Illustrations: Chemical kinetics for CO(ads) species & 2 surface reactions



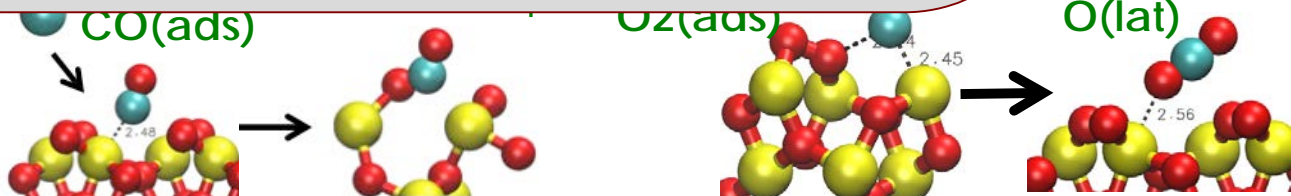
CO(g)

To do for each species on the surface (CO(ads), carb, CO₂(ads), Sn(lat), O(lat), V...) for all reactions

$$\frac{d\theta_1^{CO(ads)}}{dt} = \dots$$

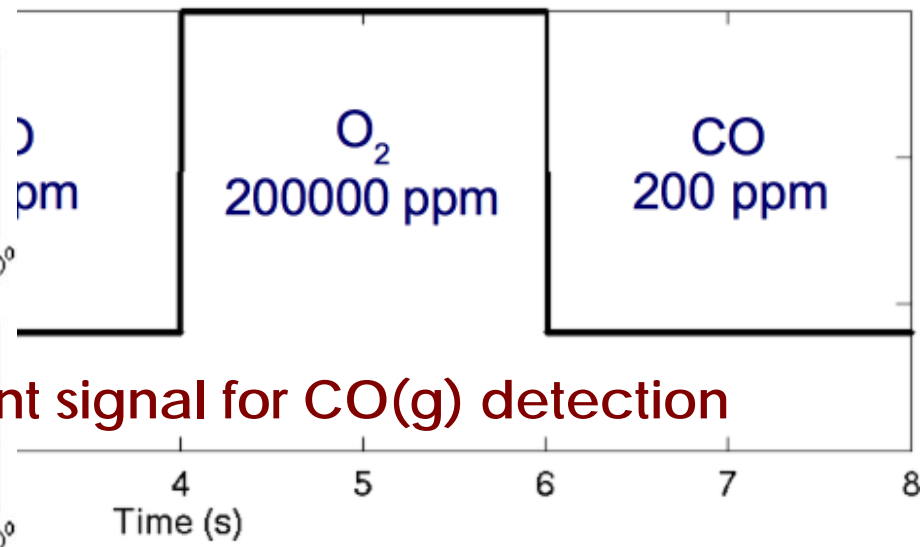
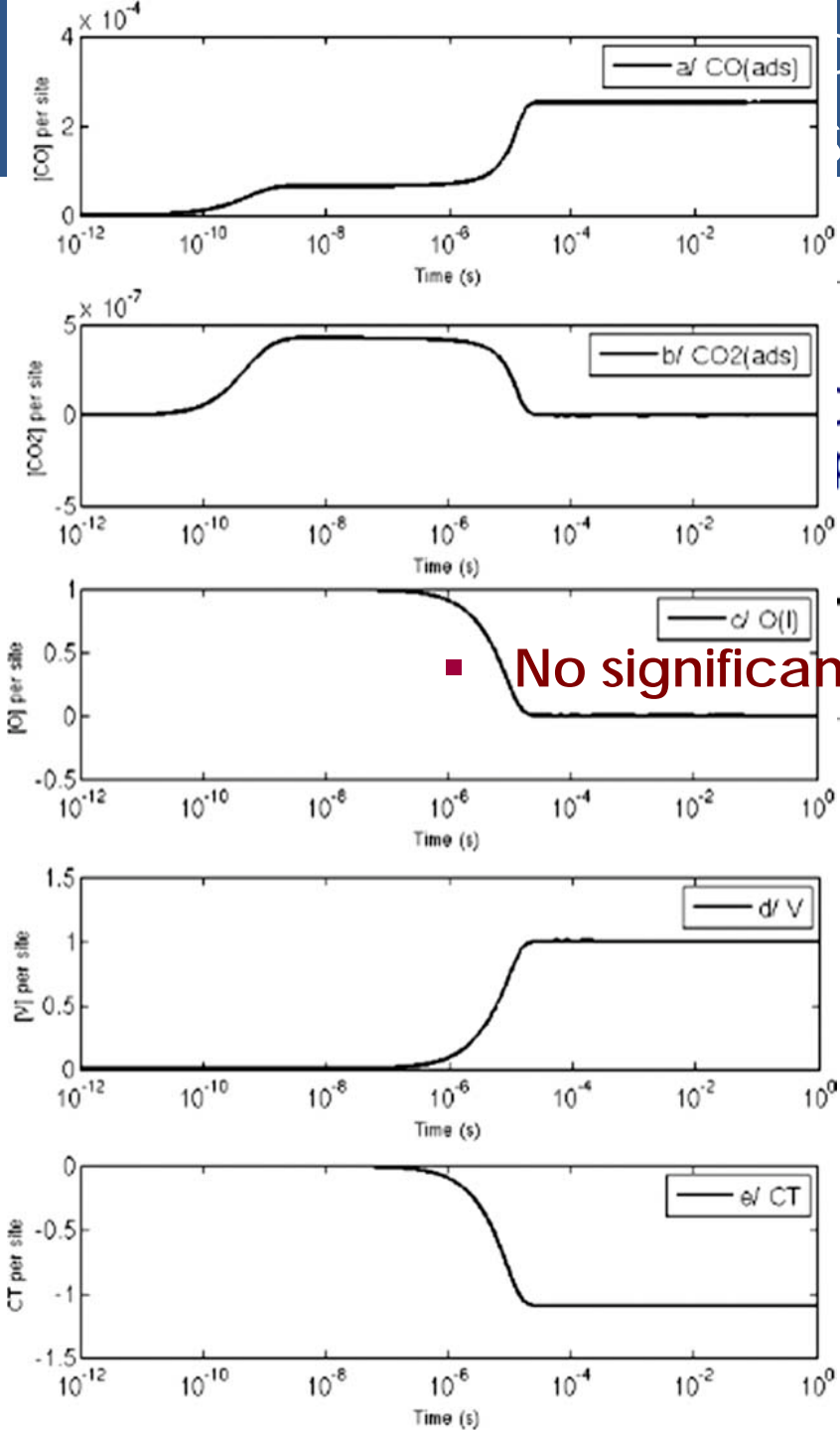
$$\theta_2 \theta_8^{O_2(ads)}$$

CO₂(ads)
O(lat)



Microscopic modeling from considerations

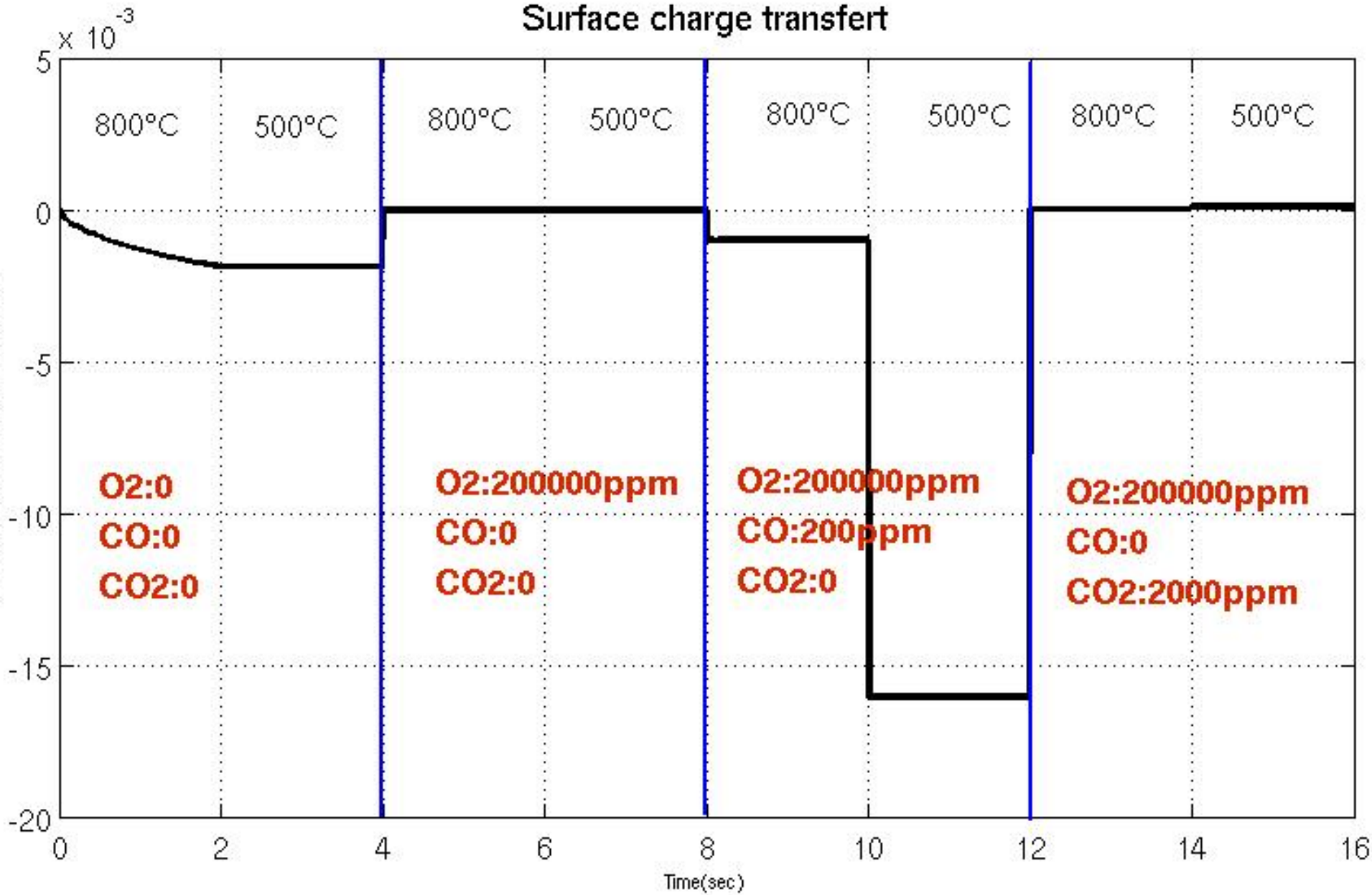
600 K $T_{\text{gas}} = 300$ K



■ No significant signal for CO(g) detection

Toward a macroscopic modeling from atomic scale considerations

Surface charge transfert



Conclusions

■ DFT

- A non exhaustive list of surface chemical reactions
- Catalytic oxidation mechanism of CO involving successive reduction and reoxidation of the oxide layer
- CO detection:
 - characterization of SnO₂-catalyzed CO combustion
 - SnO₂ reoxidation step being slower: accumulation of vacancies
→ negative charge transfer // conductivity increases
 - fast and highly exothermic reactions, large charge transfers
→ easy detection
- CO₂ detection:
 - CO₂ form stable carbonate specie
 - small charge transfers
→ small electric response *per* CO₂ → troublesome detection
- Sensitivity to interferents (H₂O)

■ Mesoscopic modelling

- CO detection by the sensor
- CO₂ detection is troublesome due to weak response
- Interfering role of H₂O

Conclusions

- **Agreement with the experimental surface characterizations and with experimental tendencies on conductivity measurement**
 - Increase of the sensor conductivity under CO(g) exposure
 - Uneasy CO₂(g) detection
 - Interfering role of H₂O
- **Multi-levels modeling** to support technological development of sensor
- To provide tool for engineer and propose new routes toward nano-engineered materials
- Water role & Thermodynamics (T, P, vibrational properties) must be fully understand to consider interplay of external parameters
→ our future modeling goal