

# Vibrational Spectroscopic Studies of Formaldehyde Adsorption on Rutile TiO<sub>2</sub>(110)

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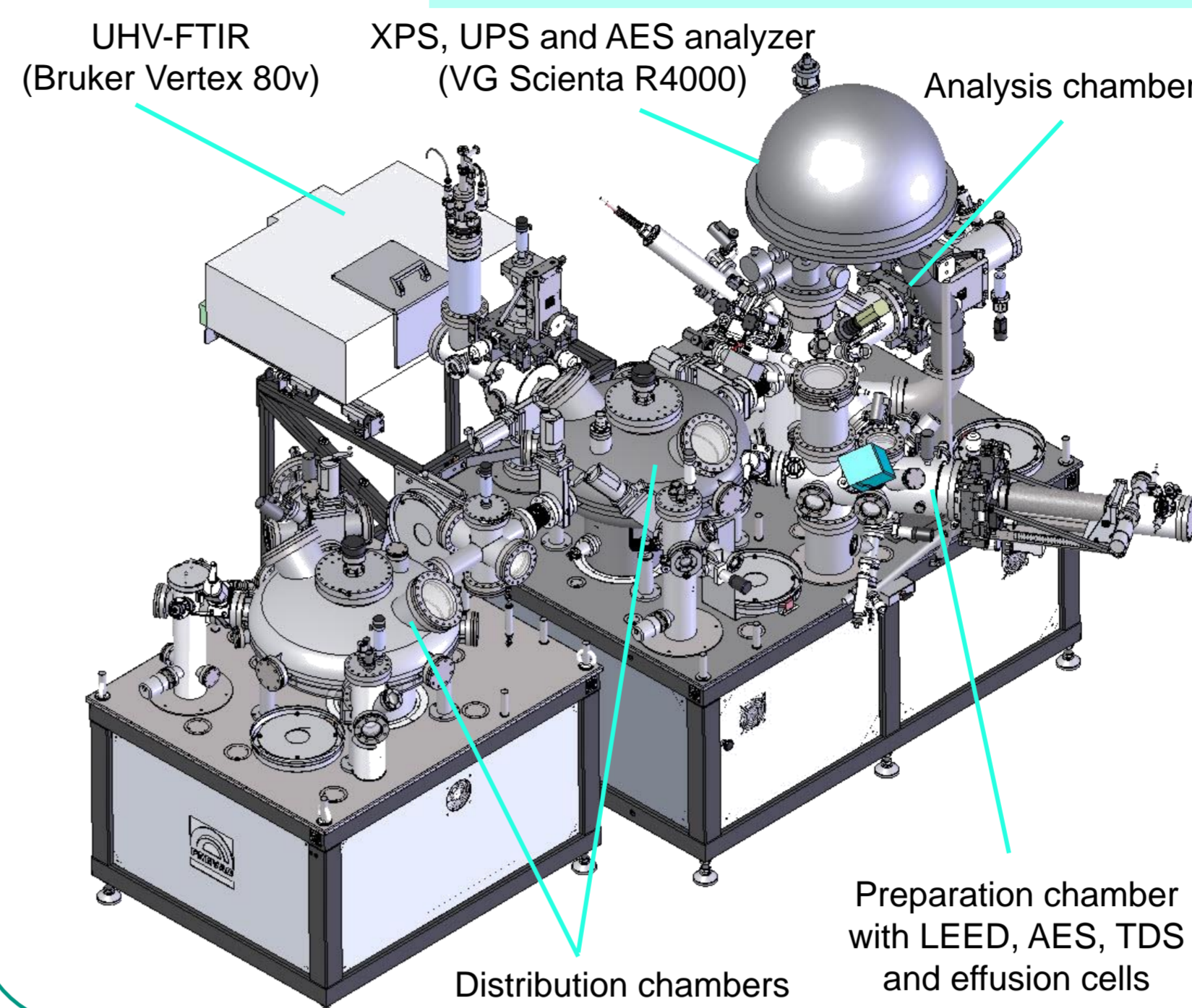
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## Introduction

TiO<sub>2</sub> is one of the most important metal oxides used in catalysis and photocatalysis. Understanding the surface chemistry of formaldehyde (CH<sub>2</sub>O) on oxide surfaces is of particular interest because CH<sub>2</sub>O is a key species (reagent, intermediate, or product) in numerous catalytic and photocatalytic reactions such as methanol synthesis, methanol oxidation and hydrocarbon production. Here, we present our systematic IR studies of the adsorption of formaldehyde (CH<sub>2</sub>O) on the oxidized rutile TiO<sub>2</sub>(110) surface using a novel ultra-high vacuum infrared reflection-absorption spectroscopy (UHV-IRRAS) apparatus.

## UHV-IRRAS apparatus



### Strategy to overcome challenge of low reflectivity:

- Attach spectrometer directly to UHV chamber.
- Do not introduce any additional optical element.
- Minimize mechanical vibrations, - crucial for time-resolved experiments.

### Additional features of "THEO":

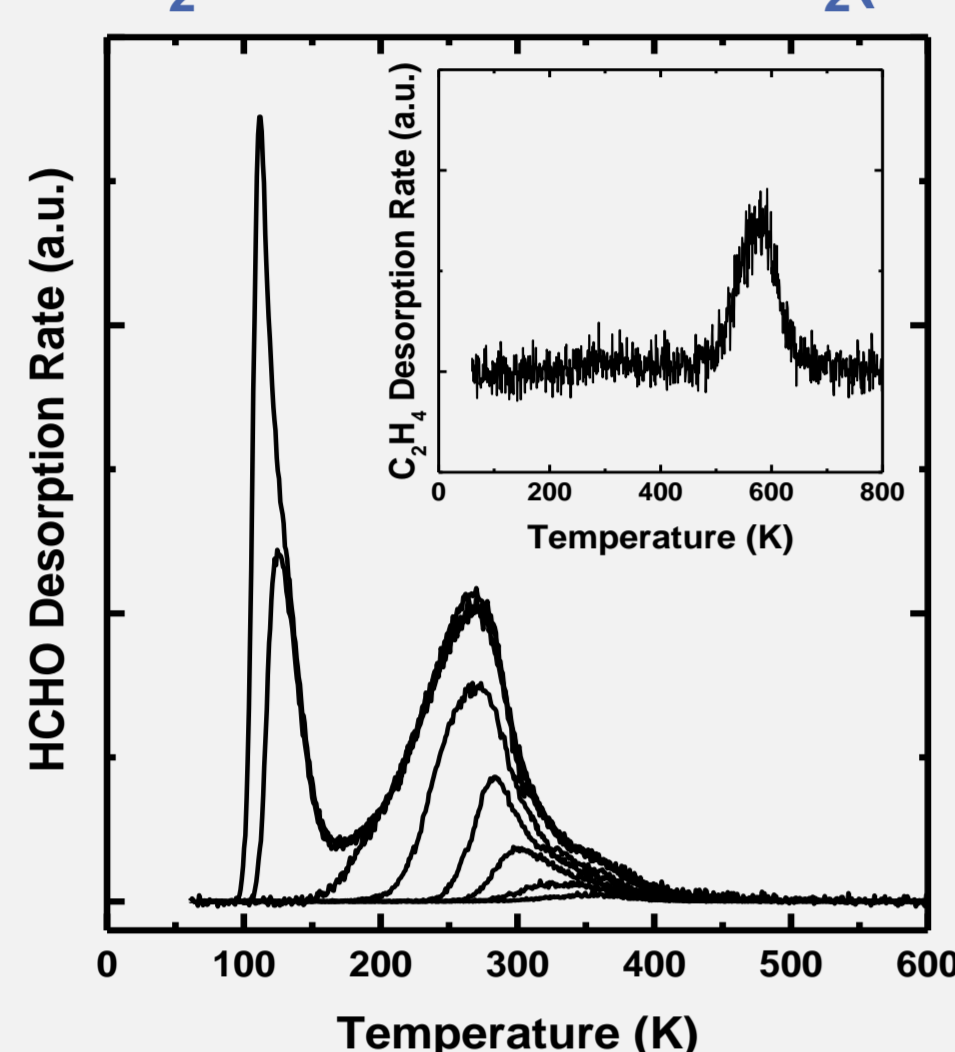
- Allows transmission measurements on powder samples.
- Cooling to 100 K (LN<sub>2</sub>) or 60 K (LHe);
- Heating up to 1200 K.
- Equipped for XPS, UPS, AES, LEIS, and LEED.

### IRRAS- Measurements:

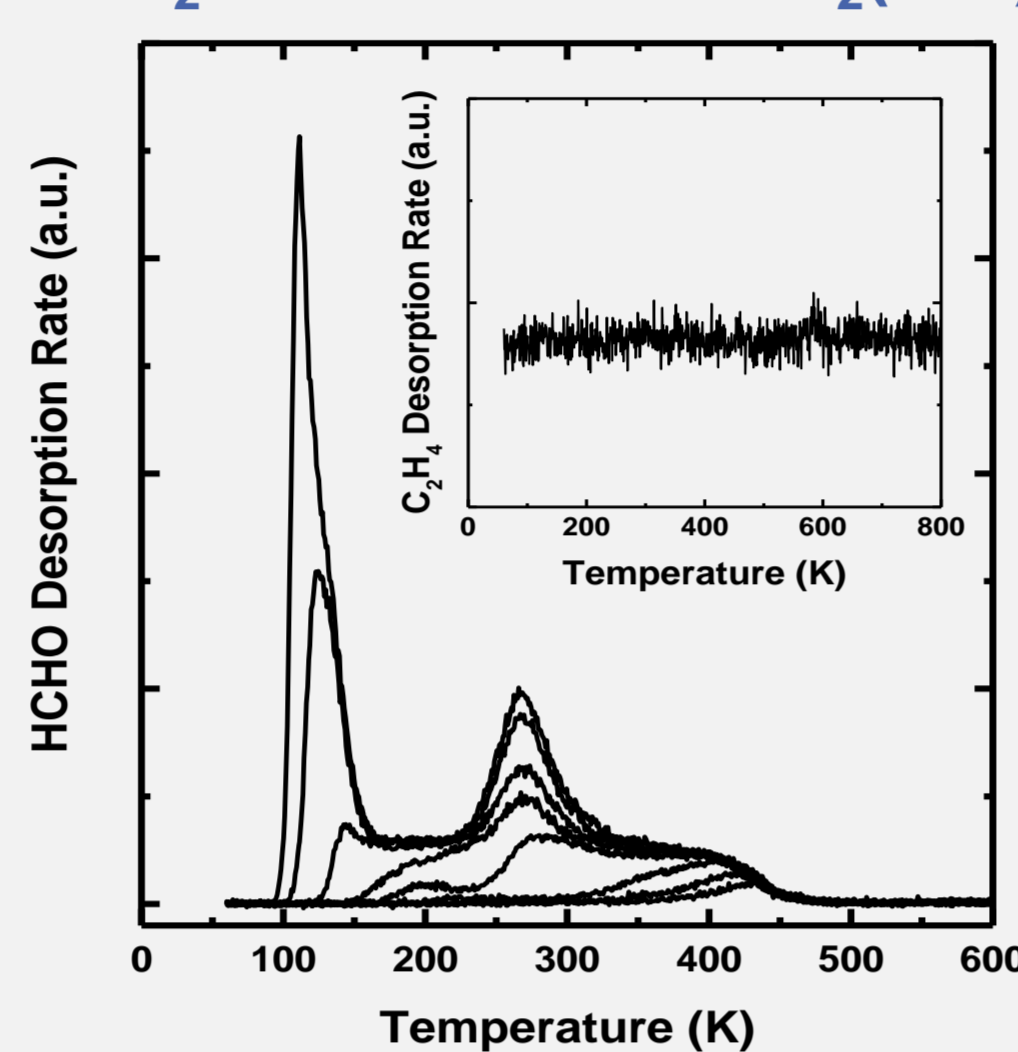
- Pressure:  $\leq 8 \times 10^{-11}$  mbar
- Reflection mode
- Grazing Incidence (80°)
- p- and s-polarized light

## TPD: CH<sub>2</sub>O adsorption on TiO<sub>2</sub>(110) at 80 K :

### CH<sub>2</sub>O on reduced TiO<sub>2</sub>(110)



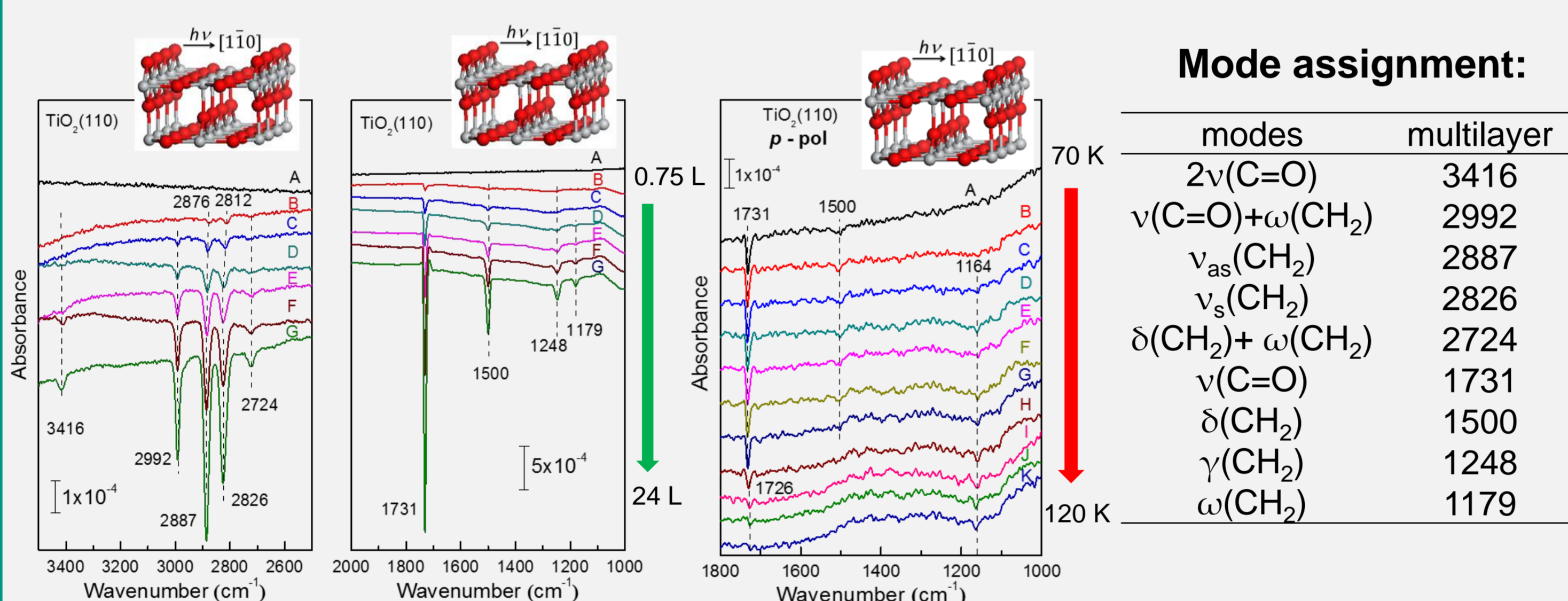
### CH<sub>2</sub>O on oxidized TiO<sub>2</sub>(110)



## CH<sub>2</sub>O adsorption on TiO<sub>2</sub>(110) : multilayer

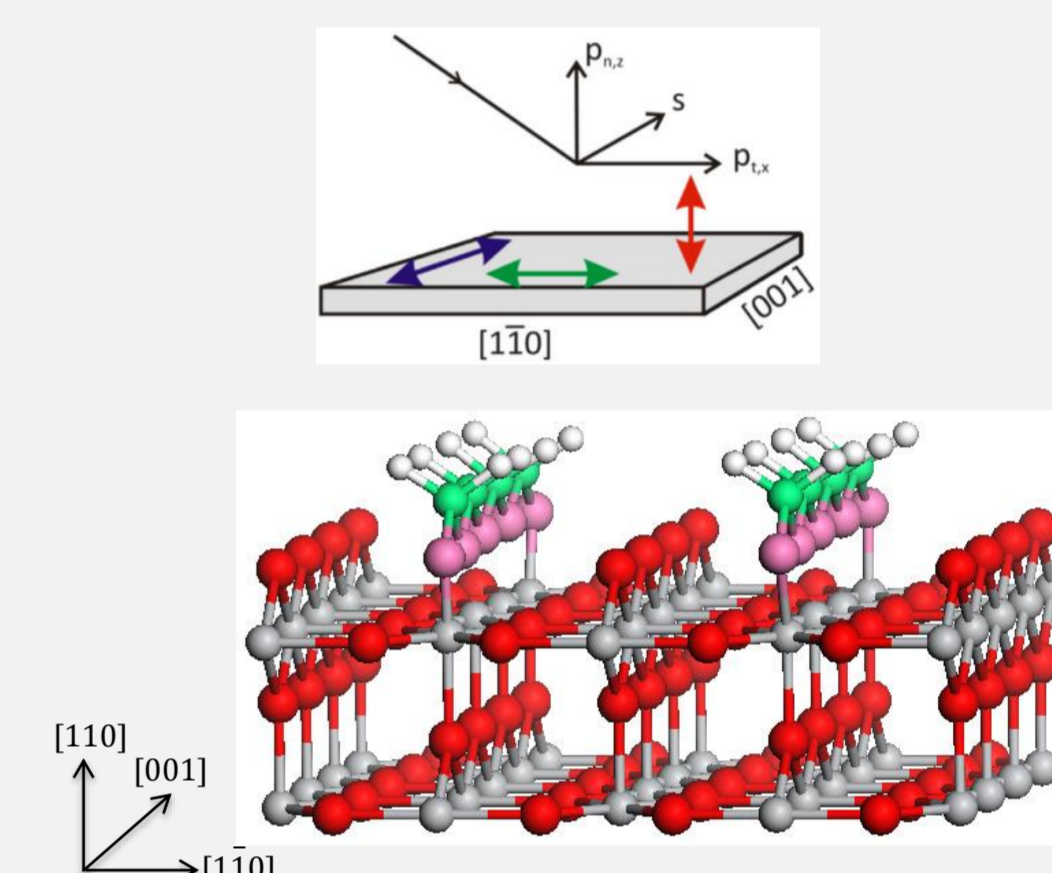
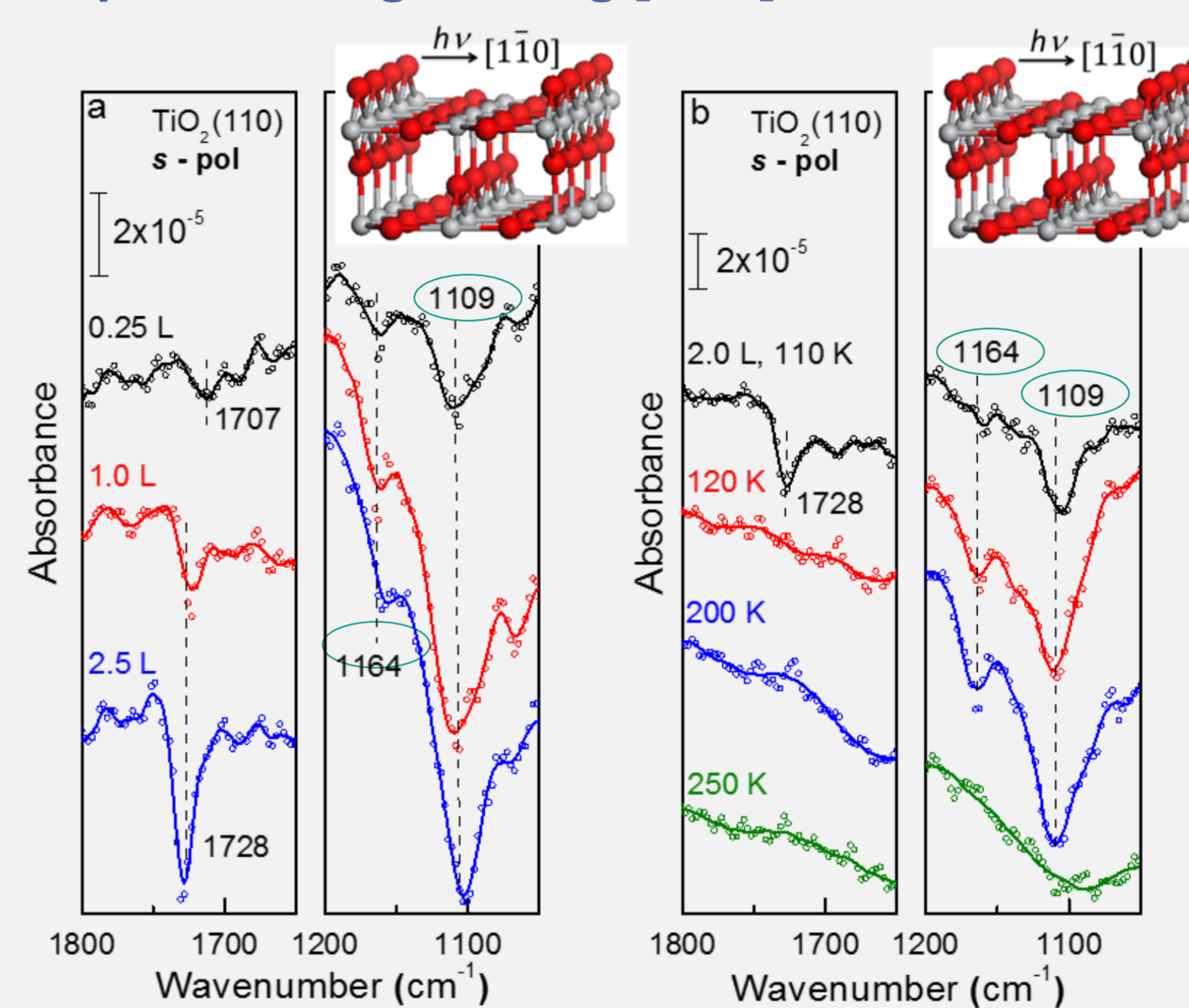
### CH<sub>2</sub>O adsorption at 65 K

### IRRAS thermal desorption data



## Paraformaldehyde

### s-polarized light along [1-10] direction

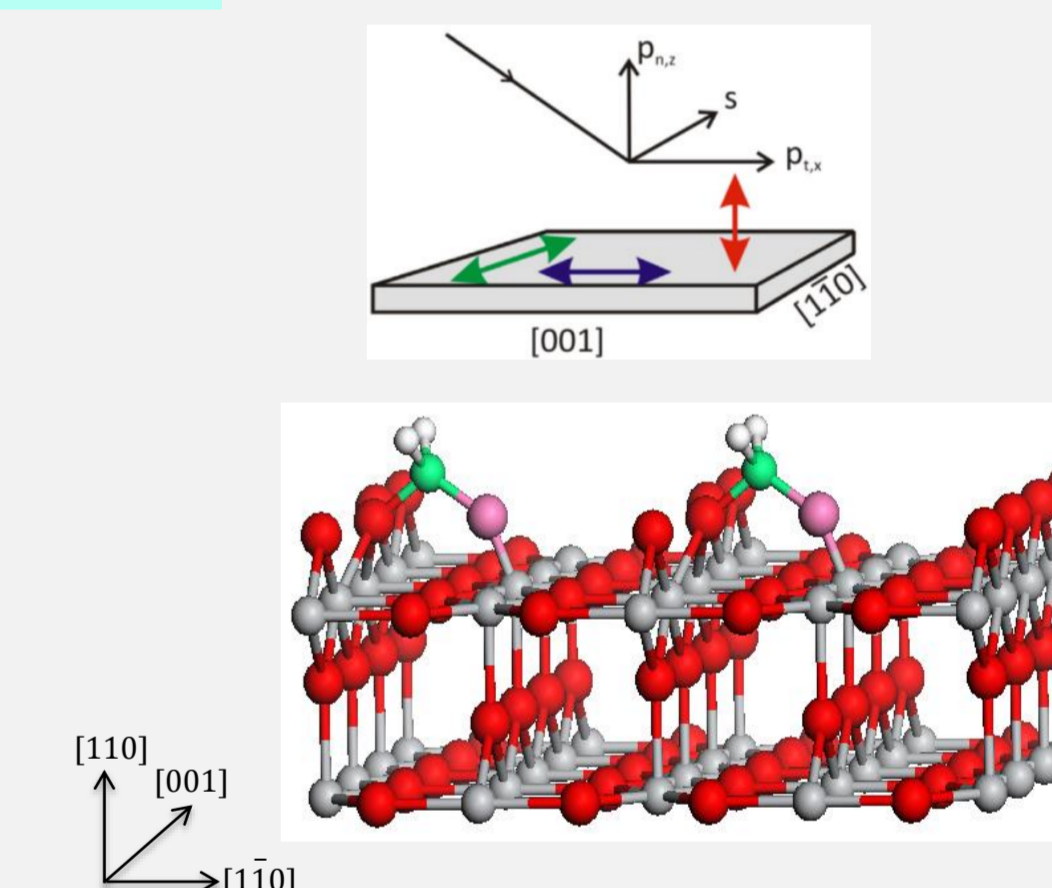
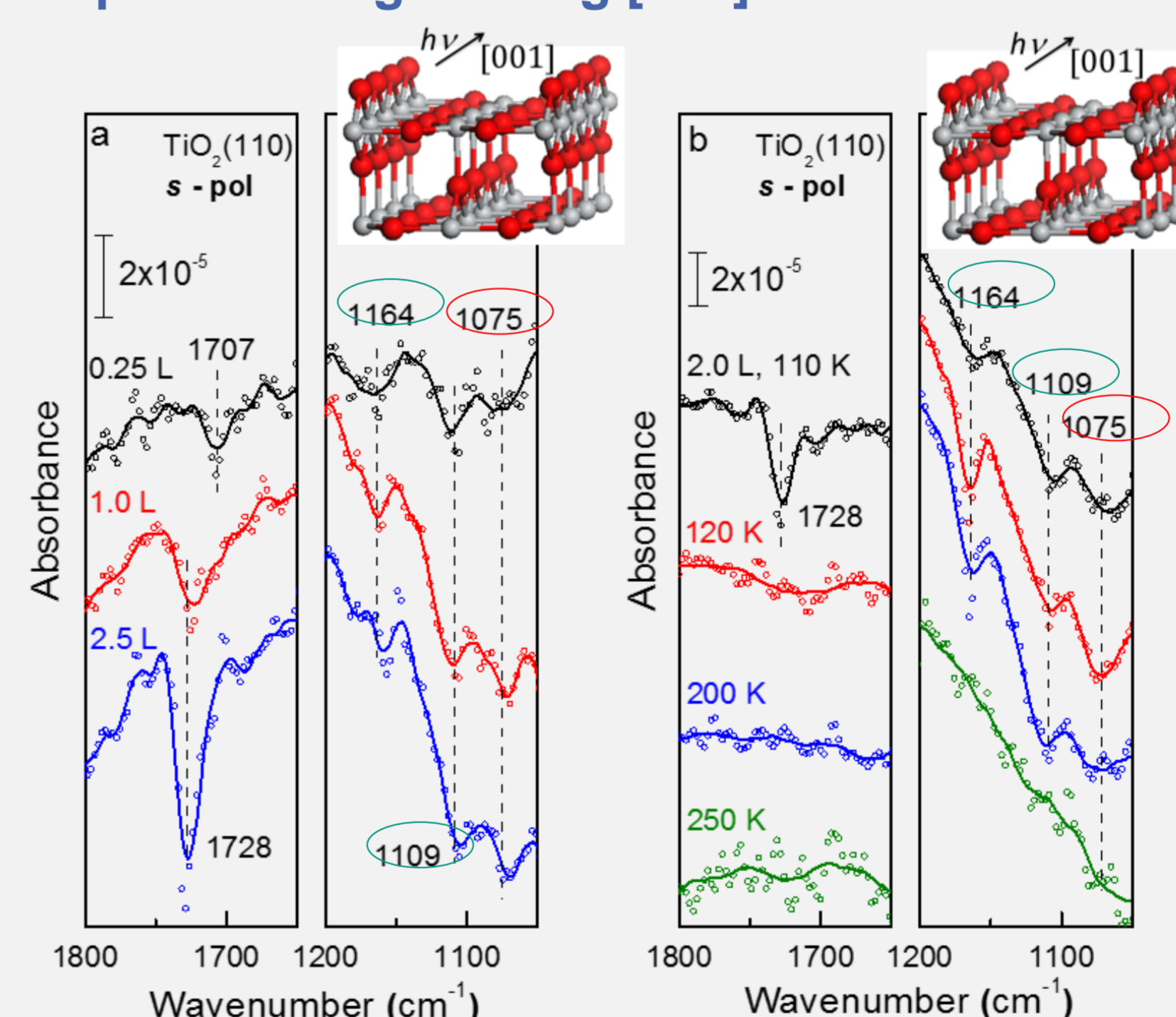


- Paraformaldehyde (POM) is formed via coupling reactions of CH<sub>2</sub>O monomers at Ti<sub>5c</sub> sites.
- The POM chain is oriented primarily along the [001] direction in a slightly disordered configuration.

ν(C-O) : 1164, 1109 cm<sup>-1</sup> (exp.)  
1158, 1120 cm<sup>-1</sup> (DFT)

## Dioxymethylene

### s-polarized light along [001] direction



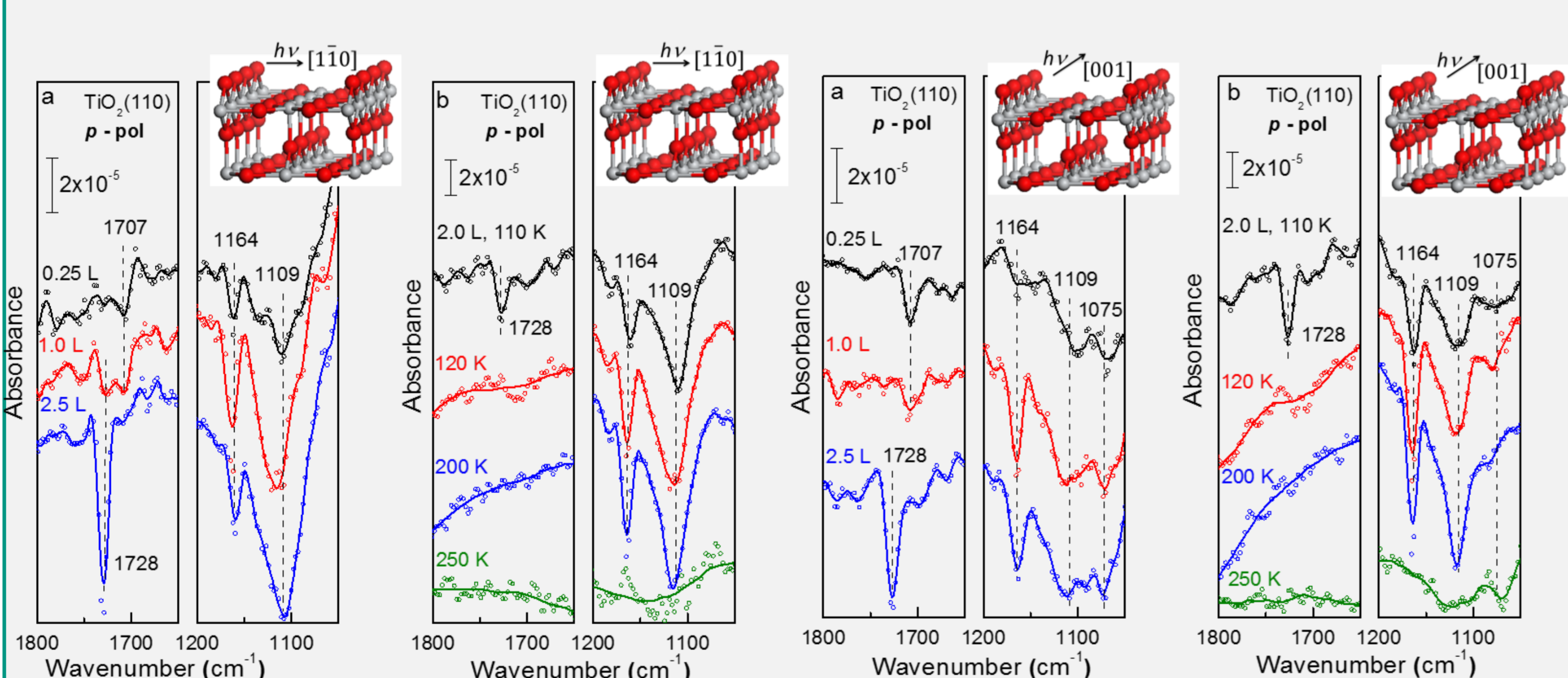
The dioxymethylene (DOM) is detected as a minority species formed via reaction of Ti<sub>5c</sub>-bound CH<sub>2</sub>O with adjacent O<sub>br</sub> along the [1-10] direction.

ν(C-O) : 1075 cm<sup>-1</sup> (exp.)  
1077, 818 cm<sup>-1</sup> (DFT)

## CH<sub>2</sub>O adsorption on TiO<sub>2</sub>(110) : monomer

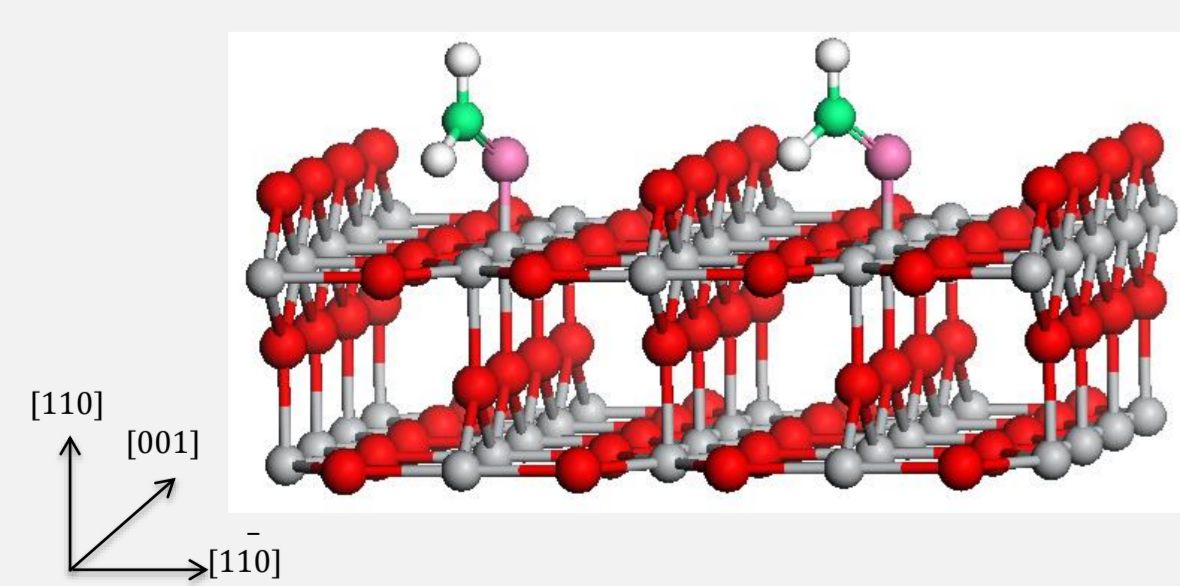
### p-polarized light along [1-10] direction

### p-polarized light along [001] direction

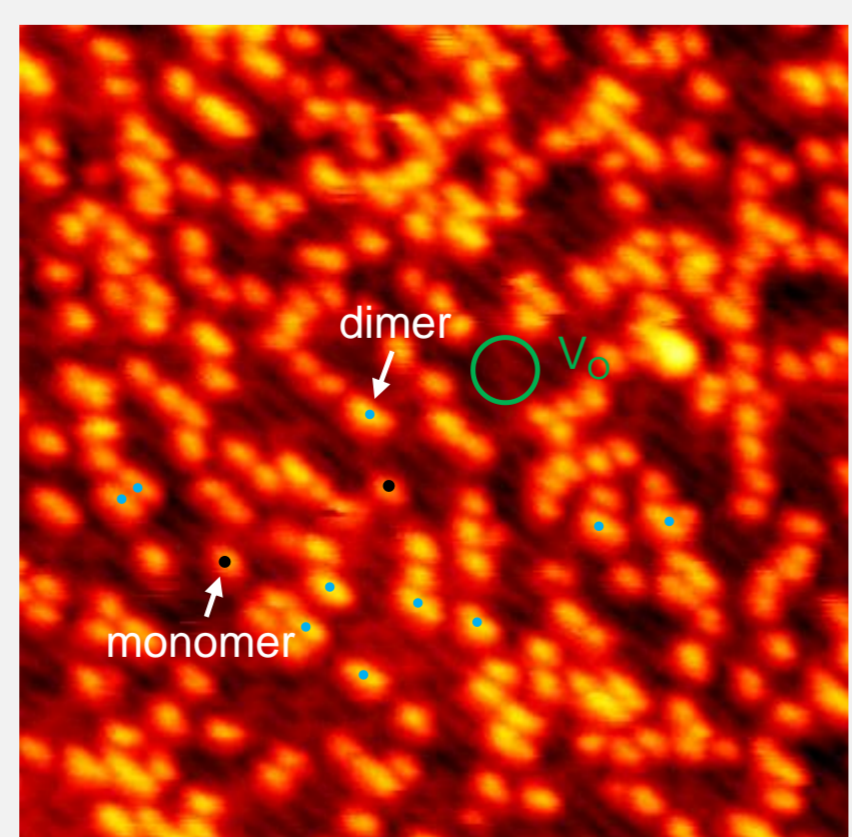


## STM

### Isolated CH<sub>2</sub>O monomer



ν(C=O) : 1707 cm<sup>-1</sup> (exp.)  
1695 cm<sup>-1</sup> (DFT)



0.07 ML CH<sub>2</sub>O at 45 K  
77 % isolated monomers at Ti<sub>5c</sub> sites  
23 % dimers at Ti<sub>5c</sub> sites

## Conclusions

- CH<sub>2</sub>O adsorption at 65 K leads to the formation of multilayer CH<sub>2</sub>O, which desorbs completely upon heating to 120 K.
- The CH<sub>2</sub>O monomer is identified after submonolayer adsorption at 110 K, in which CH<sub>2</sub>O is bound to the surface Ti<sub>5c</sub> sites via σ-donation in a tilted geometry.
- At full monolayer, paraformaldehyde is observed as a majority species formed via coupling reactions of CH<sub>2</sub>O monomers at Ti<sub>5c</sub> sites along [001] direction.
- In addition, dioxymethylene is detected as a minority one formed via reaction of CH<sub>2</sub>O with neighboring O<sub>br</sub> along [1-10] direction.

## References:

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2. K. Zhu, Y. Xia, M. Tang, Z.-T. Wang, I. Lyubintsky, Q. Ge, Z. Dohnálek, K. T. Park, Z. Zhang. J. Phys. Chem. C. 119 (2015) 18452–18457.
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