Vibrational Spectroscopic Studies of Formaldehyde Adsorption on Rutile TiO_2(110)

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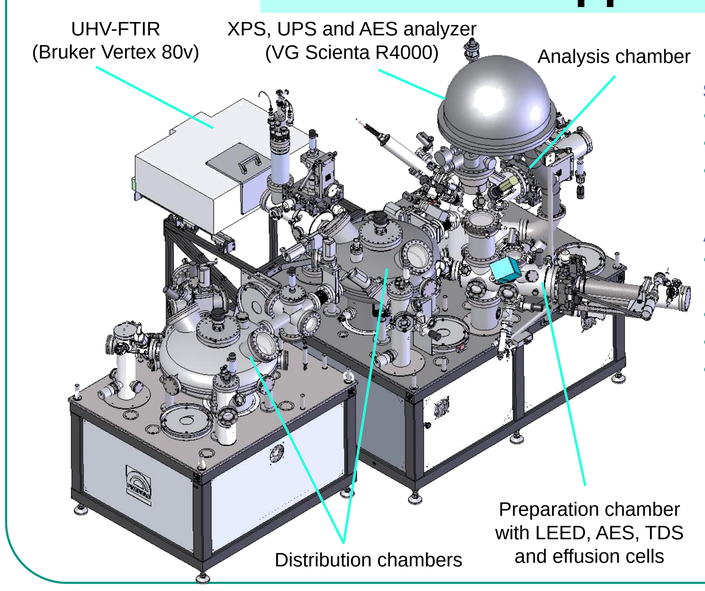
Introduction

TiO_2 is one of the most important metal oxides used in catalysis and photocatalysis. Understanding the surface chemistry of formaldehyde (CH_2O) on oxide surfaces is of particular interest because CH_2O 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_2O) on the oxidized rutile TiO_2(110) surface using a novel ultra-high vacuum infrared reflection-absorption spectroscopy (UHV-IRRAS) apparatus.

UHV-IRRAS apparatus



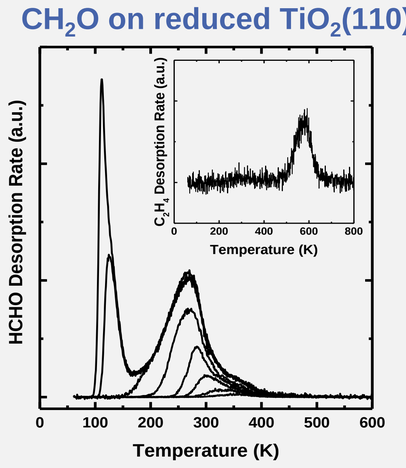
Strategy to overcome challenge of low reflectivity:
- Attach spectrometer directly to UHV chamber.
- Do not introduce any additional optical element.
- Minimize mechanical vibrations,
  - crucial for time-resolved experiments.

Additional features of "THEO":
- Allows transmission measurements on powder samples.
- Cooling to 100 K (LN_2) or 60 K (LHe);
- Heating up to 1200 K.
- Equipped for XPS, UPS, AES, LEIS, and LEED.

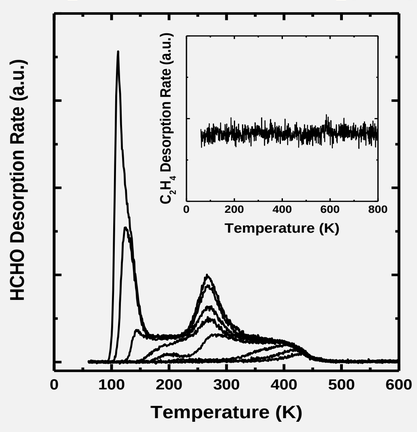
IRRAS- Measurements:
- Pressure: ≤ 8×10^{-11} mbar
- Reflection mode
- Grazing Incidence (80°)
- *p*- and *s*-polarized light

TPD: CH_2O adsorption on TiO_2(110) at 80 K :

CH_2O on reduced TiO_2(110)



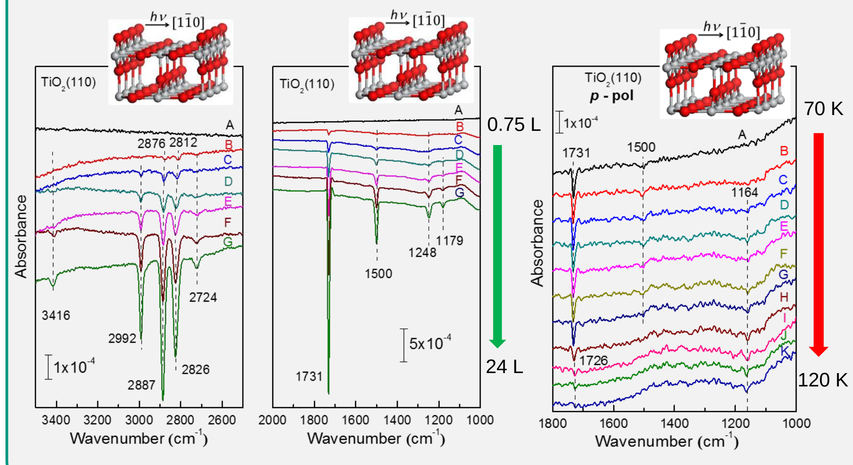
CH_2O on oxidized TiO_2(110)



CH_2O adsorption on TiO_2(110) : multilayer

CH_2O adsorption at 65 K

IRRAS thermal desorption data



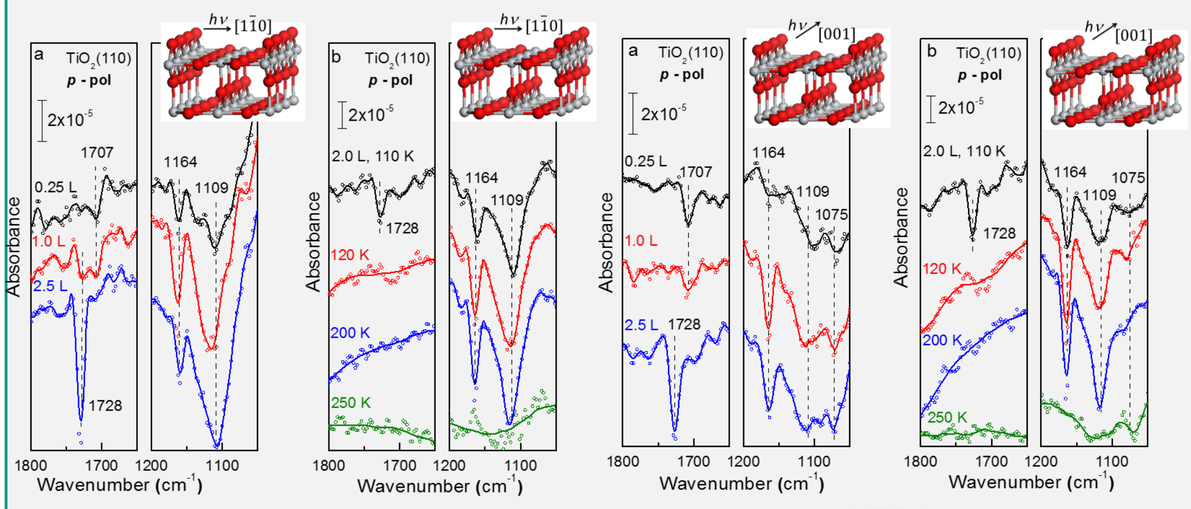
Mode assignment:

modes	multilayer
2ν(C=O)	3416
ν(C=O)+ω(CH_2)	2992
ν_{as}(CH_2)	2887
ν_s(CH_2)	2826
δ(CH_2)+ ω(CH_2)	2724
ν(C=O)	1731
δ(CH_2)	1500
γ(CH_2)	1248
ω(CH_2)	1179

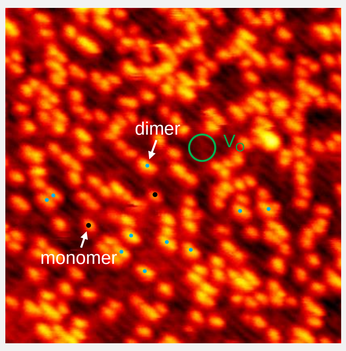
CH_2O adsorption on TiO_2(110) : monomer

p-polarized light along [1-10] direction

p-polarized light along [001] direction



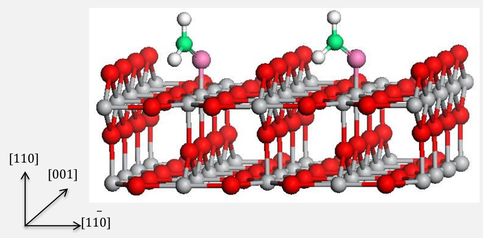
STM



0.07 ML CH_2O at 45 K

77 % isolated monomers at Ti_{5c} sites
23 % dimers at Ti_{5c} sites

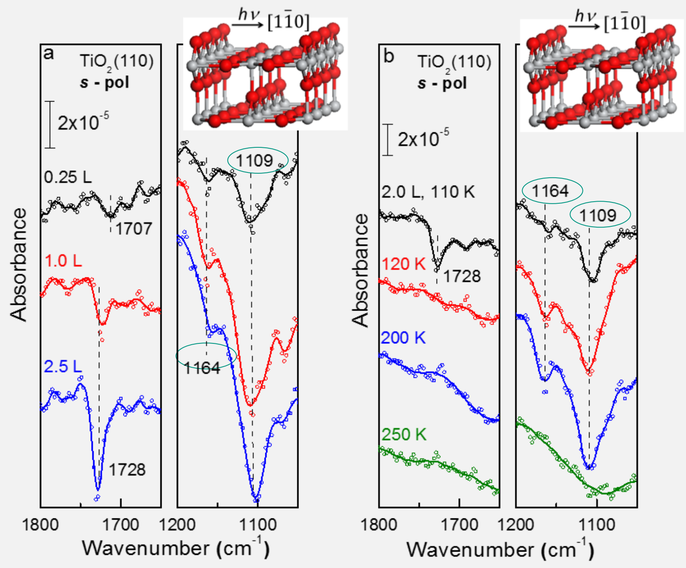
Isolated CH_2O monomer

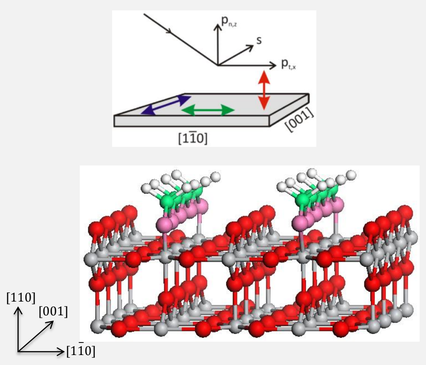


ν(C=O) : 1707 cm^{-1} (exp.)
1695 cm^{-1} (DFT)

Paraformaldehyde

s-polarized light along [1-10] direction



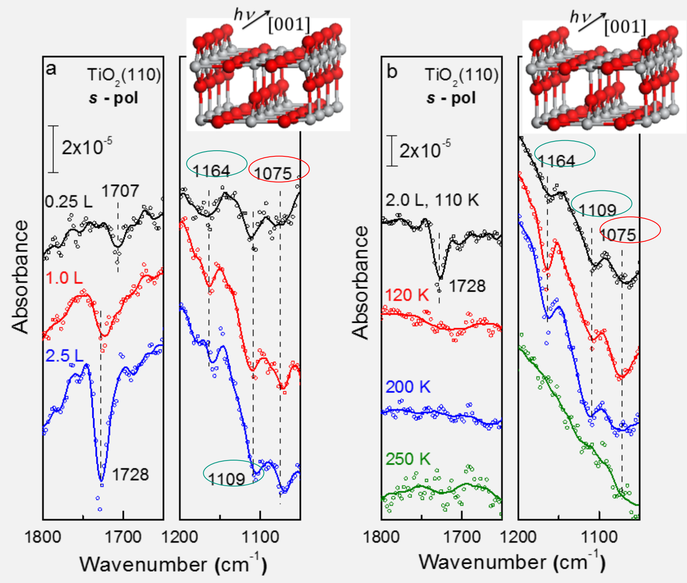


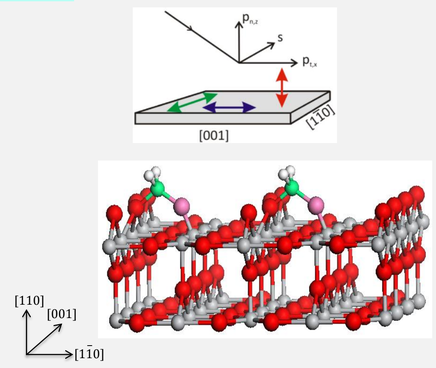
- Paraformaldehyde (POM) is formed via coupling reactions of CH_2O monomers at Ti_{5c} sites.
- The POM chain is oriented primarily along the [001] direction in a slightly disordered configuration.

ν(C-O) : 1164, 1109 cm^{-1} (exp.)
1158, 1120 cm^{-1} (DFT)

Dioxymethylene

s-polarized light along [001] direction





The dioxymethylene (DOM) is detected as a minority species formed via reaction of Ti_{5c}-bound CH2O with adjacent O_{br} along the [1-10] direction.

ν(C-O) : 1075 cm^{-1} (exp.)
1077, 818 cm^{-1} (DFT)

Conclusions

- CH_2O adsorption at 65 K leads to the formation of multilayer CH_2O, which desorbs completely upon heating to 120 K.
- The CH_2O monomer is identified after submonolayer adsorption at 110 K, in which CH_2O is bound to the surface Ti_{5c} sites via σ-donation in a tilted geometry.
- At full monolayer, paraformaldehyde is observed as a majority species formed via coupling reactions of CH_2O monomers at Ti_{5c} sites along [001] direction.
- In addition, dioxymethylene is detected as a minority one formed via reaction of CH_2O with neighboring O_{br} along [1-10] direction.

References:

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