Formaldehyde Adsorption on Rutile TiO_2(110) Surface Probed by IR Spectroscopy

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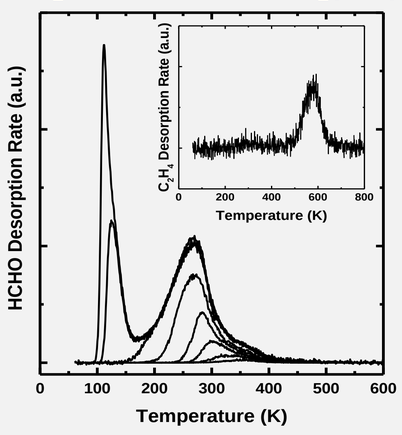
Introduction

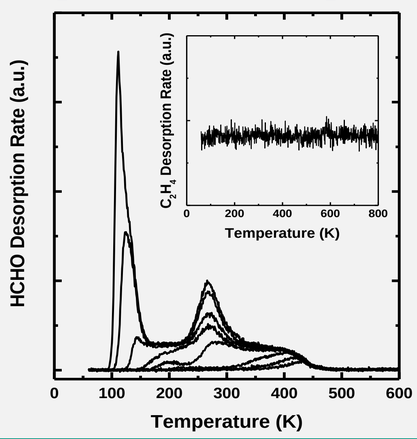
Titanium dioxide (TiO_2) is one of the most important metal oxides used in catalysis and photocatalysis. Understanding the surface chemistry of formaldehyde (CH_2O) on this material is of particular interest because CH_2O is a key species (reagent, intermediate, or product) in numerous catalytic and photocatalytic reactions such as methanol synthesis, methanol oxidation and hydrocarbon production. Here, we present a thorough surface science study on the interaction of formaldehyde (CH_2O) with the rutile TiO_2(110) surface using a novel ultra-high vacuum infrared reflection-absorption spectroscopy (UHV-IRRAS) apparatus.

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

CH_2O on reduced TiO_2(110)

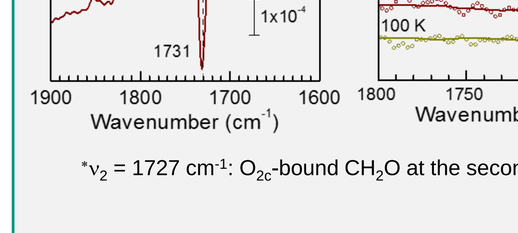


CH_2O on oxidized TiO_2(110)

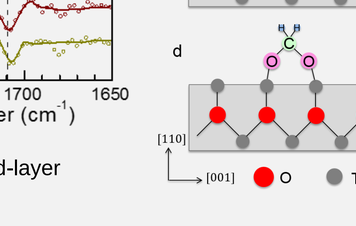


CH_2O adsorption on TiO_2(110) : Multilayers

CH_2O adsorption at 65 K



IRRAS thermal desorption data



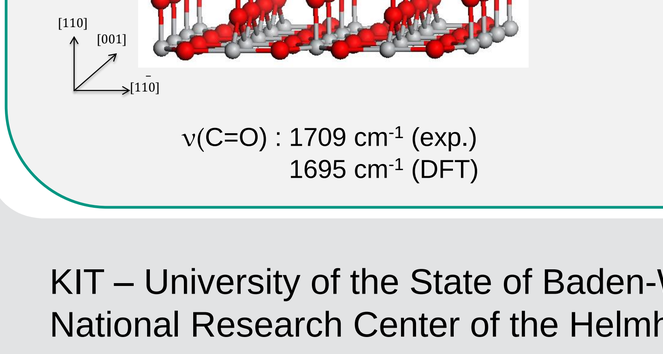
Mode assignment:

modes	gas	multilayer
$2\nu_2$	3471.7	3416
$\nu_2+\nu_5$	3000.1	2992
$2\nu_3$	2999.5	-
$\nu_{as}(CH_2)$, ν_4	2843.3	2887
$\nu_s(CH_2)$, ν_1	2782.5	2826
$\nu_3+\nu_5$	2719.2	2724
ν(C=O), ν_2	1746.1	1731
$\delta(CH_2)$, ν_3	1500.0	1500
$\omega(CH_2)$, ν_5	1249.3	1248
$\tau(CH_2)$, ν_6	1167.1	1179

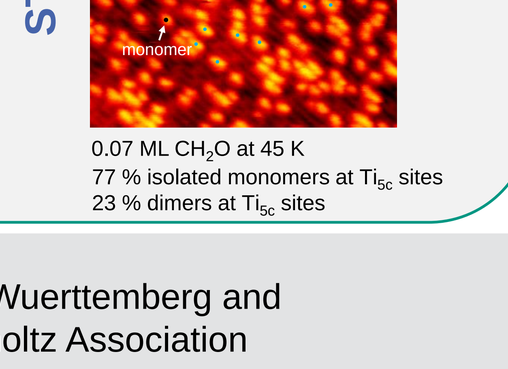
- Intermolecular interaction: dipole-dipole attractions between polar carbonyl groups
- Fermi resonance: ν_2 + ν_5 combination mode and ν_4 mode, same symmetry (B_1)

CH_2O adsorption on TiO_2(110) : Monomers

CH_2O adsorption at 65 K

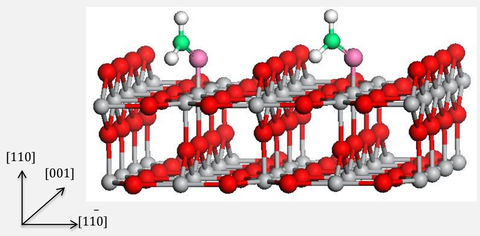


CH_2O polymerization at the Ti_{5C} rows



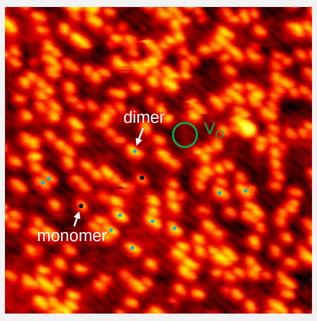
*ν_2 = 1727 cm^{-1}: O_{2c}-bound CH_2O at the second-layer

Isolated CH_2O monomer



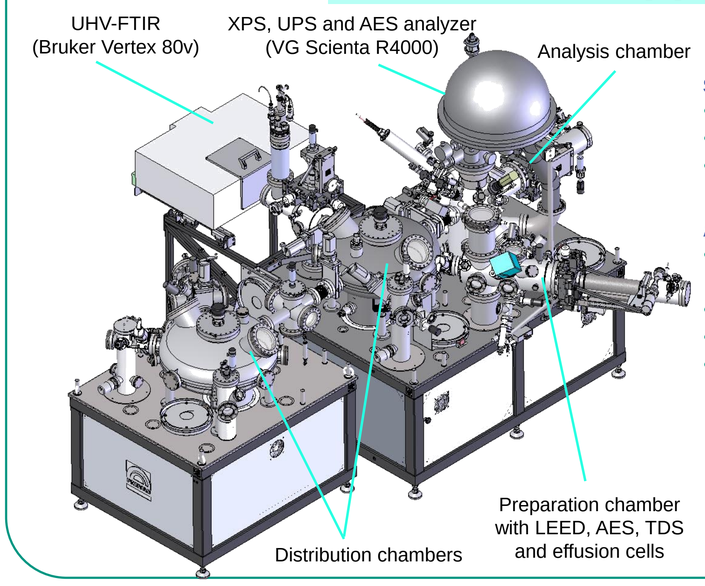
ν(C=O) : 1709 cm^{-1} (exp.)
1695 cm^{-1} (DFT)

STM



0.07 ML CH_2O at 45 K
77 % isolated monomers at Ti_{5c} sites
23 % dimers at Ti_{5c} sites

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":

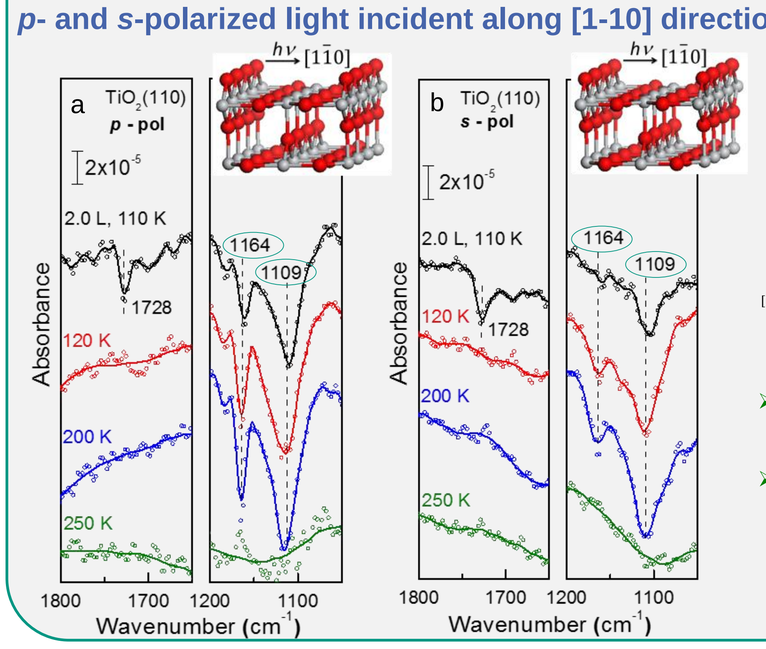
- Allows transmission measurements on powder samples.
- Cooling to 100 K (LN_2) or 60 K (LHe);
- Heating up to 1200 K.
- Equipped for XPS, UPS, AES, LEIS, and LEED.

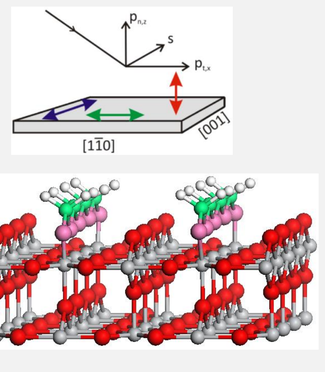
IRRAS- Measurements:

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

Paraformaldehyde

p- and *s*-polarized light incident along [1-10] direction



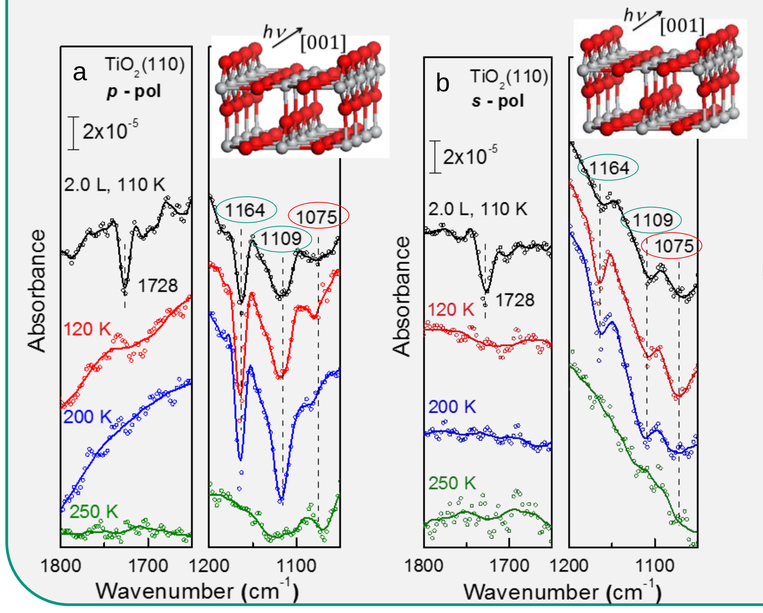


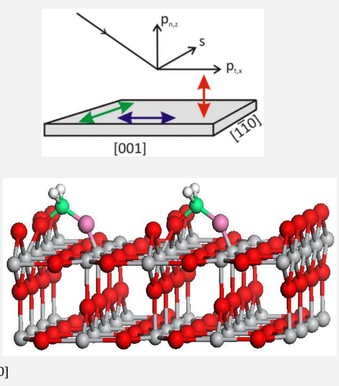
- Paraformaldehyde (POM) is formed via coupling reactions of CH_2O monomers at Ti_{5c} sites.
- The POM chain is oriented primarily along the [001] direction in a slightly disordered configuration.

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

Dioxymethylene

p- and *s*-polarized light incident along [001] direction





- Dioxymethylene (DOM) was detected as minority species formed via reaction of Ti_{5c}-bound CH_2O monomers with surface O-atoms.

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 was identified after submonolayer adsorption at 45-60 K, in which CH_2O is bound to the surface Ti_{5c} sites via σ-donation in a tilted geometry.
- Upon heating, the CH_2O monomers polymerize to form paraformaldehyde (POM) chains, oriented primarily along the Ti_{5c} rows ([001] direction).
- Dioxymethylene was detected as minority species formed via reaction of Ti_{5c}-bound CH_2O monomers with surface O-atoms.

References:

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