Karlsruhe Institute of Technology

Interaction of Formaldehyde with the Rutile TiO_2(110) Surface

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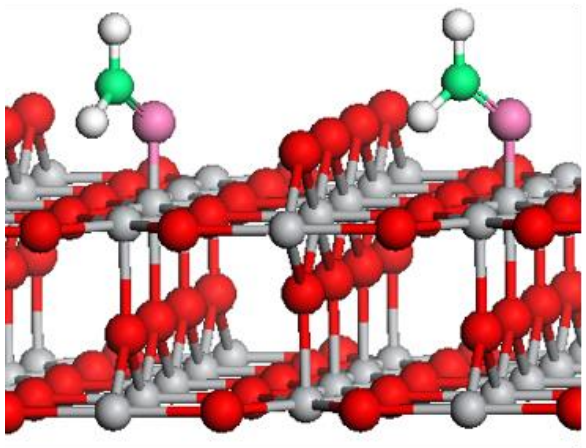
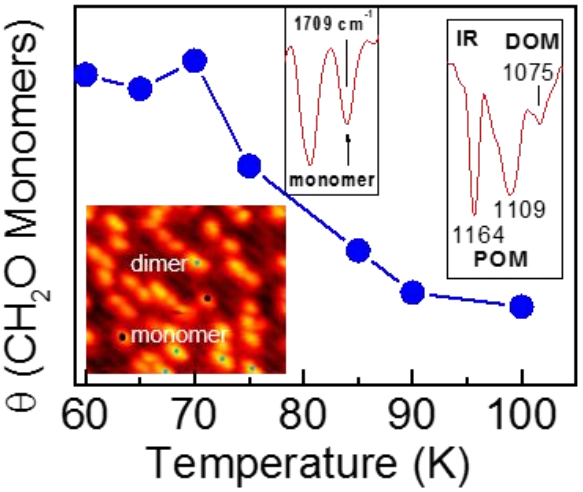
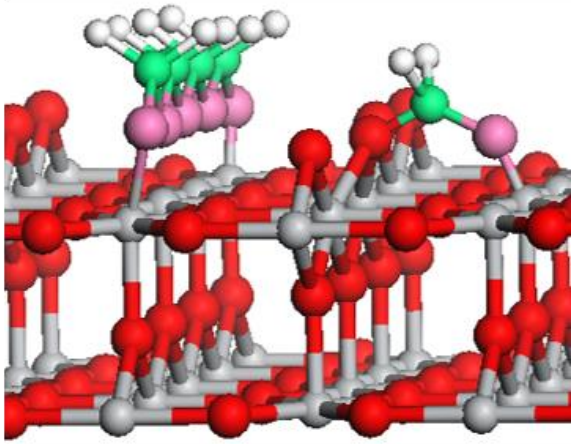
Institute of Functional Interfaces (IFG)



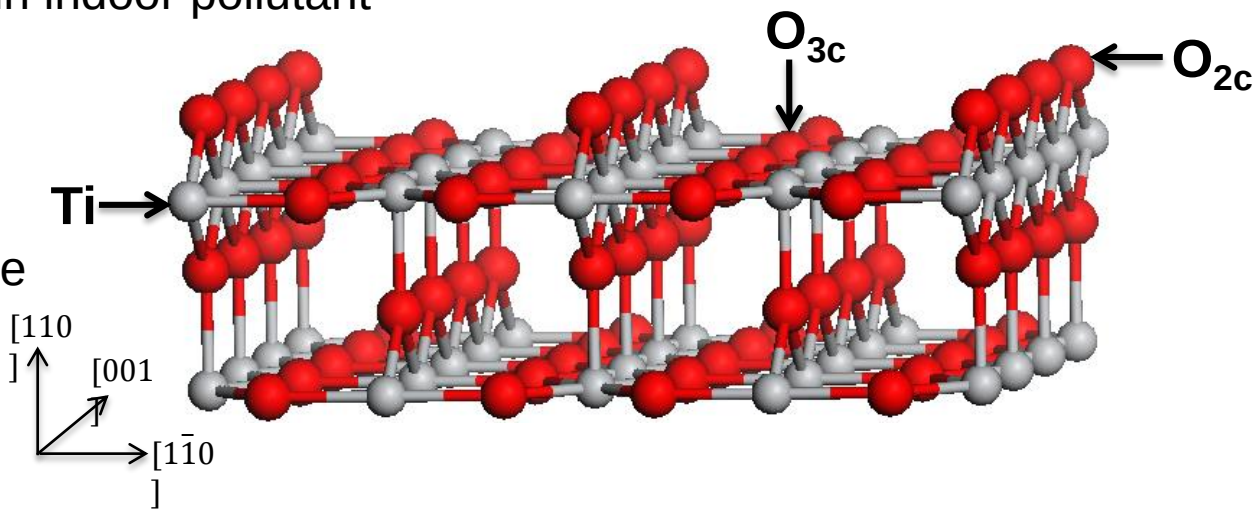




Why we study formaldehyde on titania?

- TiO_2: the most important metal oxide used in catalysis and photocatalysis
- CH_2O: a key species in catalytic and photocatalytic reactions
- CH_2O: the main indoor pollutant

TiO_2 (110) surface



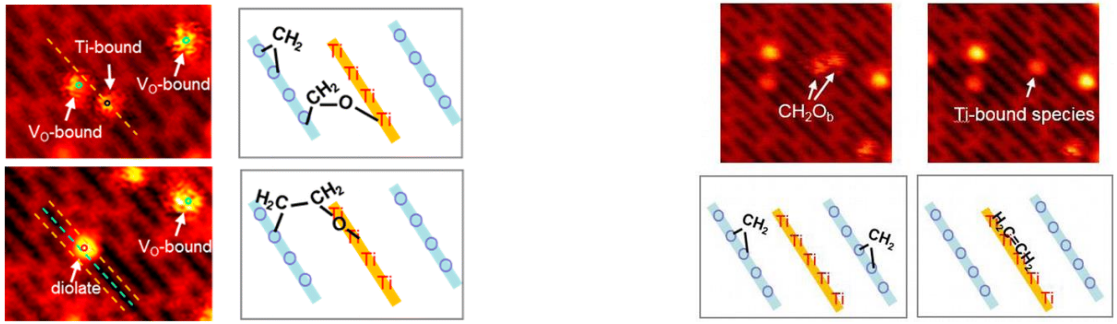
Previous theoretical research

[1] Muir, J. M. R.; Idriss, H. *Chem. Phys. Lett.* 2013, 572, 125–129
[2] McGill, P. R.; Söhnel, T. *Phys. Chem. Chem. Phys.* 2012, 14, 858–868
[3] Liu, H.; Wang, X.; Pan, C.; Liew, K. M. *J. Phys. Chem. C* 2012, 116, 8044–8053
[4] Haubrich, J.; Kaxiras, E.; Friend, C. M. *Chem. – Eur.J*. 2011, 17, 4496–4506
[5] Kieu, L.; Boyd, P.; Idriss, H. *J. Mol. Catal. A: Chem.* 2001, 176, 117–125
[6] Li, J.; Wu, L.; Zhang, Y. *Chem. Phys. Lett.* 2001, 342, 249–258

Previous experimental research on TiO_2(110)

- high resolution electron energy loss spectroscopy (HREELS) and thermal programmed desorption (TPD) [1]
  - Oxidized surface: CH_2O + TiO_2(110) paraformaldehyde (100 K) CH_2O (260 K)
    Reduced surface: $2CH_2O + 2V_O$ $-OCH_2CH_2O-$ $C_2H_2 + 2O_S$ (550 K)

- scanning tunneling microscopy (STM) [2-4]



  - Reduced surface: 75 K: $CH_2O + V_O$ CH_2O_b (the V_O-bound CH_2O)
    170 K: (1) $CH_2O_b + CH_2O_{Ti}$ $-O_bCH_2CH_2O_{Ti}-$
    (2) $2CH_2O_b$ C_2H_2 at Ti_{5c} sites (C_2H_2 desorbs at ~ 215 K)

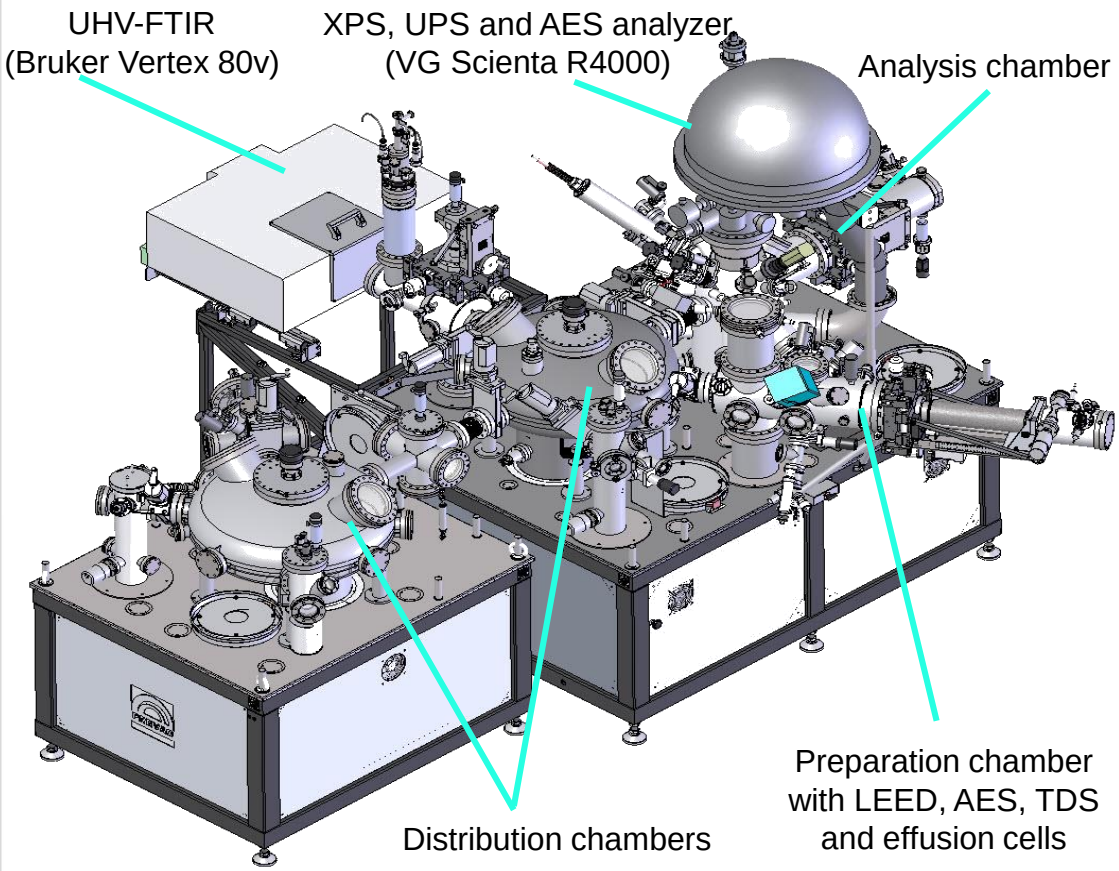
- X-ray photoemission spectroscopy (XPS) and TPD [5-7]
  - Reduced surface: C_2H_2 formation at high temperature

IR study on powder samples [8-10]

- Dioxymethylene and paraformaldehyde

[1] JPCC, 2008,112, 9828-9834; [2] JPCC, 2015, 119, 14267-14272; [3] JPCC, 2015, 119, 18452-18457;
[4] Top. Catal. 2015, 58, 103-113; [5] JPCC, 2014, 118, 20420-20428; [6] JPCL, 2013, 4, 2668-2673;
[7] JPC, 1994, 98, 11733-11738; [8] JACS, 1987, 109, 5197−5202; [9] J. Mol. Catal. 1987, 42, 205−213; [10] Kinet. Catal 2000, 41, 885−891

UHV-IRRAS apparatus (THEO)



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":

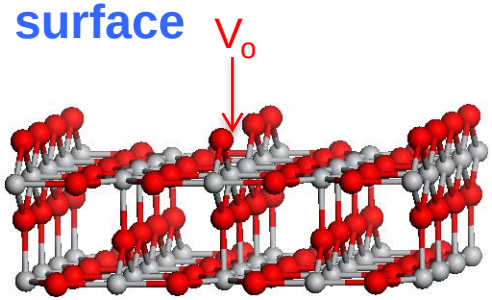
- Allows transmission measurements on powder samples.
- Cooling to 100 K (LN_2) or 60 K (LHe);
- Heating up to 1200 K.
- Equipped for XPS, UPS, AES, LEIS, and LEED.

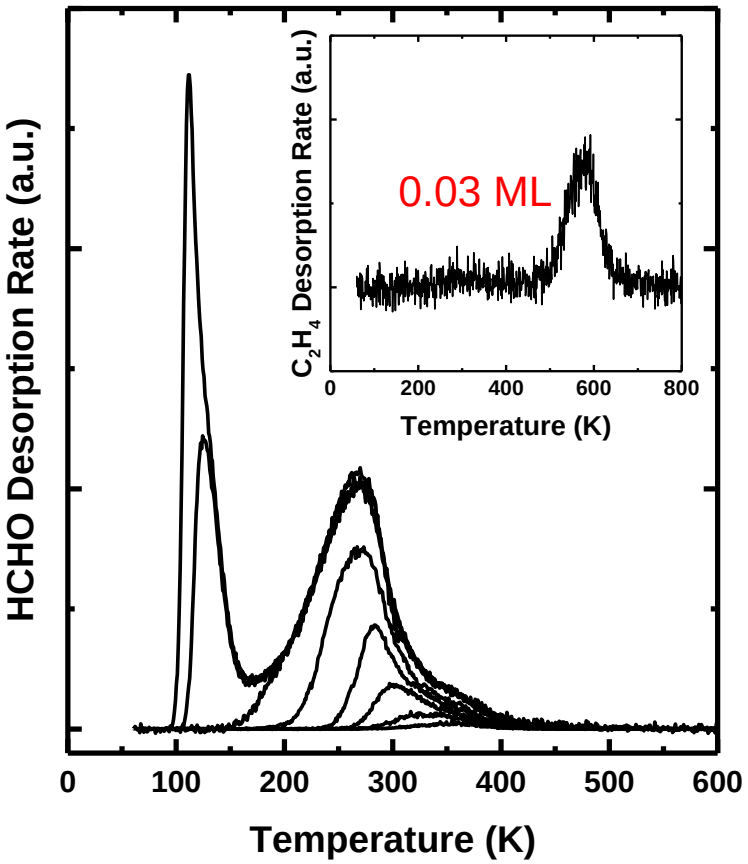
IRRAS-Measurements:

- Pressure: ≤ 8×10^{-11} mbar (LN_2) or 3×10^{-11} mbar (LHe)
- Reflection mode
- Grazing Incidence (80°)
- *p*- and *s*-polarized light

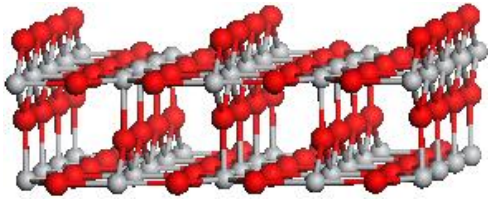
TPD: CH_2O adsorption on TiO_2(110) at 80 K

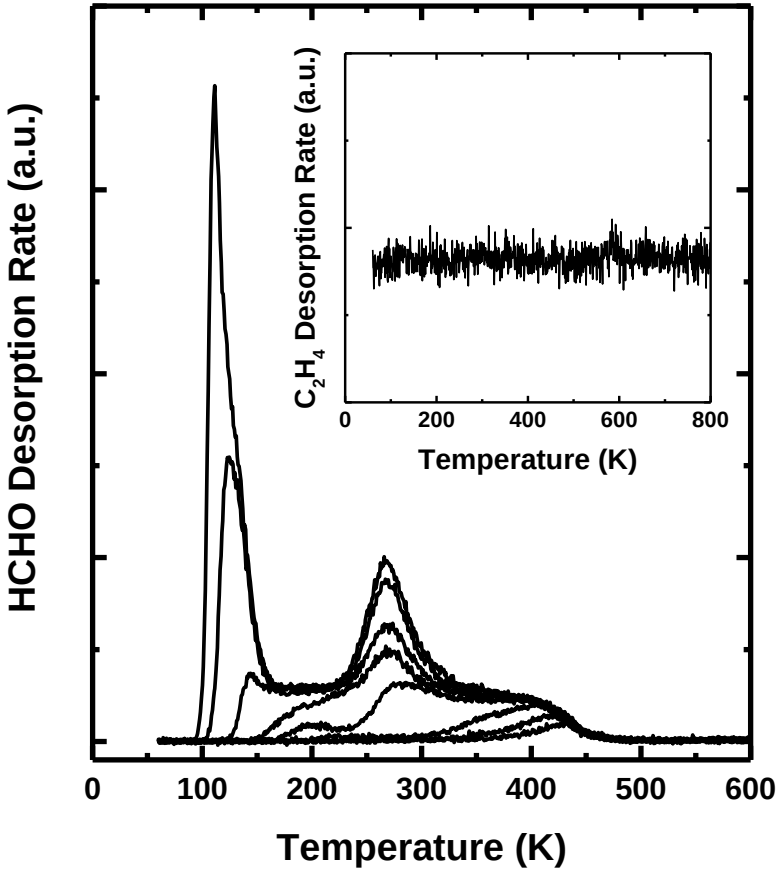
Reduced surface



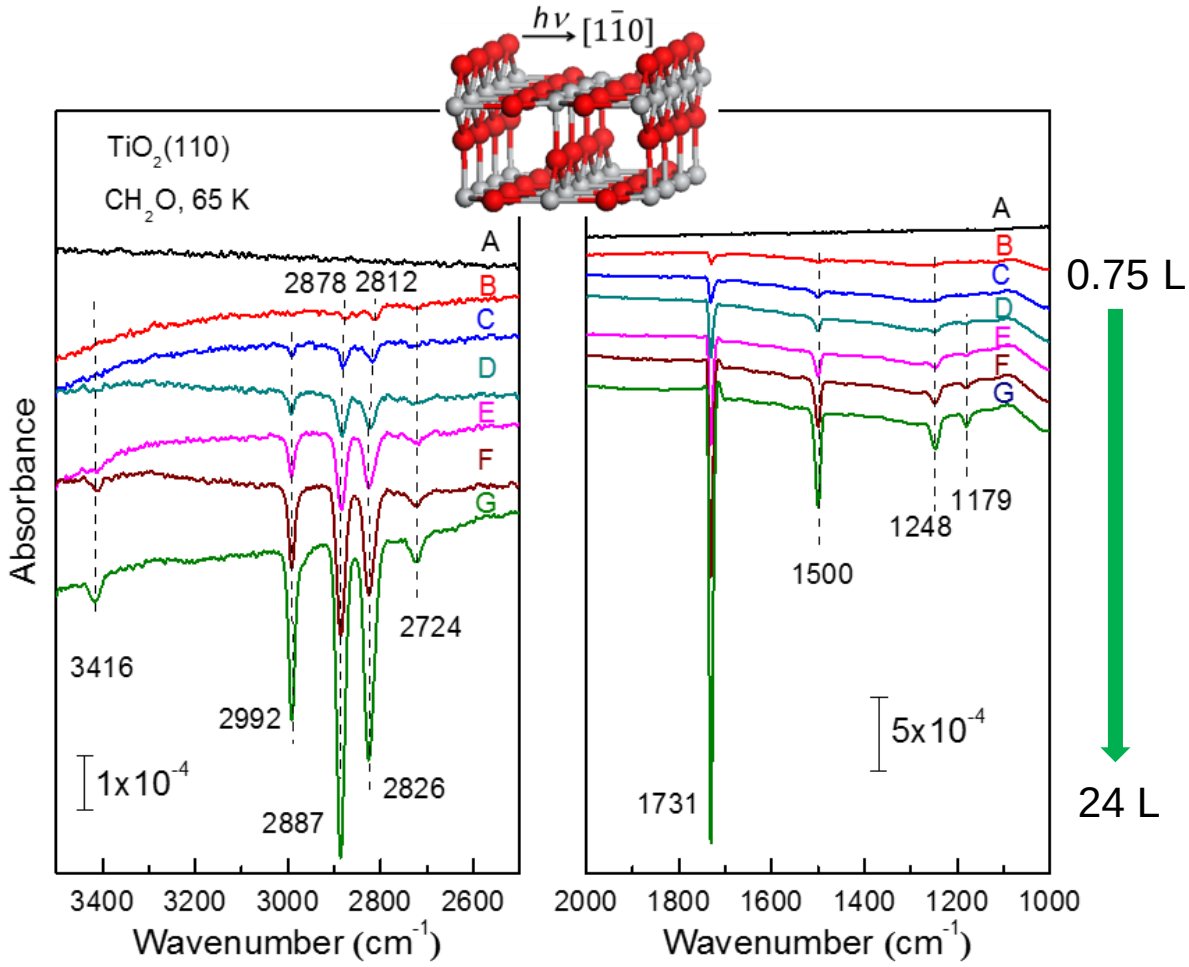


Oxidized surface





CH_2O adsorption on TiO_2(110): multilayer (65 K)



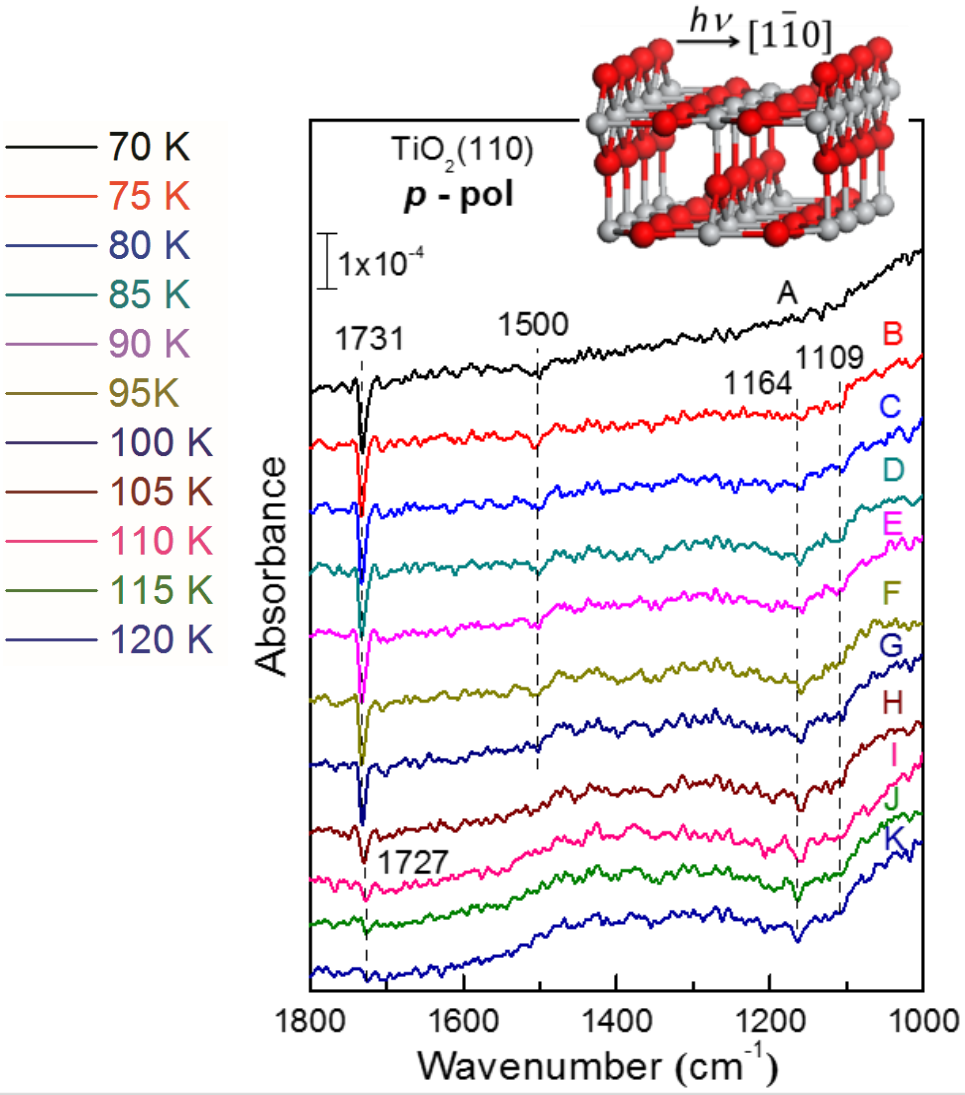
modes	gas	multilayer
$2\nu_2$	3471.7	3416
$\nu_2+\nu_5$	3000.1	2992
$2\nu_3$	2999.5	-
$\nu_{as}(CH_2)$, ν_4	2843.3	2887
$\nu_s(CH_2)$, ν_1	2782.5	2826
$\nu_3+\nu_5$	2719.2	2724
ν(C=O), ν_2	1746.1	1731
$\delta(CH_2)$, ν_3	1500.0	1500
$\omega(CH_2)$, ν_5	1249.3	1248
$\tau(CH_2)$, ν_6	1167.1	1179

(A) clean surface and (B-G) exposure to CH_2O: (B) 0.75 L, (C) 1.5 L, (D) 3 L, (E) 6 L, (F) 12 L, (G) 24 L

- Intermolecular interaction: dipole-dipole attractions between polar carbonyl groups

CH_2O adsorption on TiO_2(110): multilayer

Temperature-dependent IRRAS data

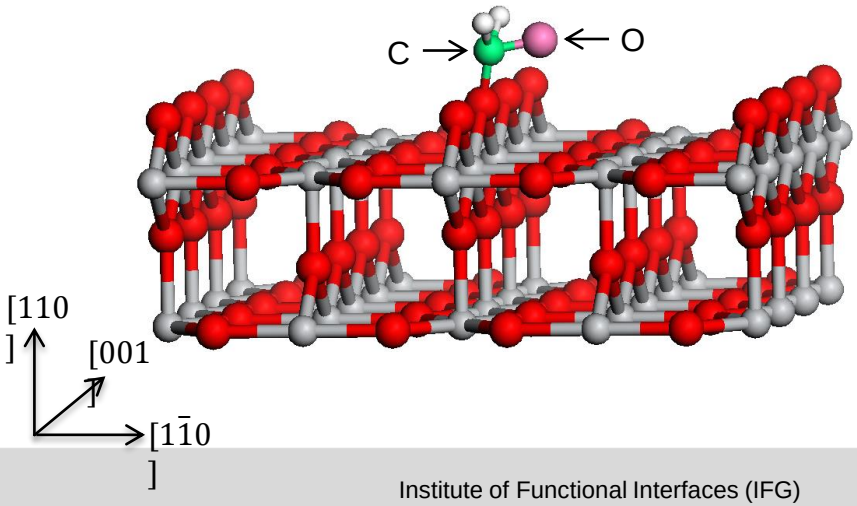


- ν(C=O):

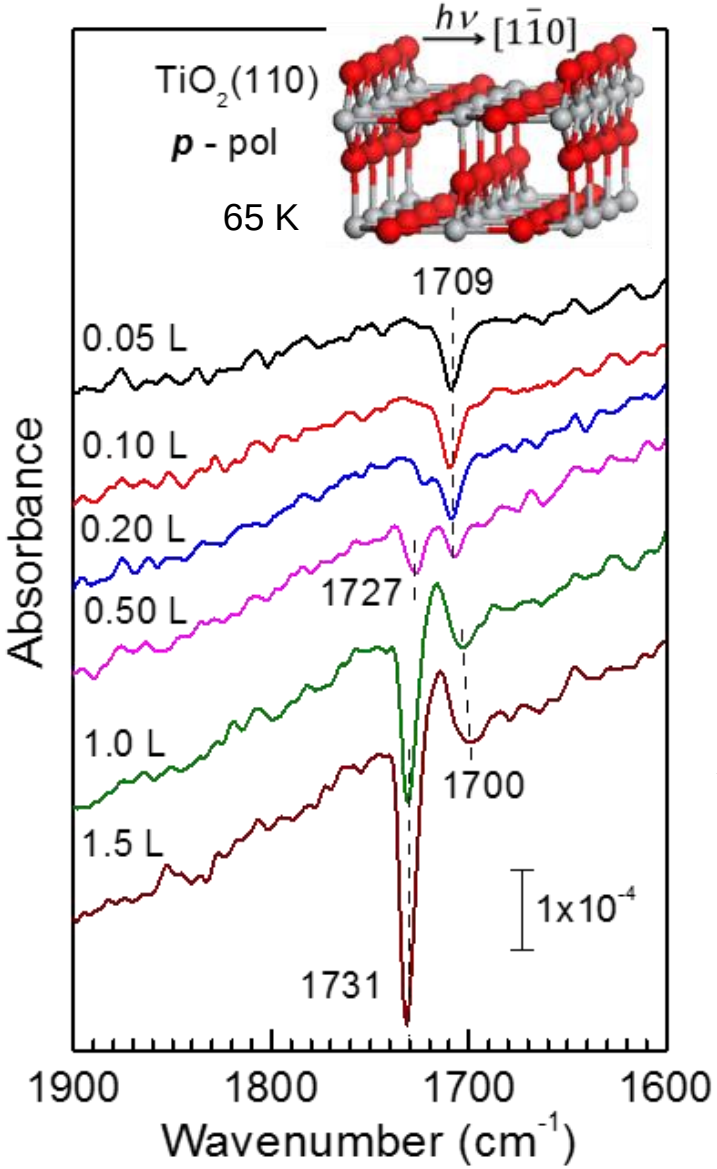
  1731 cm^{-1} ⟶ 1727 cm^{-1} (110 K)
  second-layer of multilayer CH_2O

- 120 K:
  the desorption of multilayer CH_2O

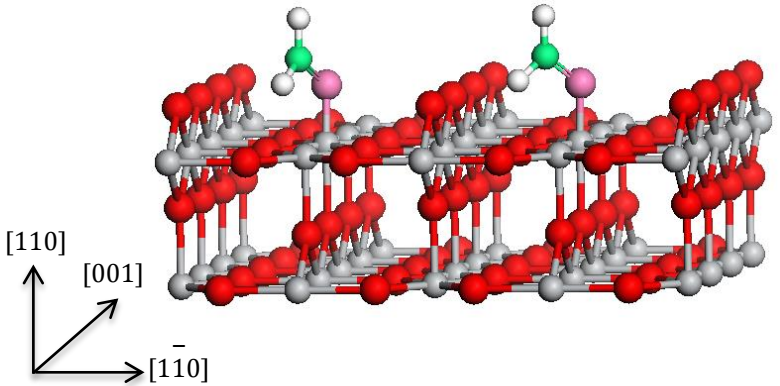
- Two new bands show up at 1164 and 1109 cm^{-1}



CH_2O adsorption on TiO_2(110): monomers

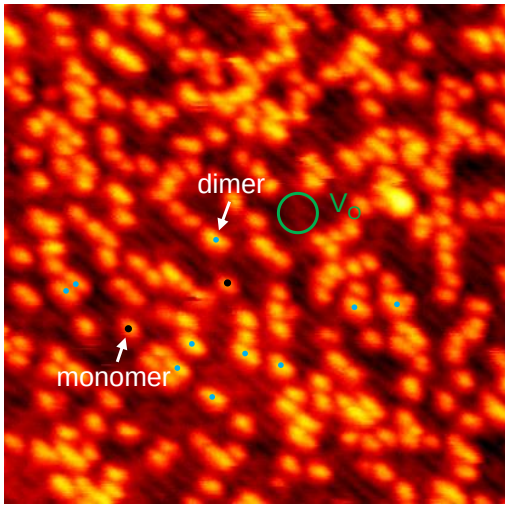


Isolated CH_2O monomer



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

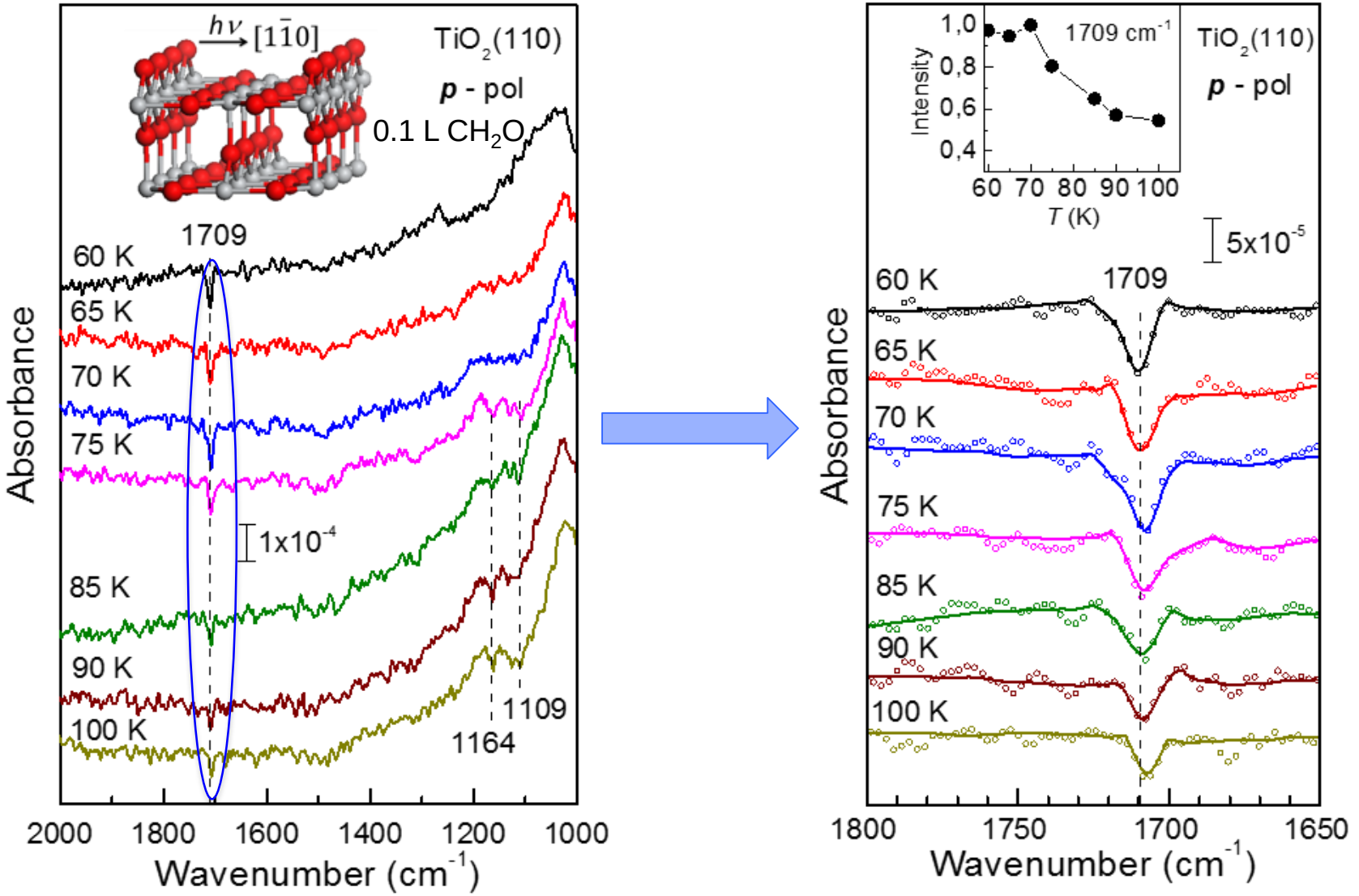
STM



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

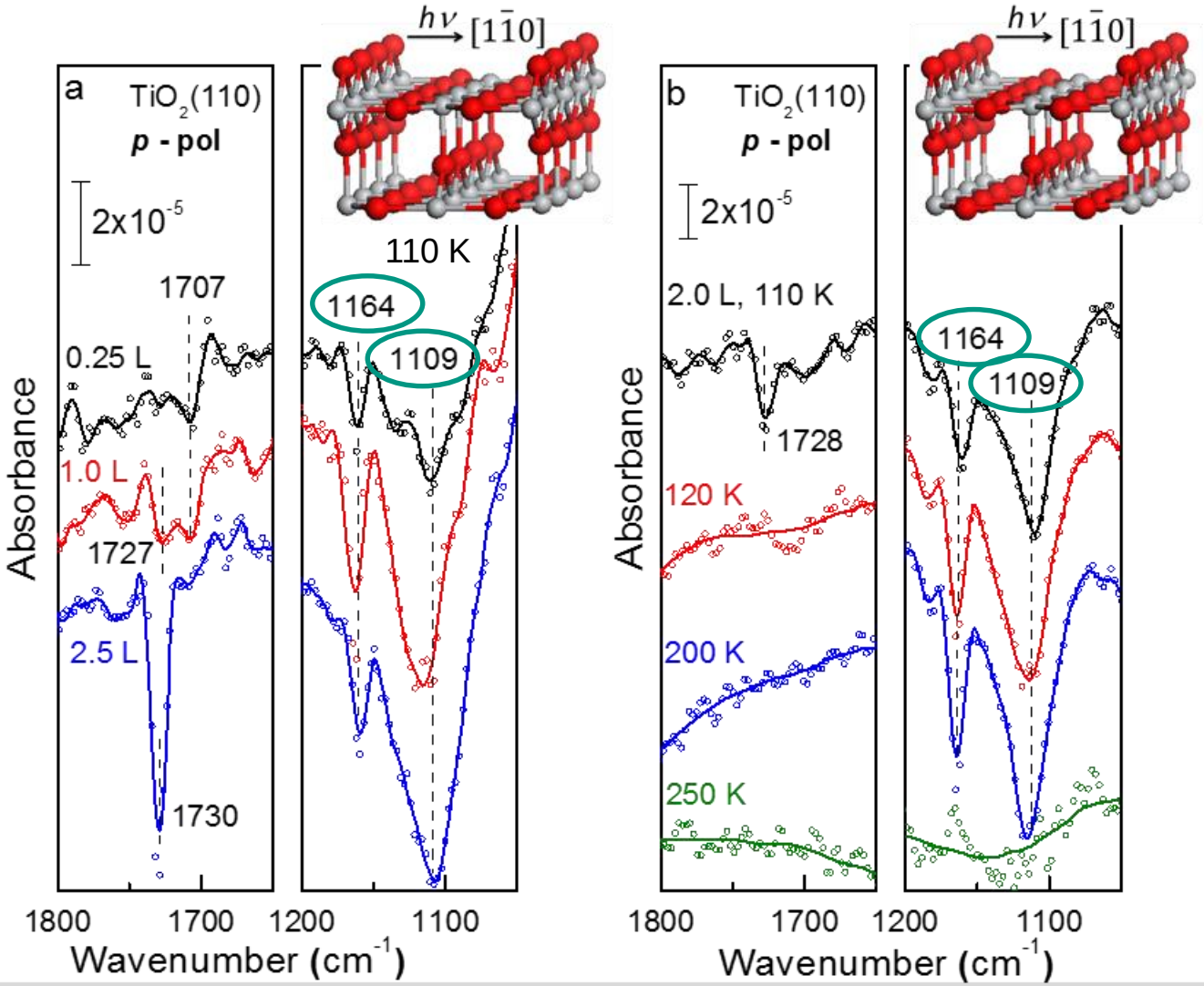
CH_2O adsorption on TiO_2(110): monomers

Temperature-dependent IRRAS data



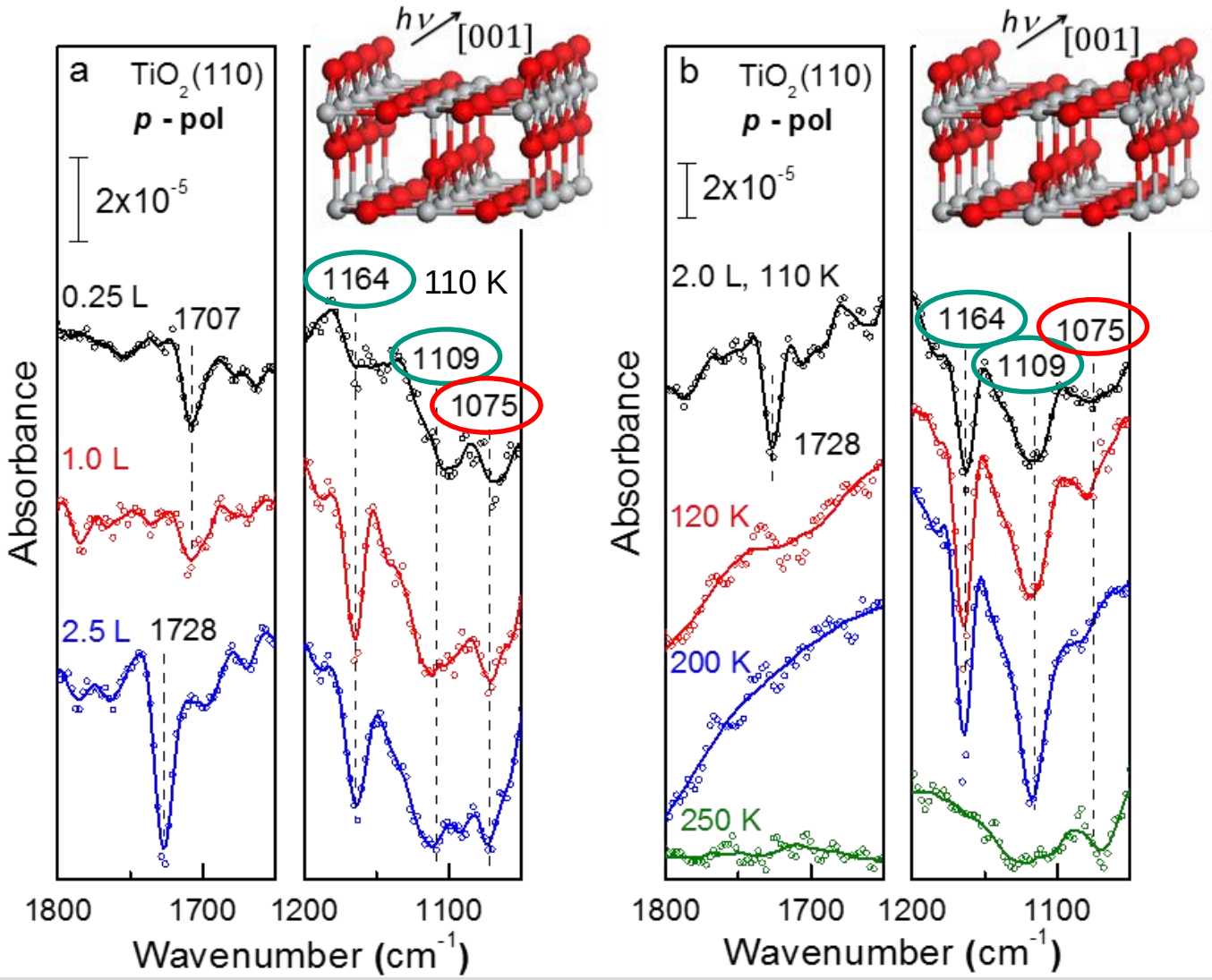
Paraformaldehyde and dioxymethylene

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



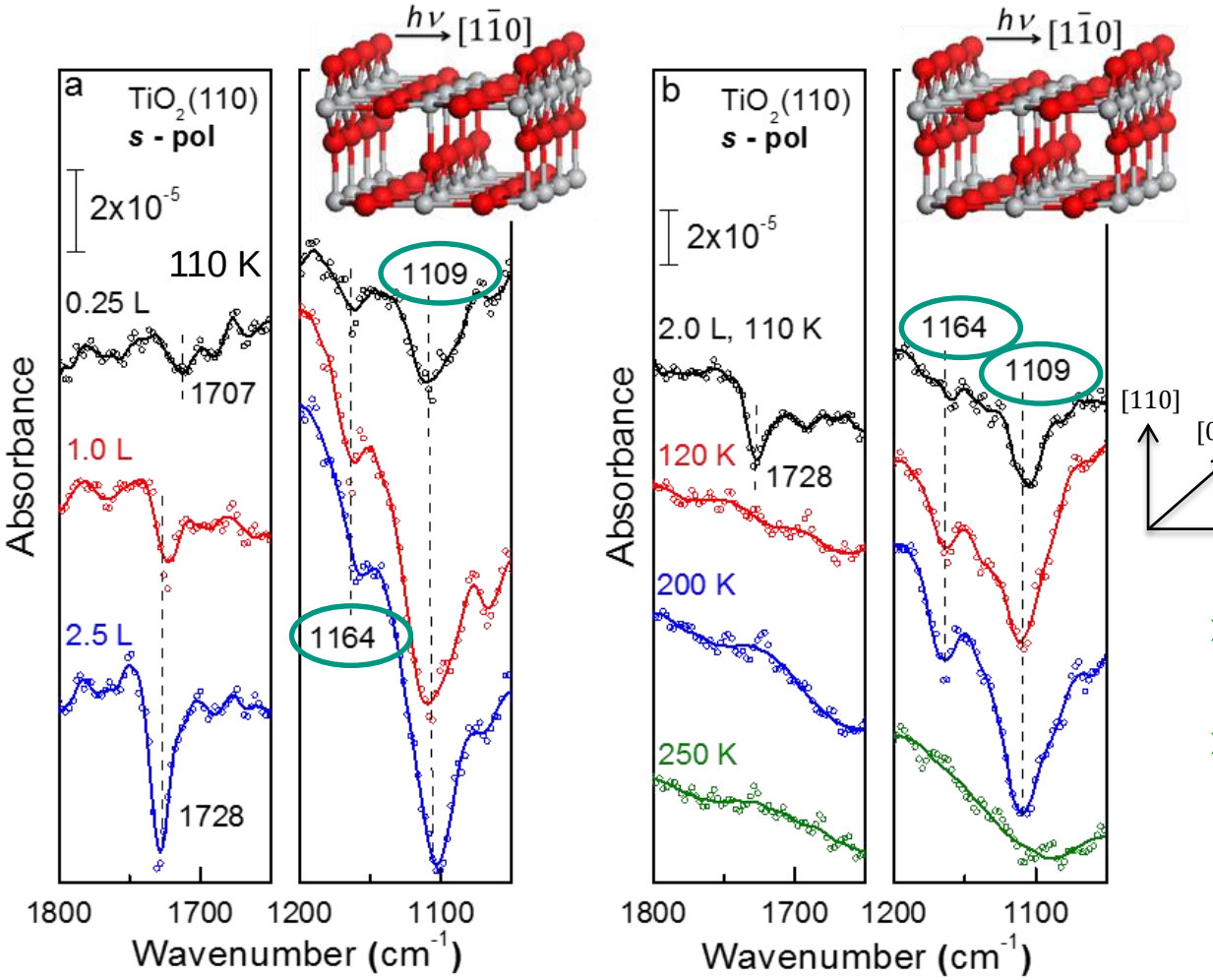
Paraformaldehyde and dioxymethylene

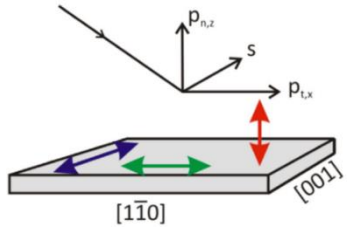
p - polarized light incident along [001] direction

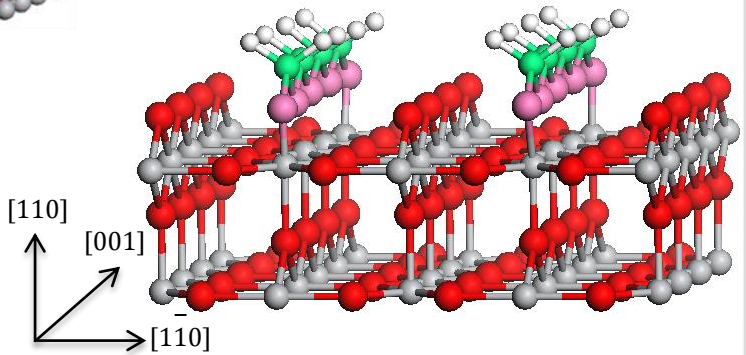


Paraformaldehyde and dioxymethylene

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



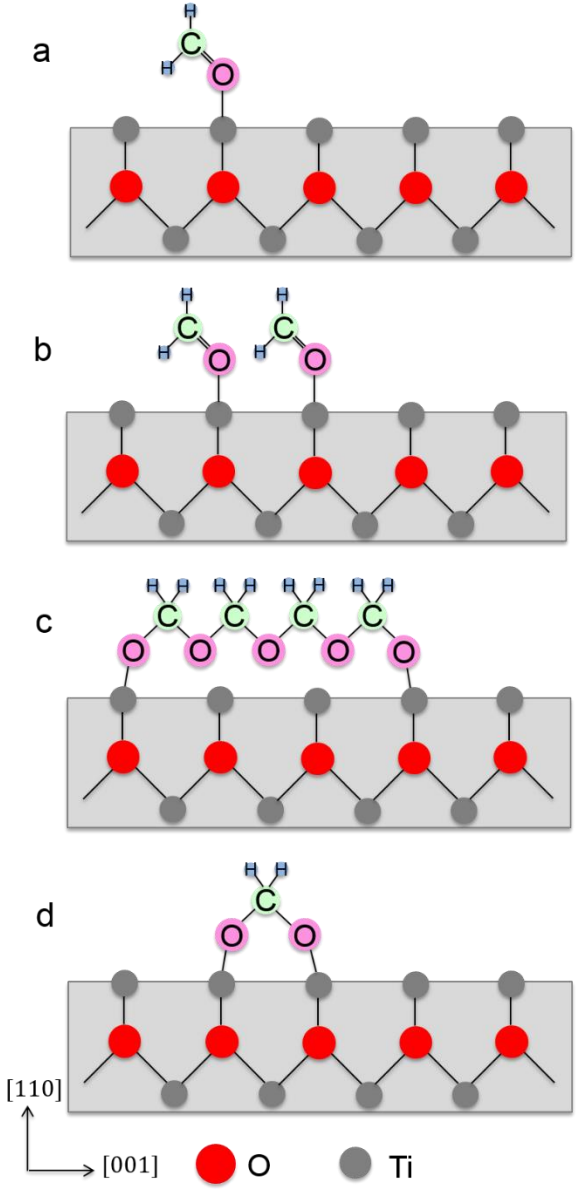


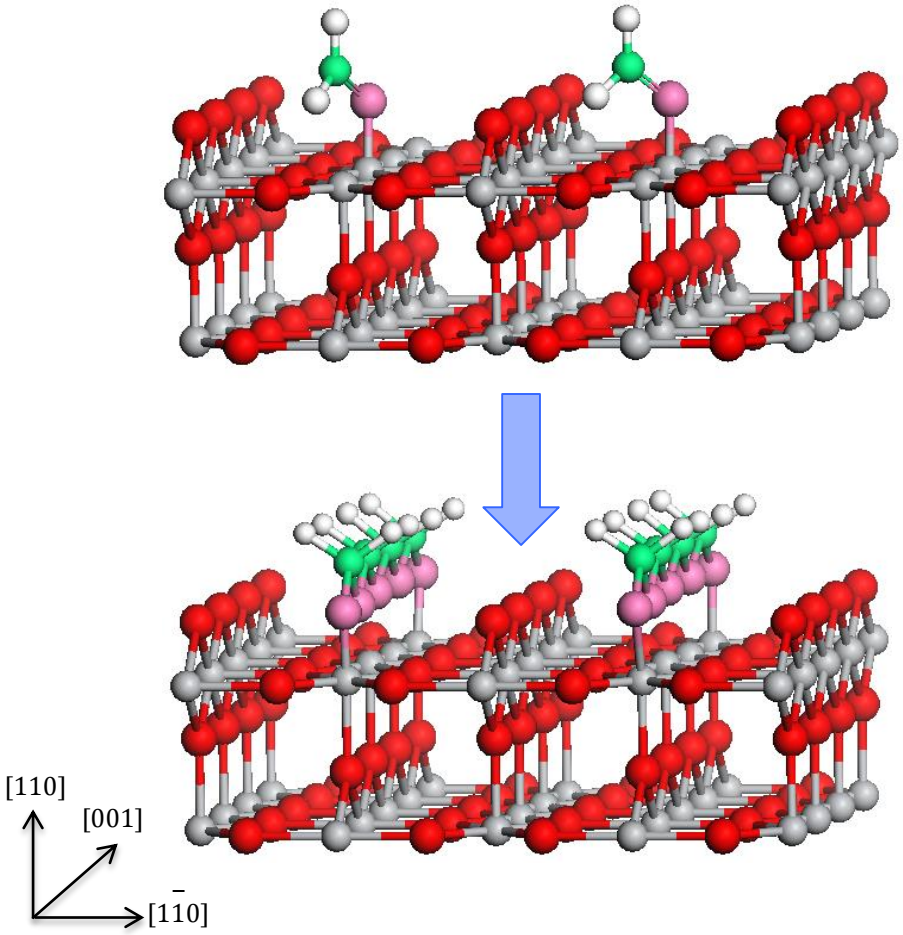


- Paraformaldehyde (POM) is formed via coupling reactions of CH_2O monomers at Ti_{5c} sites.
- The POM chain is oriented primarily along the [001] direction in a slightly disordered configuration.

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

Paraformaldehyde and dioxymethylene

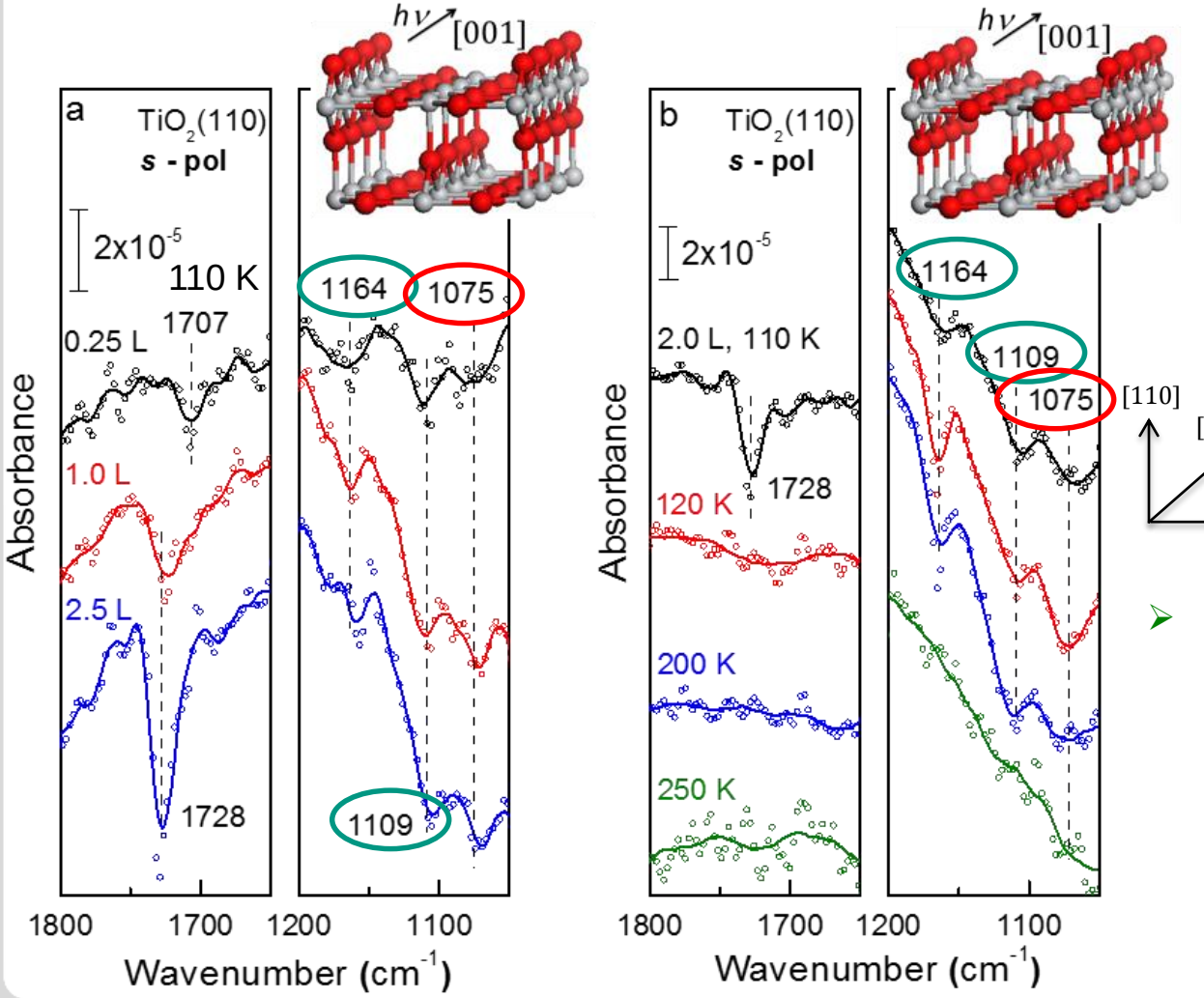


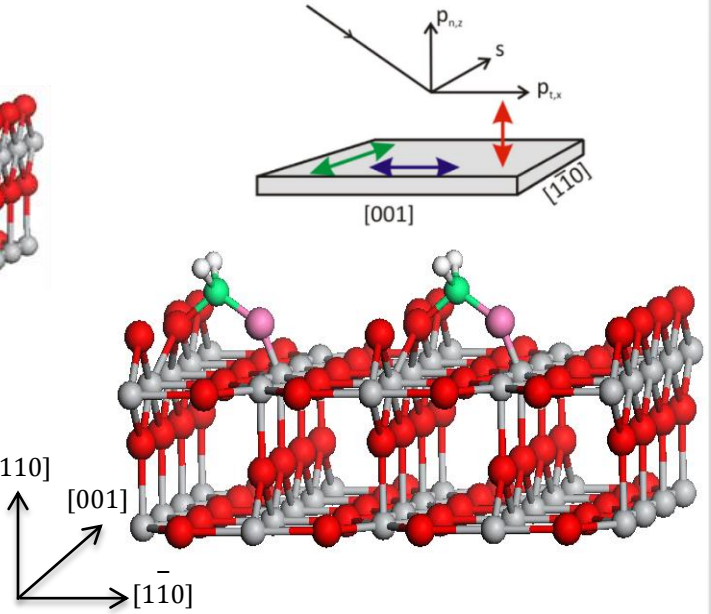


(a) CH_2O monomer in η^1(O) configuratio (b) CH_2O dimer; (c) paraformaldehyde; (d) dioxymethylene

Paraformaldehyde and dioxymethylene

s - polarized light incident along [001] direction





- Dioxymethylene (DOM) is 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

- Multilayer CH_2O

  ν(C=O) :1731, 1727 cm^{-1}
  (1727 cm^{-1}: O_{2c}-bonded second-layer CH_2O)
  Desorption temperature: 120 K

- CH_2O monomer

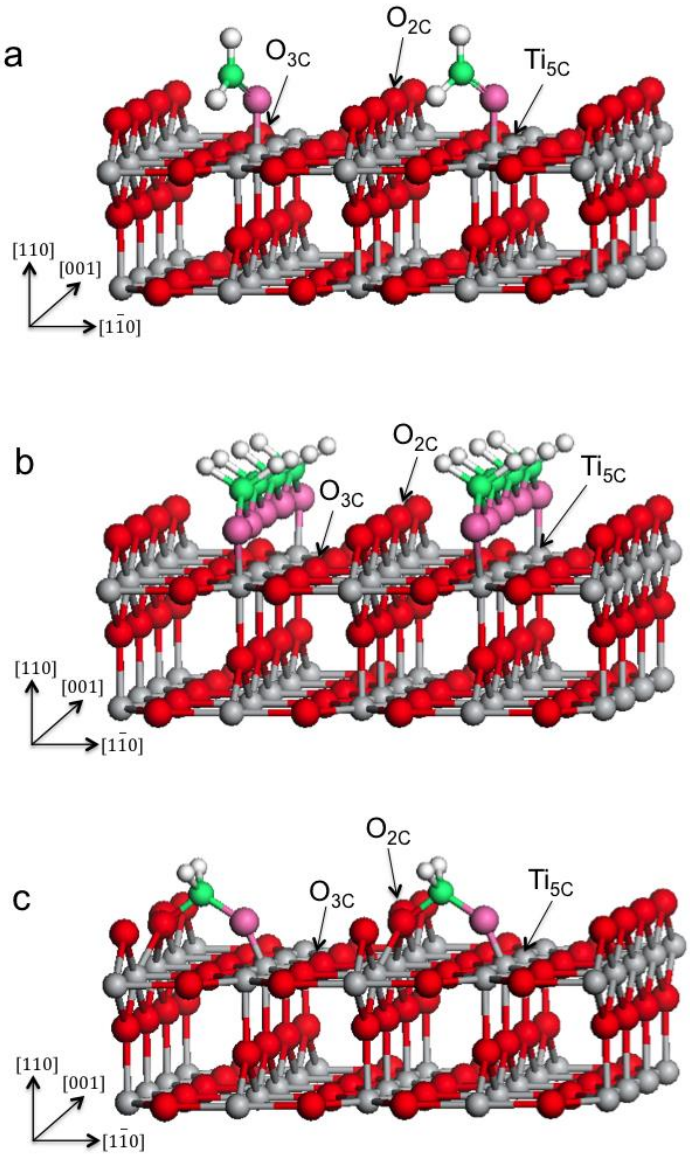
  ν(C=O) :1709 cm^{-1}
  Thermal conversion at 70 K

- Paraformaldehyde (POM)

  ν(C=O) :1164, 1109 cm^{-1}
  mainly oriented along the [001] direction

- Dioxymethylene (DOM)

  ν(C=O) :1075,1065 cm^{-1}
  formed via reaction with substrate O_{2c} ions
  or oxygen adatoms (O_{ad}) located at Ti_{5c} sites



(a) CH_2O monomer in η^1(O) configuration;
(b) paraformaldehyde; (c) dioxymethylene.

Acknowledgements

KIT-IFG

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Thanks for your attention !