Karlsruhe Institute of Technology

Insights into water adsorption on ZnO(10-10) surfaces: an IRRAS study

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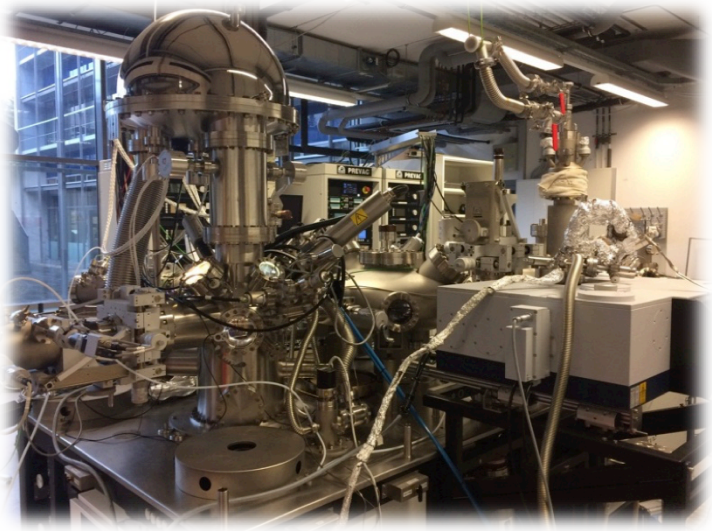
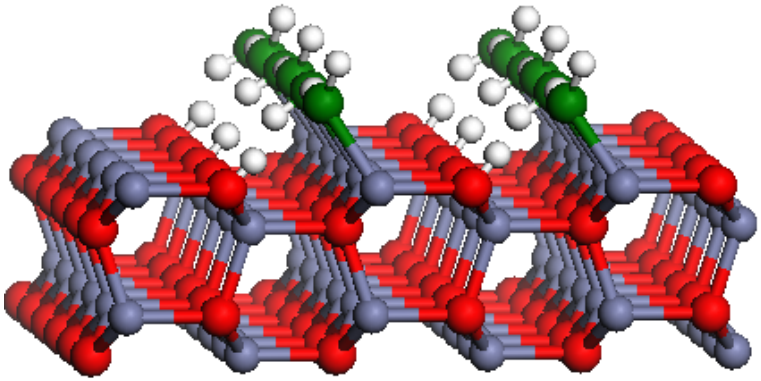
Institute of functional interfaces, Chemistry of oxydic and organic Interfaces

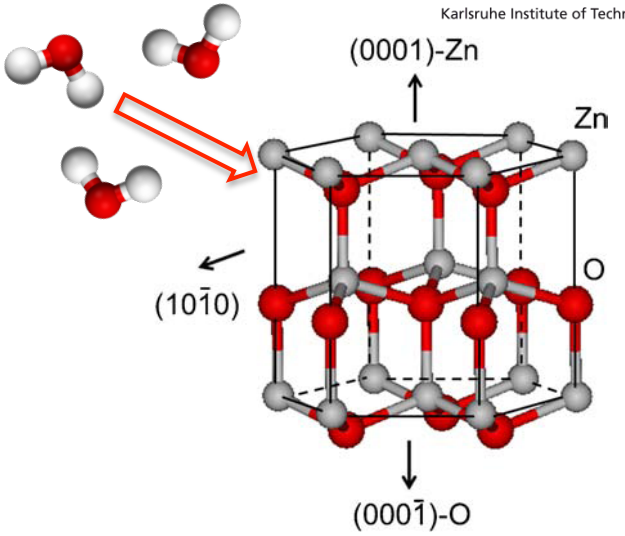




Introduction

Motivation

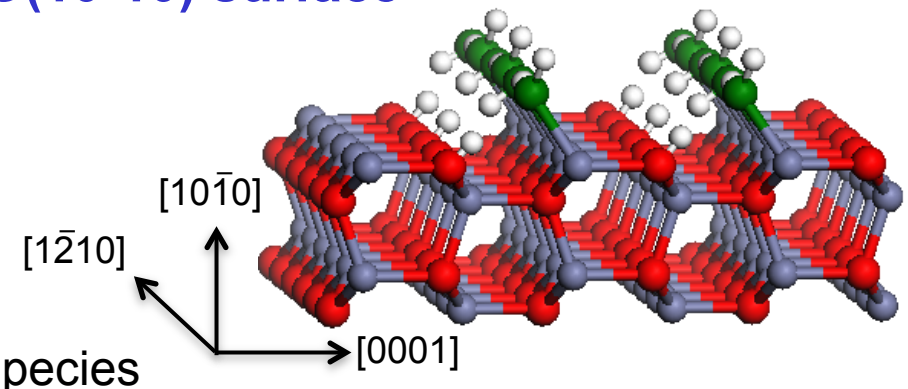
- water in chemical reactions: reactant, product, solvent, contamination
- hydration process of ZnO surfaces in catalysis reactions: methanol production from synthesis gas, water-gas shift reaction



Wurtzite ZnO

Previous research of water on ZnO(10-10) surface

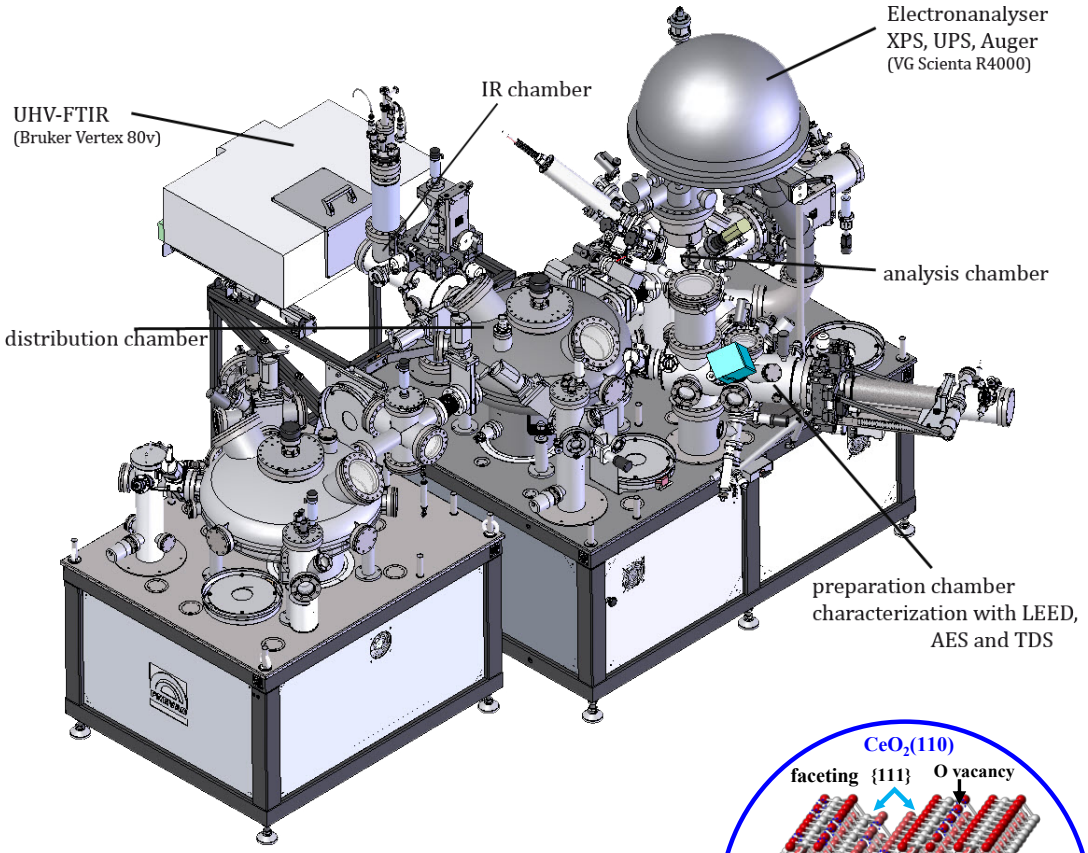
- TDS and UPS[1]
  water adlayer bound to Zn^{2+} sites
- HAS, LEED, STM, He-TDS and DFT[2-4]
  well ordered (2×1) superstructure
- HREELS[5]
  coexistence of intact H_2O and hydroxyl species



Zn: grey, O: red, O(H_2O): green, H: white

[1] Zwicker, G.; Jacobi, K. *Surf. Sci. Lett.* **1983**, *131*, 179. [2] Meyer, B. et al. *Angew. Chemie Int. Ed.* **2004**, *43* (48), 6641. [3] Dulub, O. et al. *Phys. Rev. Lett.* **2005**, *95* (13), 1–4. [4] Meyer, B. et al *Phys. Chem. Chem. Phys.* **2006**, *8* (13), 1513. [5] Wang, Y. et al. *Phys. Chem. Chem. Phys.* **2006**, *8* (13), 1521.

Experimental

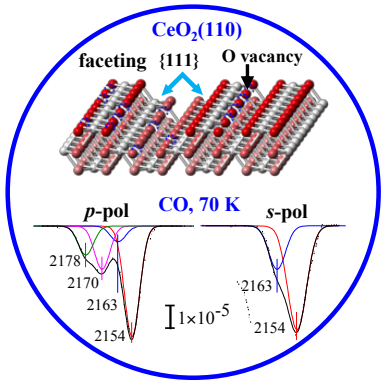


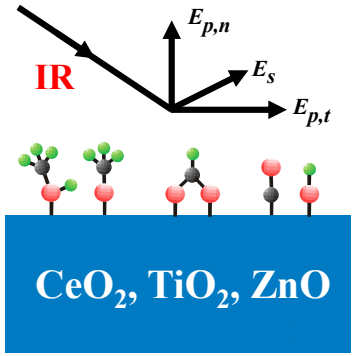
Sample Preparation

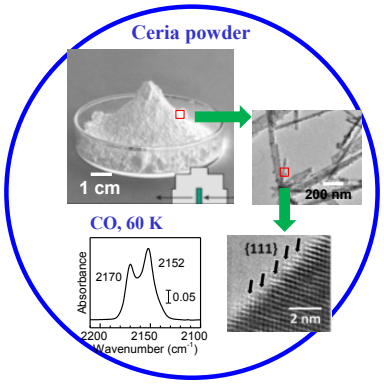
- Sputter-Anneal-Cycles
- XPS: sample cleanliness/oxidation

IRRAS-Measurements

- Pressure: < 1×10^{-10} mbar
- Reflection mode
- p- and s- polarization
- Grazing incidence (80°)
- T_{sample}: down to 110 K (LN_2)





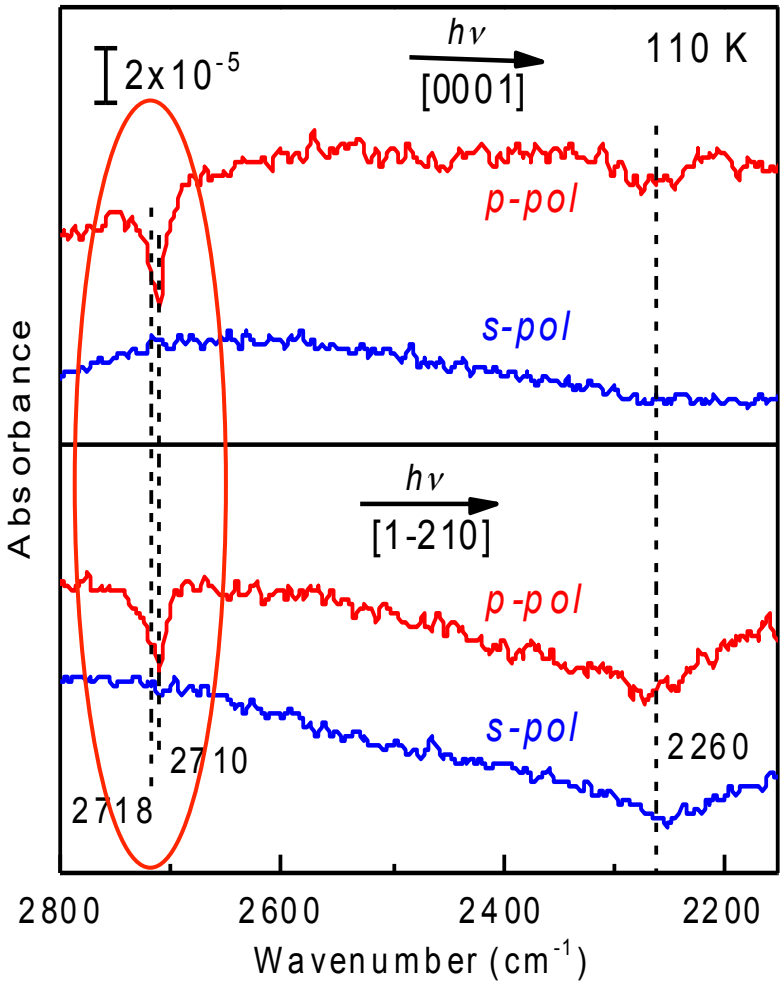


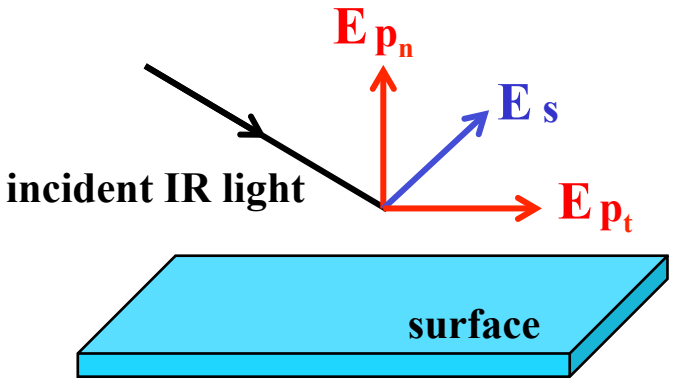
Yuemin Wang and Christof Wöll, *Chem. Soc. Rev.* **2017**, 46, 1875-1932.

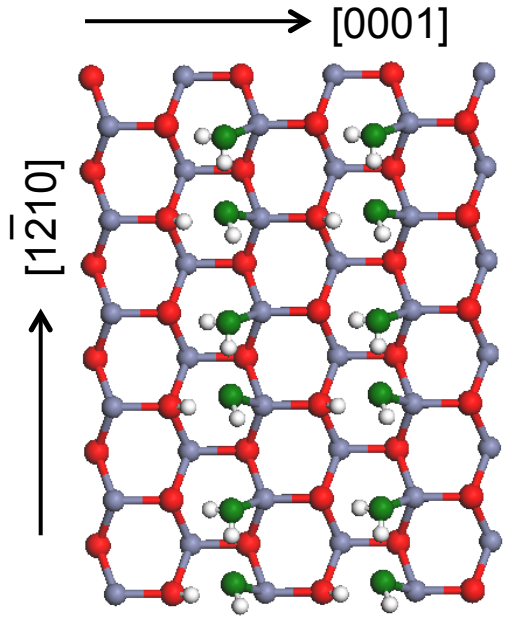
Single crystals

Nanoparticles

D_2O on ZnO(10-10): monolayer



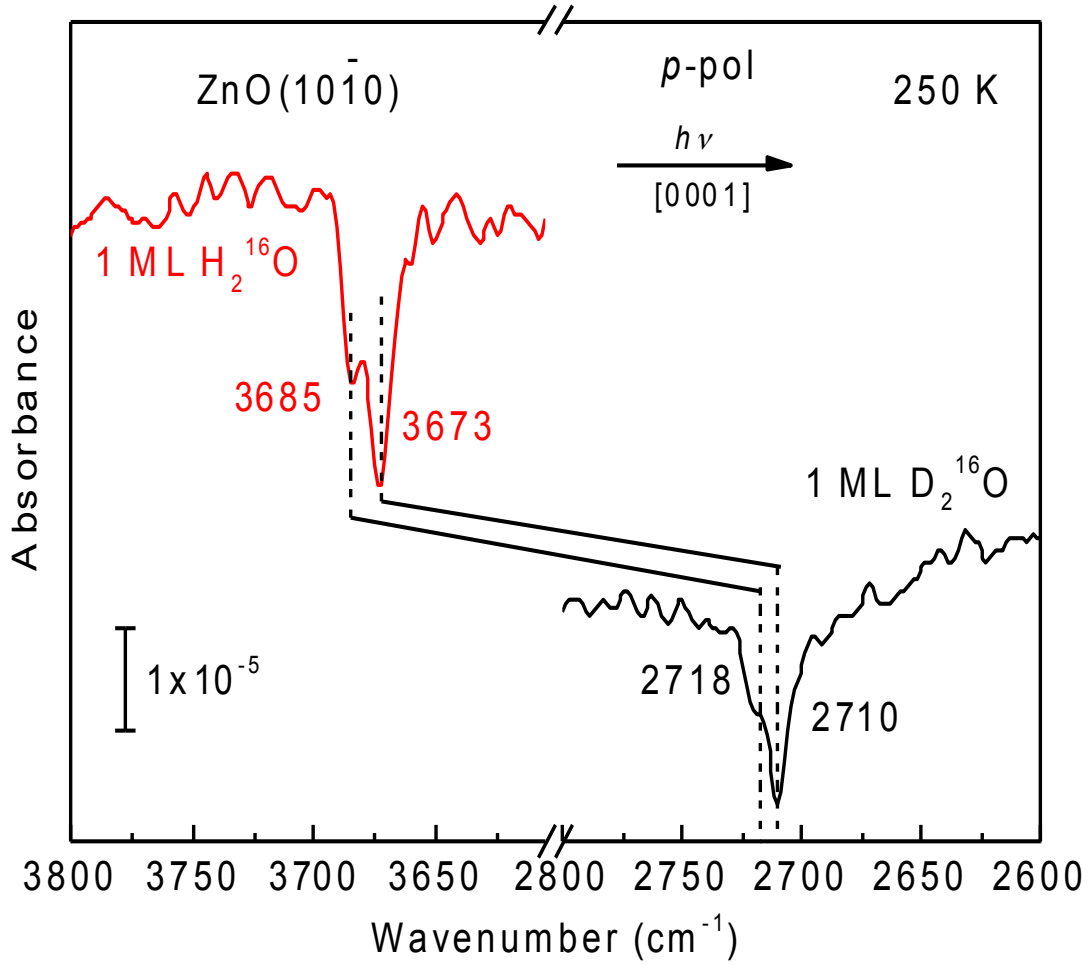


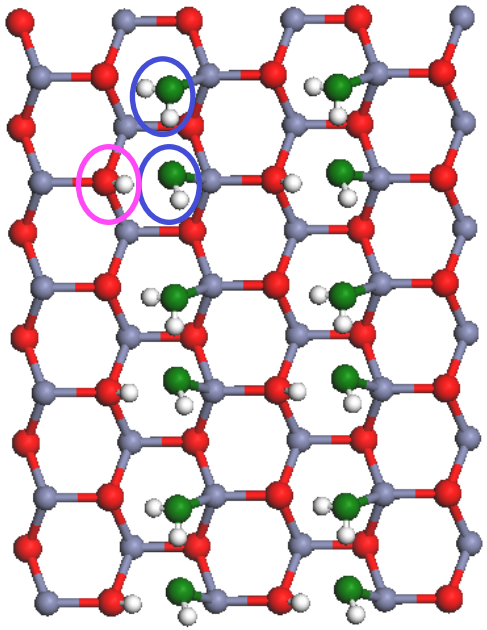


Polarization- and azimuth-resolved IRRAS data obtained after D_2O adsorption of one monolayer on ZnO(10-10) at 110 K.

Zn: grey, O: red, O(H_2O): green, H: white

H_2O/D_2O on ZnO(10-10): monolayer

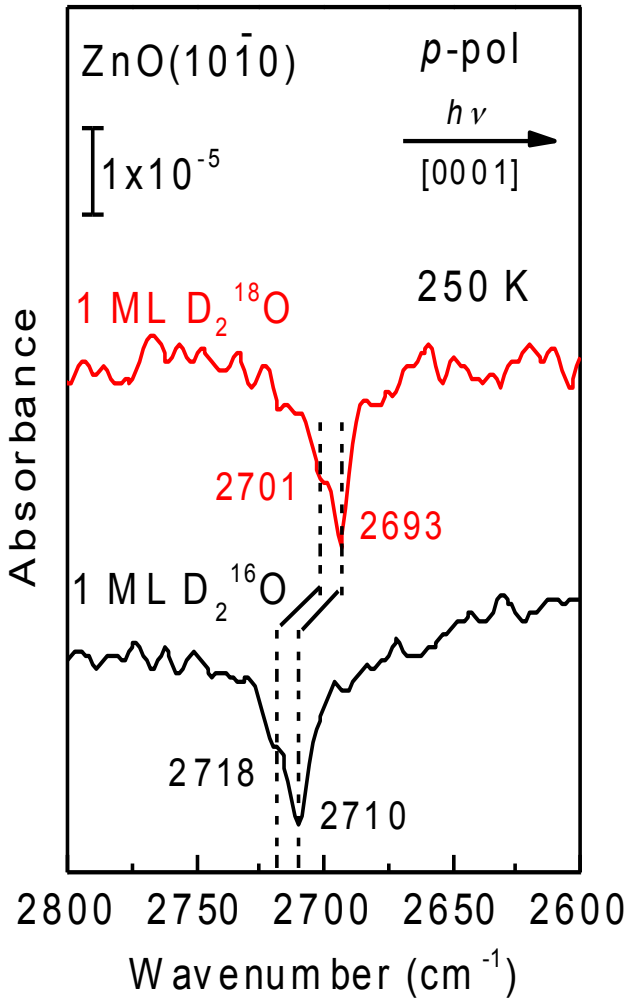


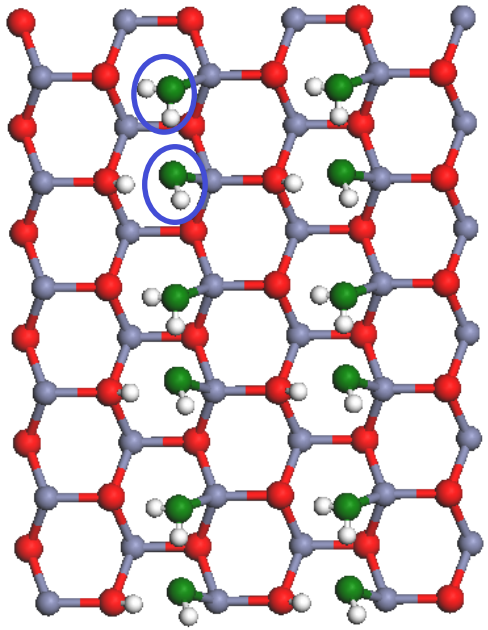


Zn: grey, O: red, O(H_2O): green, H: white

IRRAS spectra recorded after exposing the clean ZnO(10-10) surface to one monolayer $D_2{}^{16}O$ or $H_2{}^{16}O$ at 250 K with p-polarized light incident along [0001] azimuth.

$D_2{}^{18}O/D_2{}^{16}O$ on ZnO(10-10): monolayer





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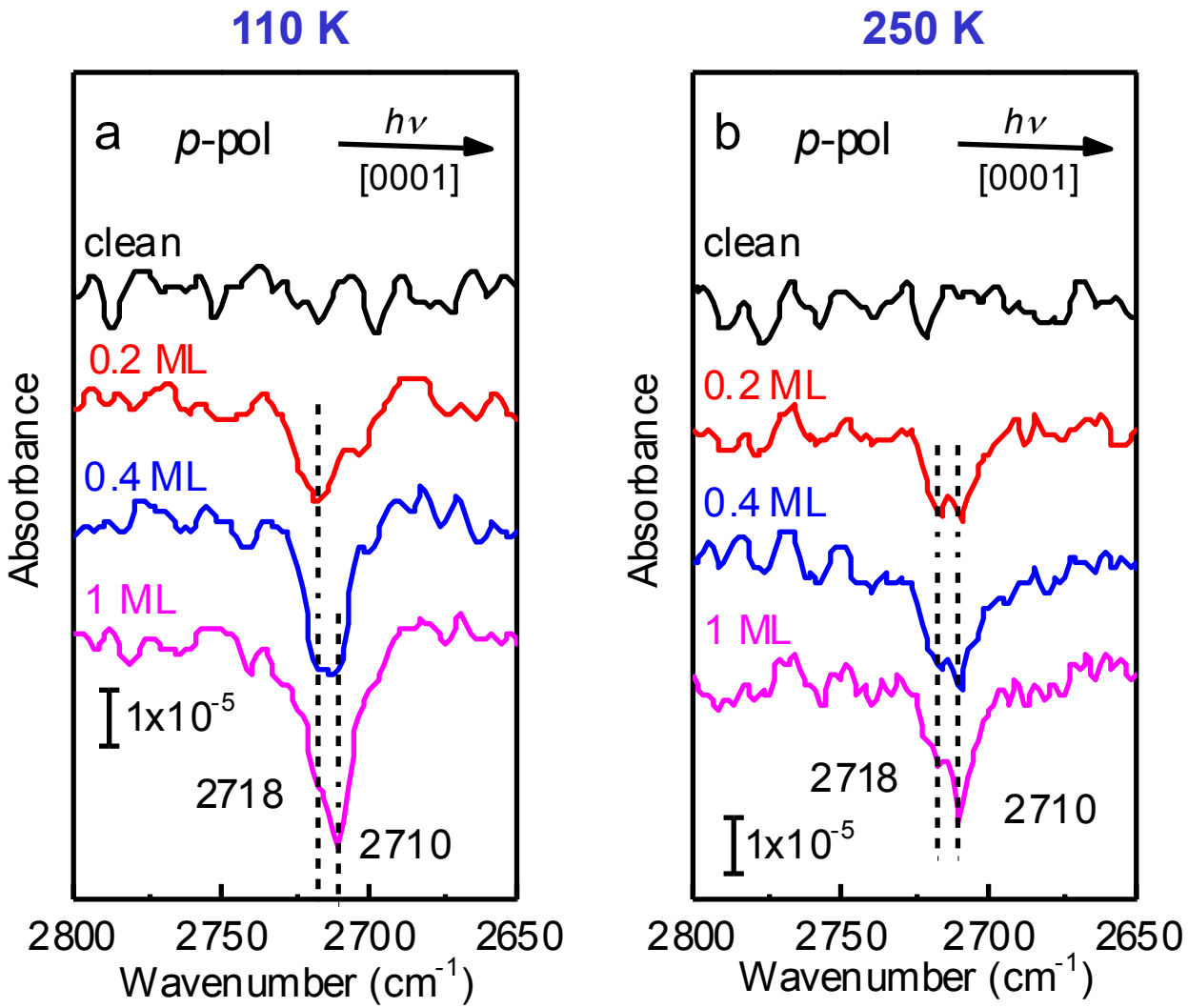
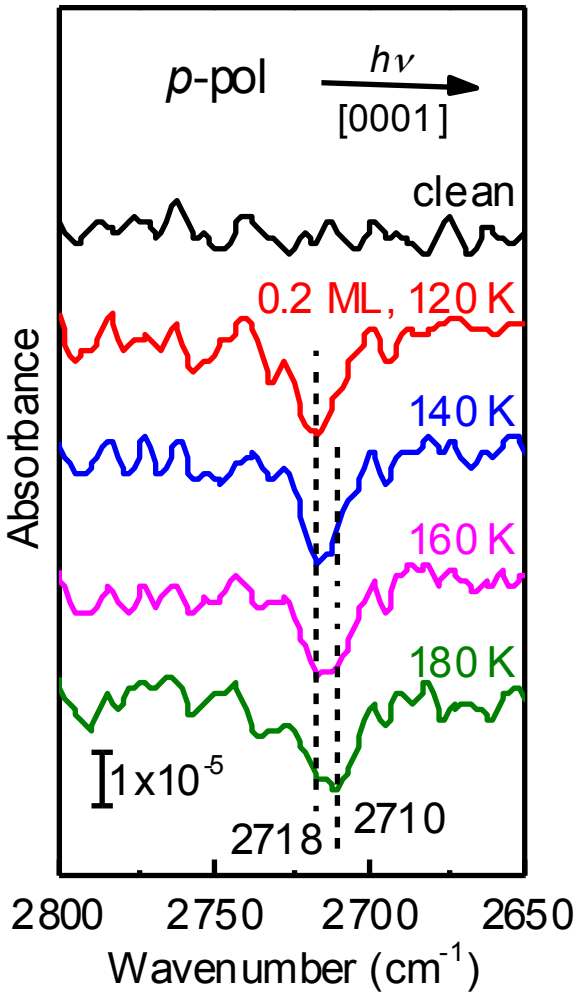
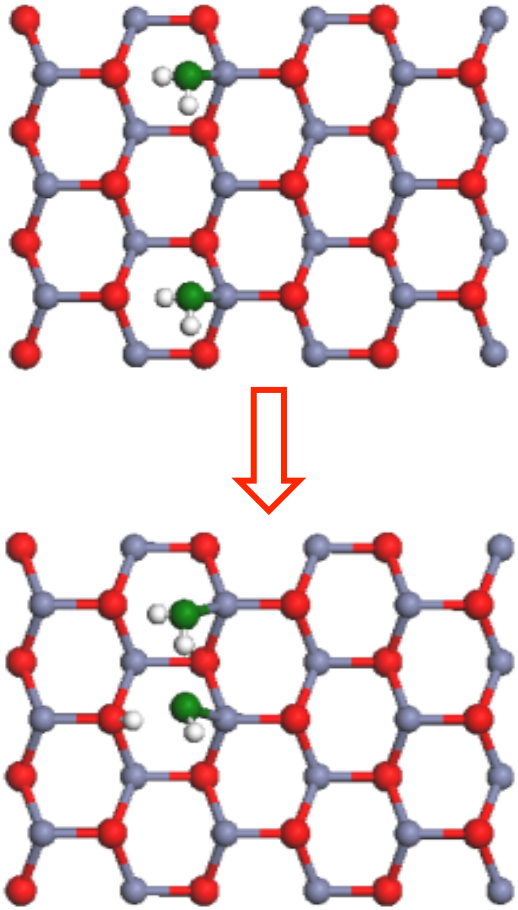
D_2O on ZnO(10-10): monomer ➡ monolayer



IRRAS spectra recorded after exposing the clean ZnO(10-10) surface to different doses of $D_2{}^{16}O$ at (a) 110 K and (b) 250 K with p-polarized light incident along [0001] azimuth.

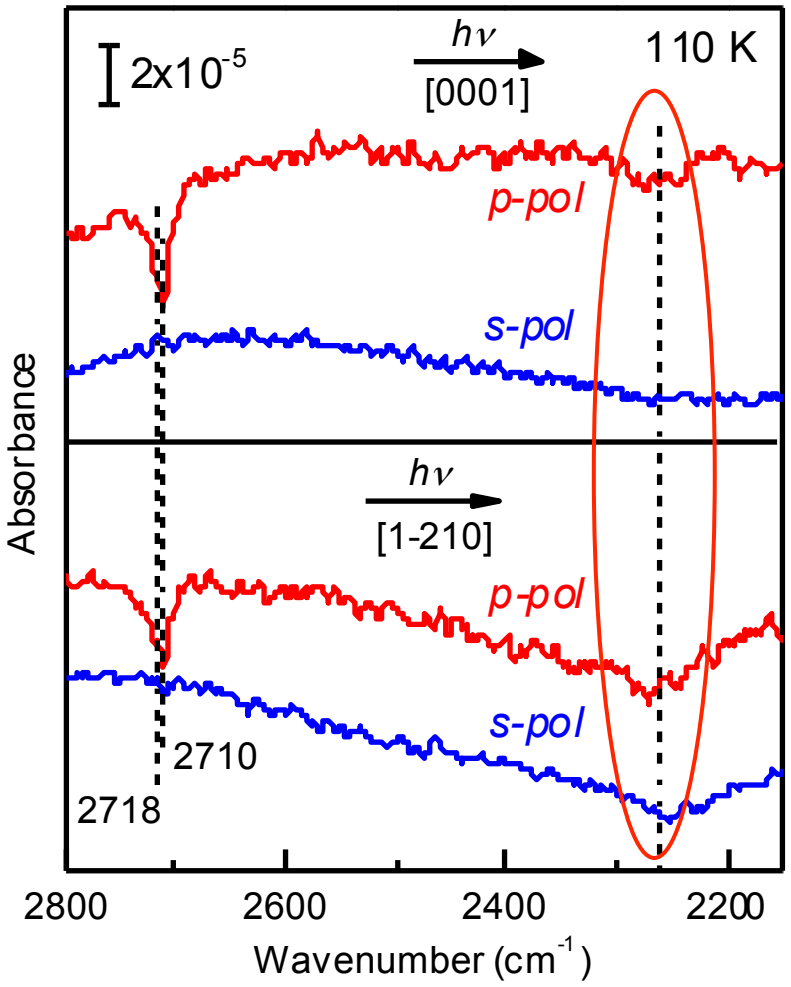
D_2O on ZnO(10-10): monomer

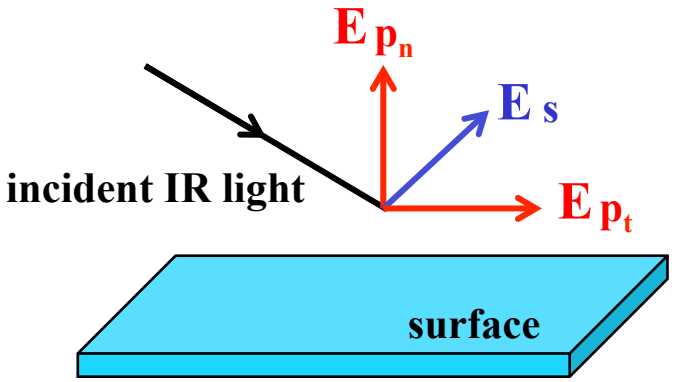


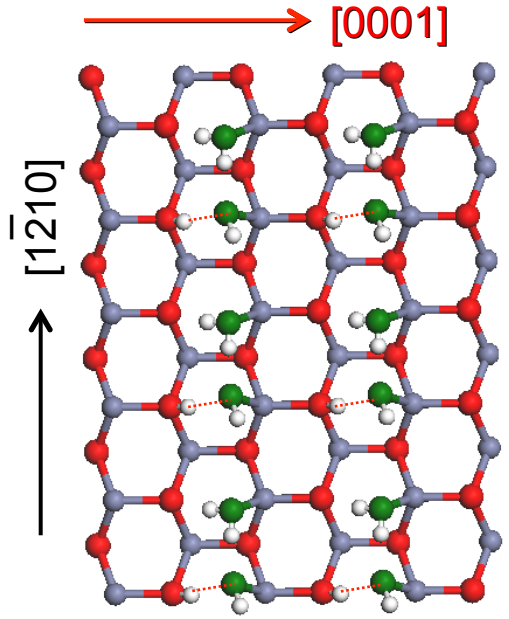


IRRAS spectra obtained after exposing the clean ZnO(10-10) surface to 0.2 ML $D_2{}^{16}O$ at 120 K and heating gradually to indicated temperatures. All spectra were measured with p-polarized light incident along [0001] azimuth at 120 K.

D_2O on ZnO(10-10): monolayer







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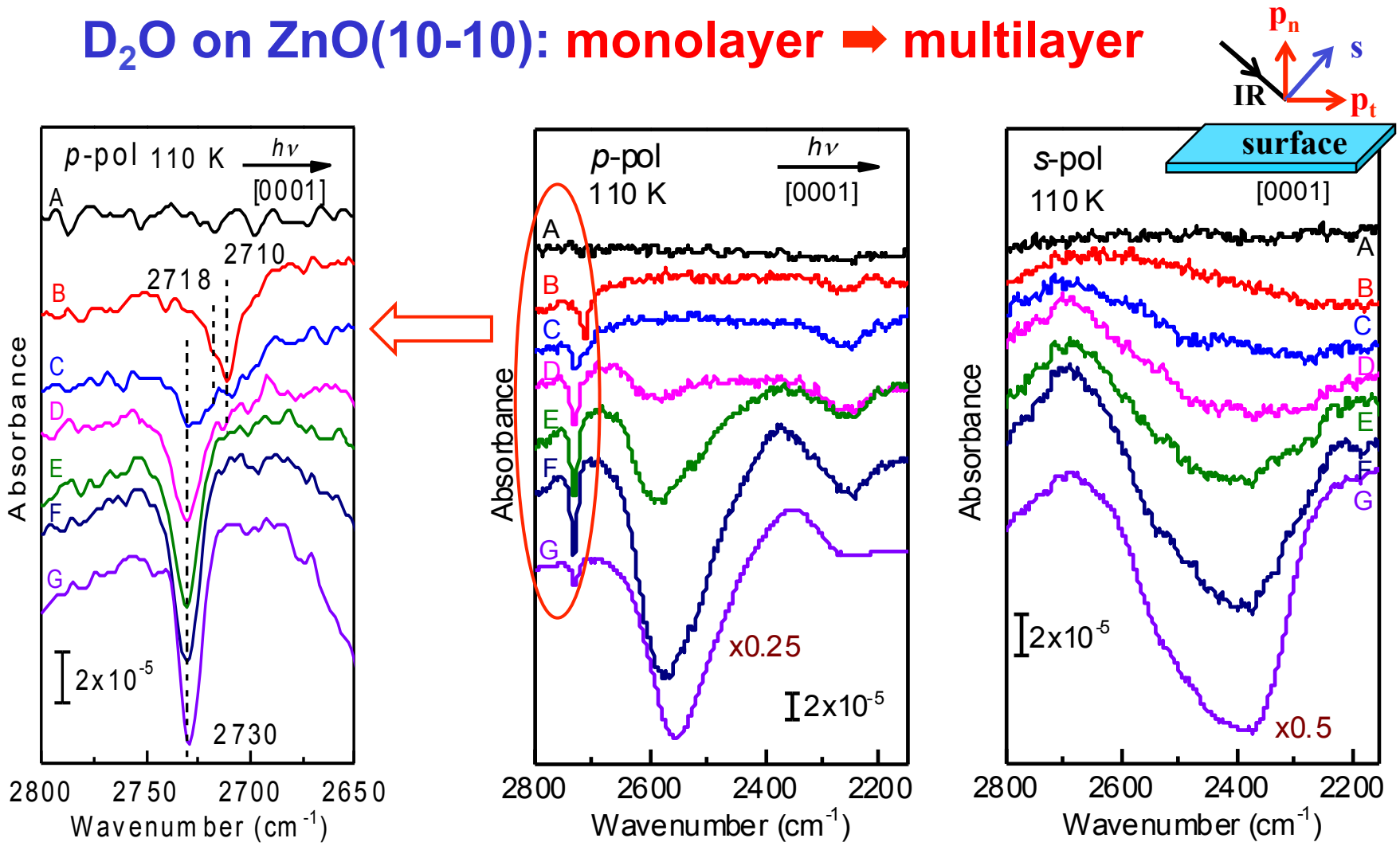
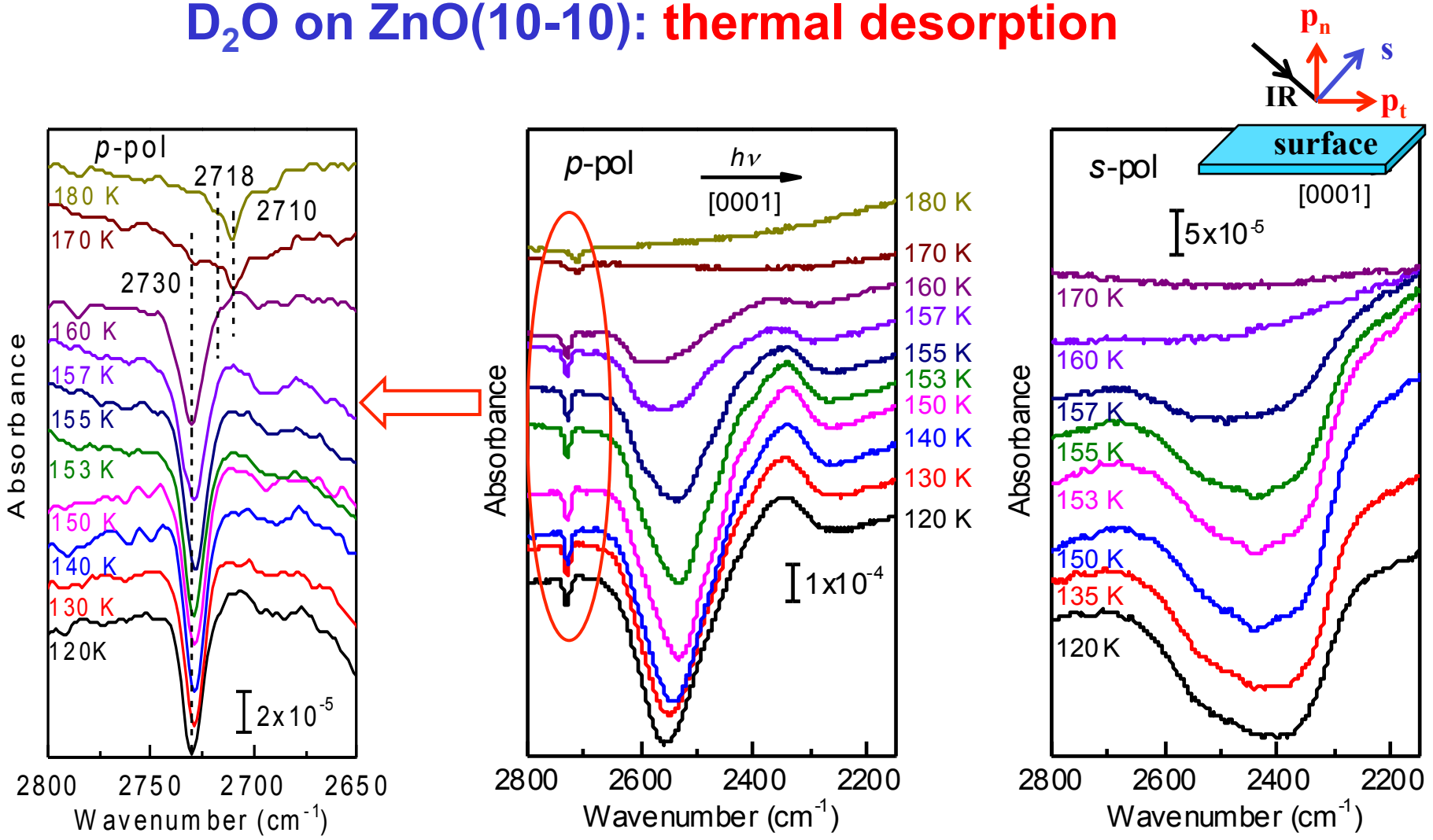
D_2O on ZnO(10-10): monolayer ➡ multilayer



For multilayer water adsorption, no difference between [0001] and [1-210] azimuths.

IRRAS spectra recorded after exposing (A) the clean ZnO(10-10) surface to (B) 1 ML, (C) 2 ML, (D) 3 ML, (E) 4 ML, (F) 6 ML, (G) 12 ML D_2O at 110 K. The spectra were recorded with p- and s-polarized light incident along [0001] azimuth.

D_2O on ZnO(10-10): thermal desorption

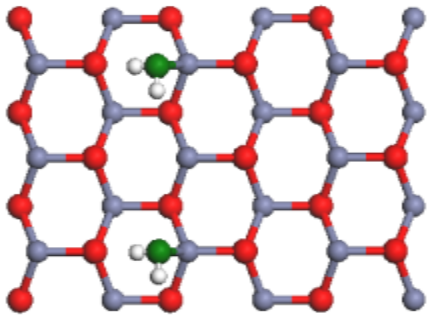


IRRAS spectra recorded after exposing the clean ZnO(10-10) surface to 10 ML D_2O at 120 K and heating gradually to indicated temperatures. All spectra were measured with p- and s-polarized light incident along [0001] azimuth at 120 K.

Conclusions

- D_2O monomer (T<140 K; 0.2 ML)

  ν(O-D) : 2718 cm^{-1}

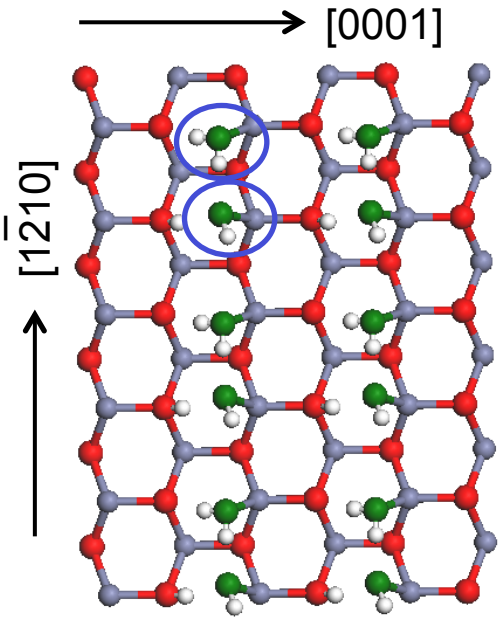


- D_2O monolayer

  ν(O-D) : 2710, 2718 cm^{-1}

  OD groups and non-H-bonded OD (“dangling”) groups in D_2O formed by partial dissociation

  hydrogen bond : 2200-2300 cm^{-1}



- D_2O bilayers and multilayers

  ν(O-D) : 2730 cm^{-1}

  hydrogen bond : 2650-2350 cm^{-1}

Thank you for your attention!