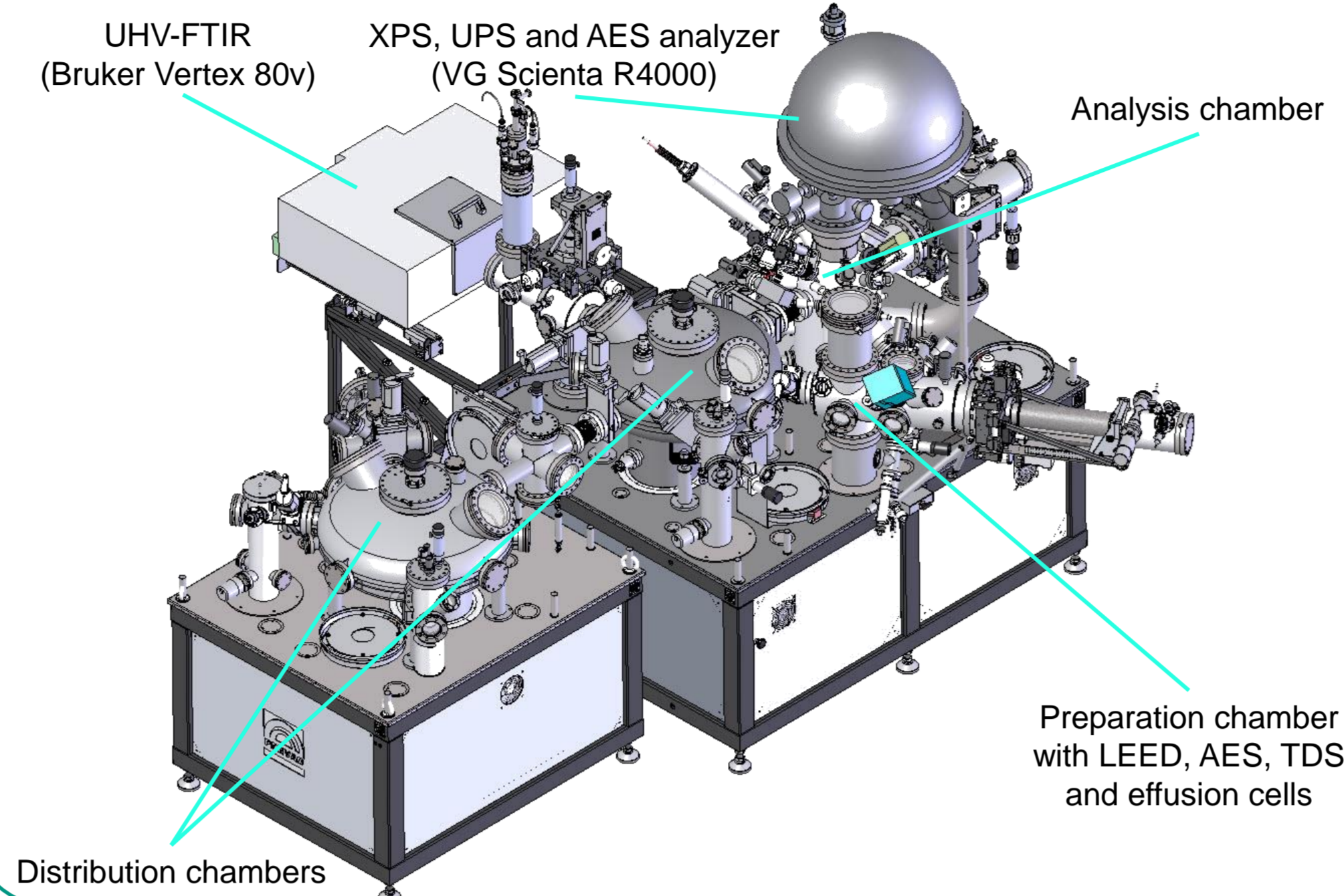


Motivation

Due to the oxygen mobility and the reducibility of cerium ions, ceria and related materials have extensive catalytic applications.^[1] Studying the interaction of methanol with ceria surfaces taking the so-called surface science approach is of crucial importance to gain a fundamental understanding of the oxidation of alcohols to aldehydes.^[2] Here, we use a novel apparatus^[3] combining a state-of-the-art FTIR spectrometer attached to a dedicated UHV-chamber to monitor the adsorption of methanol on CeO₂(111) surfaces. The system allows acquiring spectra in both reflection at grazing incidence on single crystals and in transmission geometry on polycrystalline powders. A precise interpretation of the complicated infrared spectra for adsorbates on powders can only be reached from comparison to data obtained on well-defined single crystal model systems.

We find evidence for methanol adsorbing dissociatively at 120 K on the defective CeO₂(111) surface to yield surface methoxy species. IR spectra, in particular the corresponding frequencies of the C-O stretch vibrations, provide information about the coordination of the methoxy species in respect to the oxide surface.

UHV-IR/XPS apparatus



Experimental

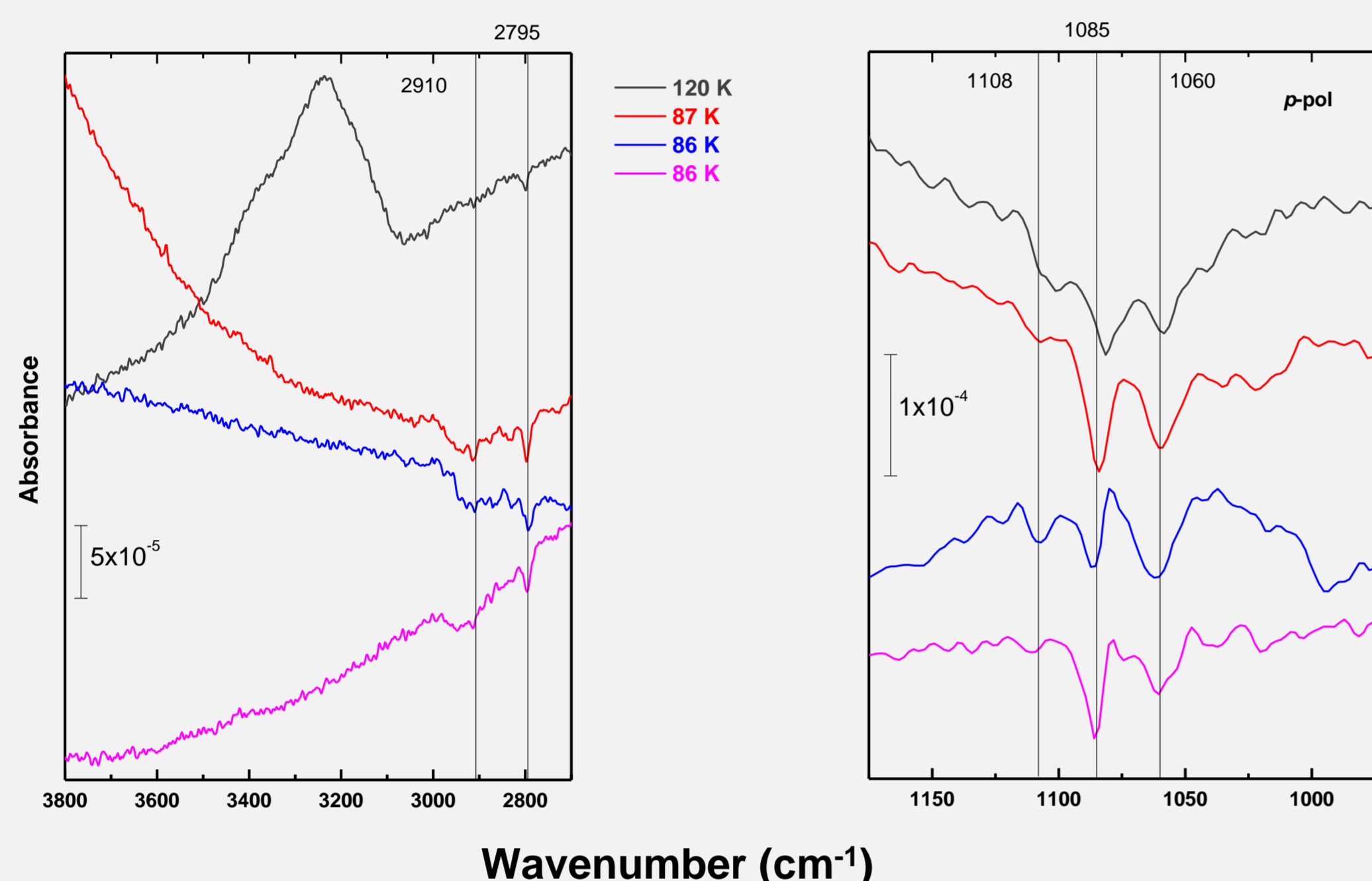
The infra-red reflection absorption spectroscopy (IRRAS) measurements were carried out using a novel UHV-IR/XPS apparatus at the KIT. A CeO₂ single crystal was mounted on the sample holder with electron beam heating. A liquid helium cryostat connected to the sample holder via copper braids allowed for cooling the sample below 100 K. The CeO₂(111) single crystal surface was prepared by repeated cycles of sputtering with 1 keV Ar⁺ ions and annealing at 800 K for 15 min in an O₂ atmosphere (partial pressure of 1×10⁻⁵ mbar) to form a stoichiometric surface. Alternately, annealing without O₂ was employed to create a reduced surface. For temperature monitoring, a K-type thermocouple was clamped directly onto the sample surface.

Methanol was cleaned via several pump-freeze-thaw cycles before use. Exposure to methanol was performed at low sample surface temperatures by achieved by backfilling the IR-chamber. IRRAS spectra only were acquired after achieving the desired Ce oxidation state and high surface crystallinity as judged from XPS and LEED. Typical base pressures during acquisition of IRRAS spectra were below 1×10⁻¹⁰ mbar.

Experimental Results

CH₃OH adsorption on the oxidized surface

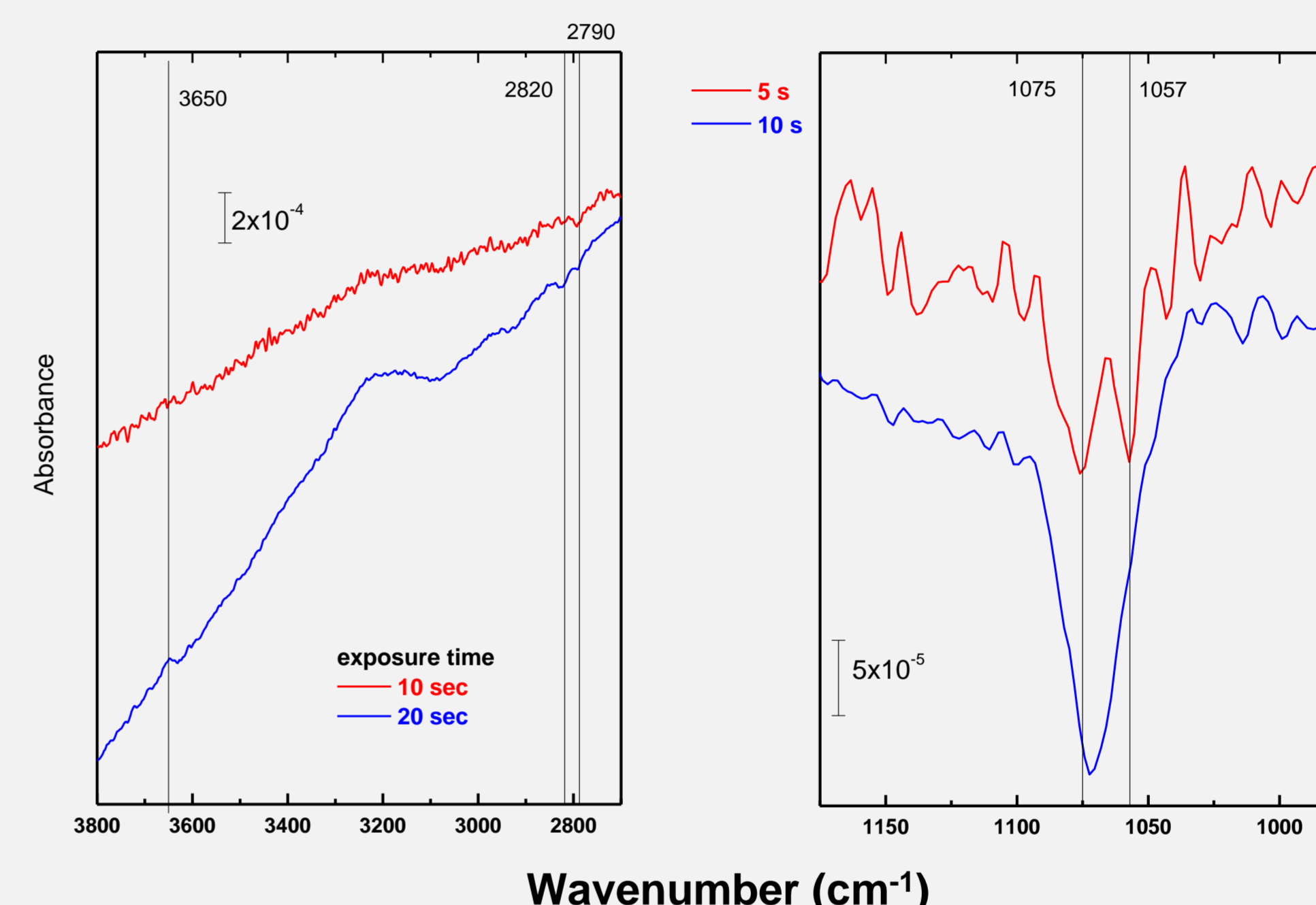
exposure pressure 1.3×10⁻¹⁰ mbar, exposure time 5 second.



- Three bands are visible in the ν(C-O) region at 1108 cm⁻¹, 1082 cm⁻¹ and 1058 cm⁻¹.

CH₃OH adsorption on the reduced surface (oxygen vacancy density ~10%)

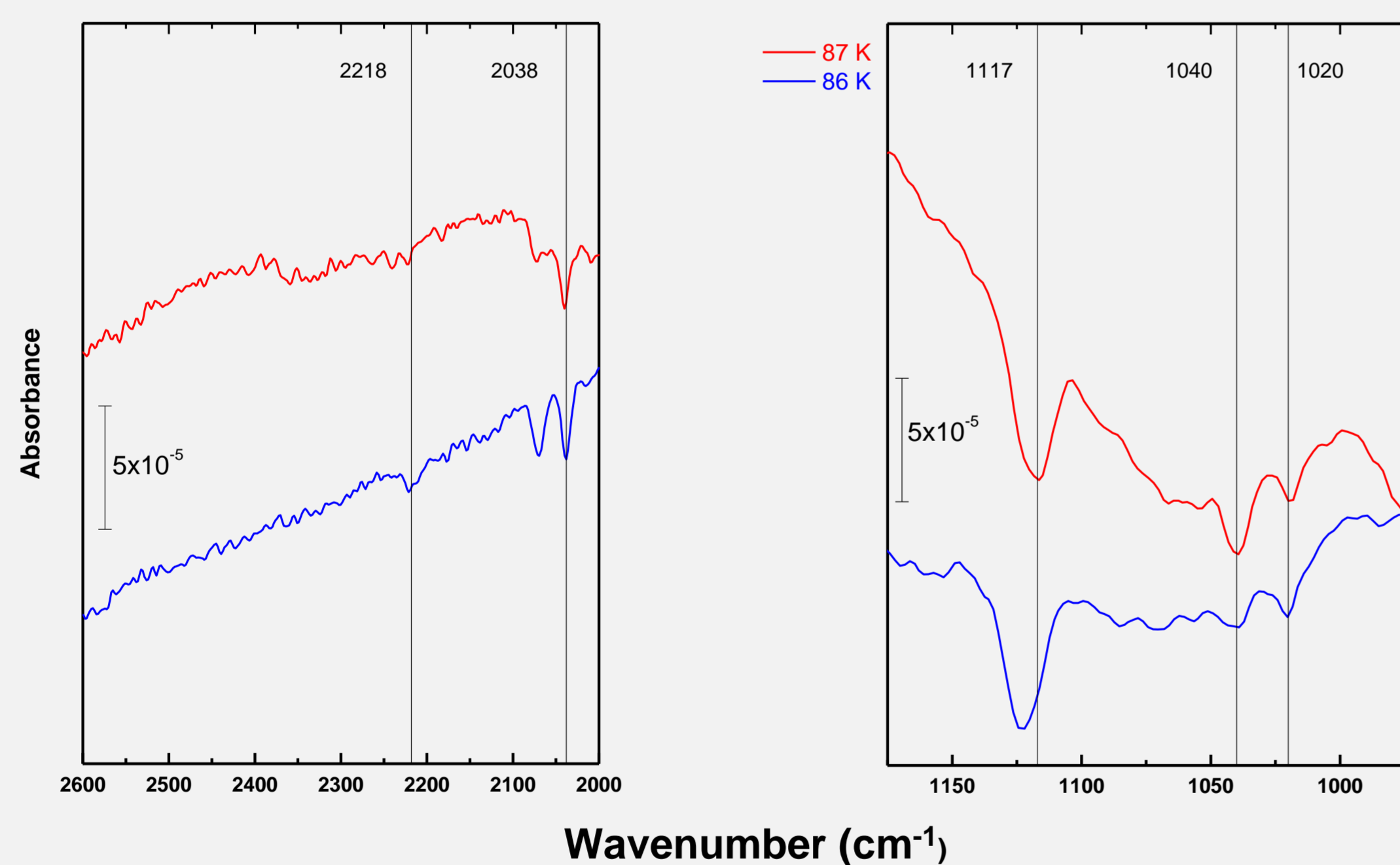
exposure pressure 1.3×10⁻¹⁰ mbar



- Two intense bands at 1075 cm⁻¹ and 1057 cm⁻¹ are apparent in the ν(C-O) region.
- A positive ν(O-H) band is visible at 3650 cm⁻¹, especially after larger exposure.

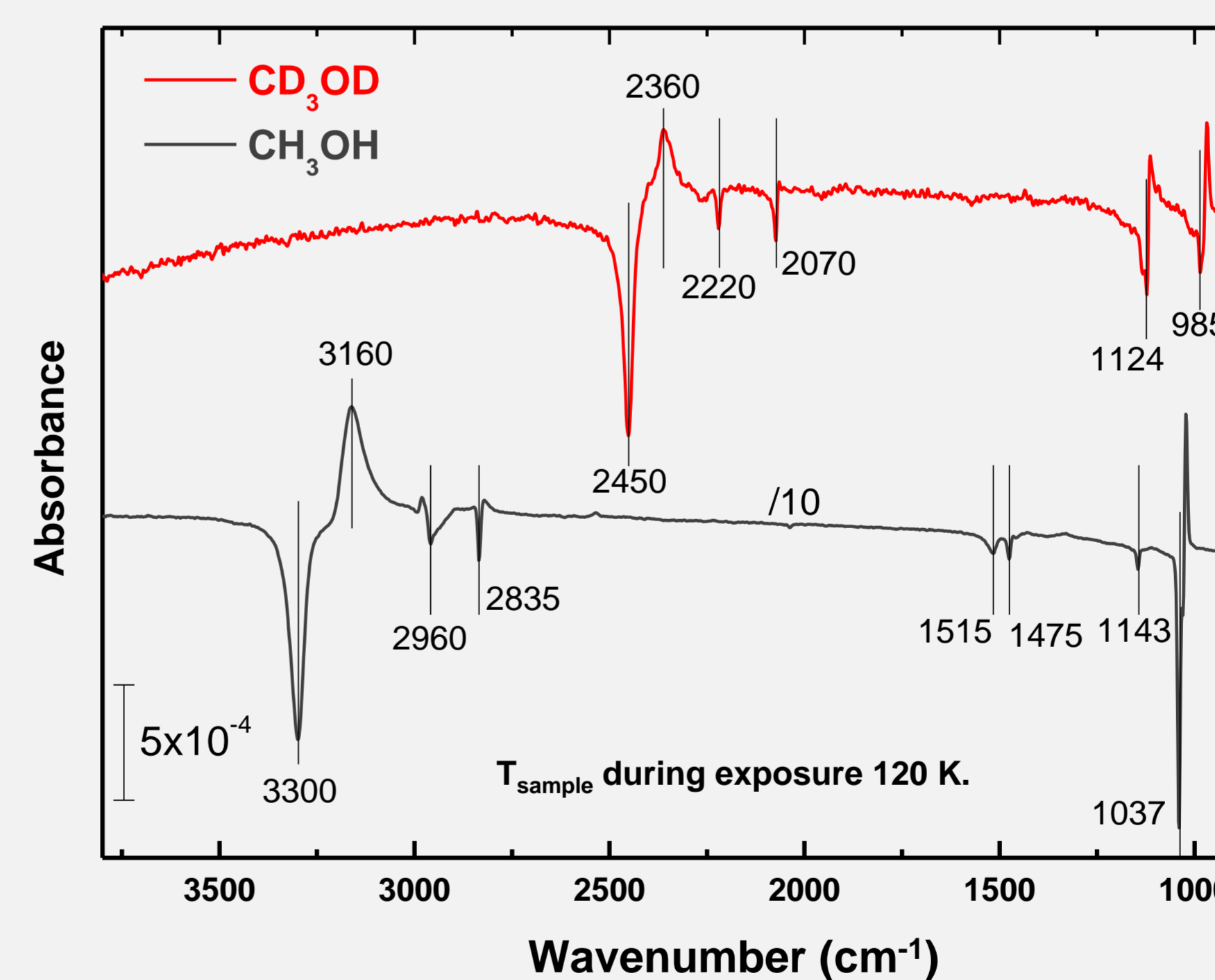
CD₃OD adsorption on the oxidized surface

exposure pressure 1.3×10⁻¹⁰ mbar, time 5 second.



- The very strong feature at 1117 cm⁻¹ is assigned to CD₃ s-deform.
- The bands at 1082 cm⁻¹ and 1058 cm⁻¹ for CH₃OH adsorption shift isotopically to 1040 cm⁻¹ and 1020 cm⁻¹, respectively, for CD₃OD.

CH₃OH/CD₃OD multilayers on the oxidized surface



MeOD	
2450 and 2360	OD stretch
2220	CD ₃ as-stretch
2070	CD ₃ s-stretch
1124	CD ₃ s-deform
985	CO stretch

MeOH	
3300 and 3160	OH stretch
2960	CH ₃ as-stretch
2835	CH ₃ s-stretch
1515	CH ₃ d-deform
1475	CH ₃ s-deform
1143	CH ₃ rock
1037	CO stretch

Assignments of bands in the ν(C-O) region

Comparison to previous assignments

Table 1. O-CH₃ species adsorbed on ceria oxidized surfaces

	O-CH ₃ monodentate	O-CH ₃ bidentate	O-CH ₃ tridentate
single crystal	1108	1082, 1058	—
thin film ^[4]	1105	1054	1015-1025
powder ^[5]	1103	1061-1065	1015

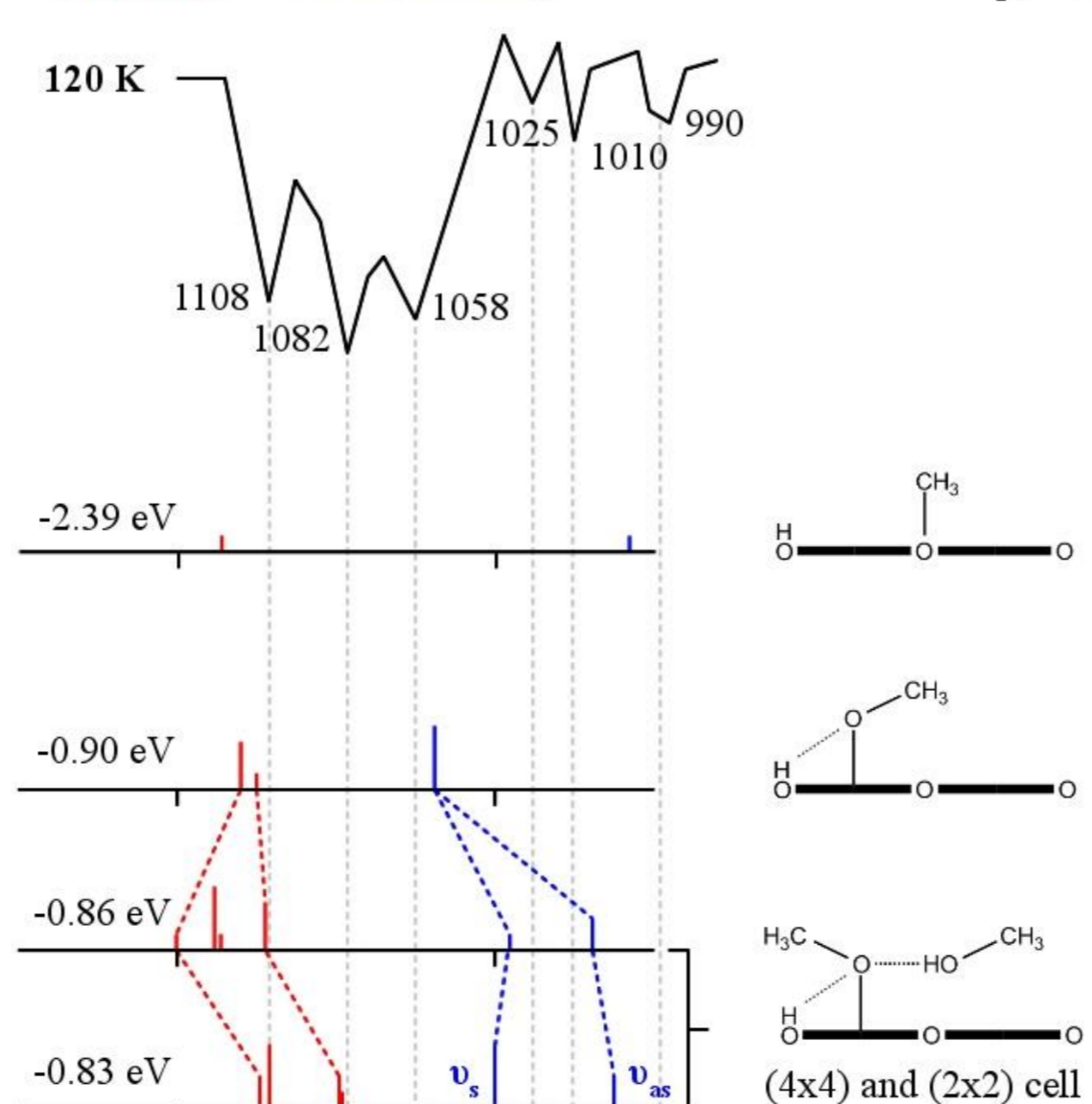
Table 2. O-CH₃ species adsorbed on ceria reduced surfaces

	O-CH ₃ monodentate	O-CH ₃ bidentate	O-CH ₃ tridentate
single crystal	—	1075, 1057	—
thin film ^[4]	1117	1067	1045
powder ^[5]	1115	1075-1083, 1065	1040

The experimental data for the thin film do not agree with our data for ceria single crystal, but are consistent with those obtained for powders. This indicates that the thin film surface exhibits numerous defects.

Theoretical calculations

Rocking and C-O Stretching Modes for MeOH at CeO₂(111)



Conclusions

- Methanol adsorbs dissociatively at CeO₂(111) surfaces to yield surface methoxy species.
- The sharp ν(O-H) band at 3650 cm⁻¹ observed for methanol adsorption on the reduced surface is possibly due to the existence of a larger amount of isolated hydroxyl groups. These groups seem to be more abundant on the reduced surface compared to the oxidized surface, where they aren't visible in the spectra.
- The bands in the ν(C-O) region for methanol adsorption on CeO₂(111) were assigned based on theoretical calculations: the band at 1108 cm⁻¹ is assigned to the CH₃ rocking mode and the bands at 1057-1085 cm⁻¹ are assigned to C-O stretch vibrations with different coordination numbers of hydrogen bonding.

References

- [1] A. Trovarelli, P. Fornasiero (Ed.), Catalysis by Ceria and Related Materials (2nd edition), Imperial College Press, London, 2013.
- [2] J. M. Vohs, Chemical Reviews, 2013, 113, 4136.
- [3] C. Yang, L. Yin, F. Bebensee, M. Buchholz, H. Sezen, S. Heissler, J. Chen, A. Nefedov, H. Idriss, X. Gong, C. Wöll, Physical Chemistry Chemical Physics, 2014, 16, 24165.
- [4] A. Siokou, R. M. Nix, J. Phys. Chem. B, 1999, 103, 6984.
- [5] A. Badri, C. Binet, J.-C. Lavelley, J. Chem. Soc., Faraday Trans., 1997, 93, 1159.