

Motivation

N₂O together with other nitrogen oxide species (NO, NO₂) is formed in the engine and also in the catalytic converter by the reaction of N₂ with adsorbed oxygen atoms. The destruction of these gases (DeNO_x process) via reduction of NO_x to N₂ is of great significance due to their environment and health impact. Especially for nitrous oxide (N₂O) has been considered as the single most important ozone-depleting substance emitted and is expected to remain the largest throughout the 21st century. Specifically, NO and NO₂ have to be firstly converted into N₂O characterized by the high inertness, and then N₂O further liberates oxygen to finally generate environmentally benign N₂, where the latter is the rate determining step of DeNO_x process. Reducible oxides, such as TiO₂, CeO₂ and Fe₂O₃, have shown the reactivity to convert N₂O to N₂ presumably at oxygen vacancy sites.

In this study, we monitored the conversion of N₂O to N₂ over the model catalyst oxide support, namely CeO₂ by using photoemission spectroscopy (PES), near edge x-ray absorption fine structure spectroscopy (NEXAFS) and ultra-high-vacuum infra-red reflection absorption spectroscopy (UHV-IRRAS), which also enables us to determine the kinetics of this process.

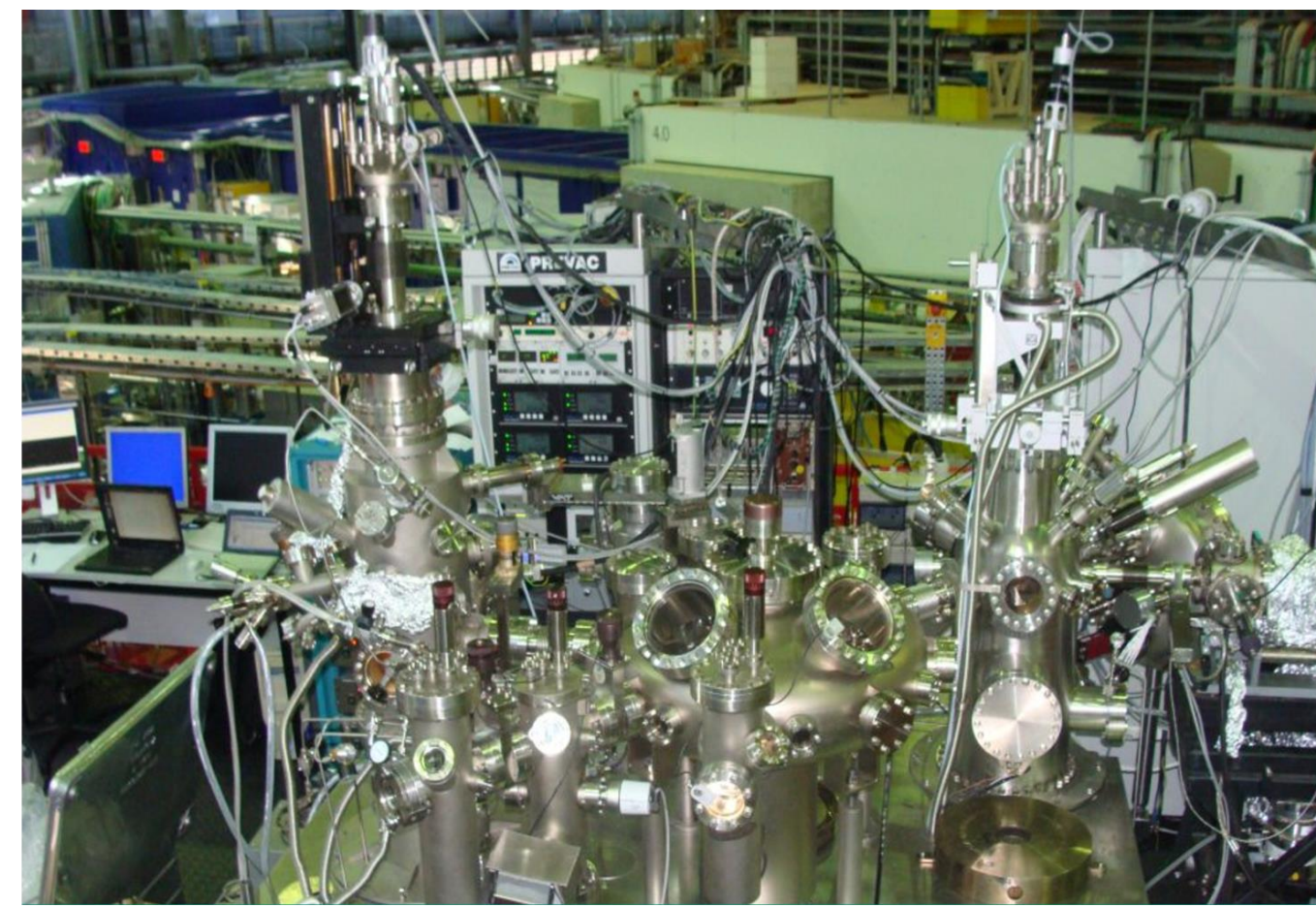
Experimental

The CeO₂ single crystals were prepared by repeated cycles of sputtering with 1 keV Ar⁺ and annealing at 800 K for 15 min in an O₂ atmosphere of 1×10⁻⁵ mbar for forming stoichiometric surfaces, and then annealed at 800 K to obtain reduced surfaces, i.e., surfaces with oxygen vacancies. The reduced ceria powders were obtained by stepwise annealing from 800 K to 1000 K for 30 min.

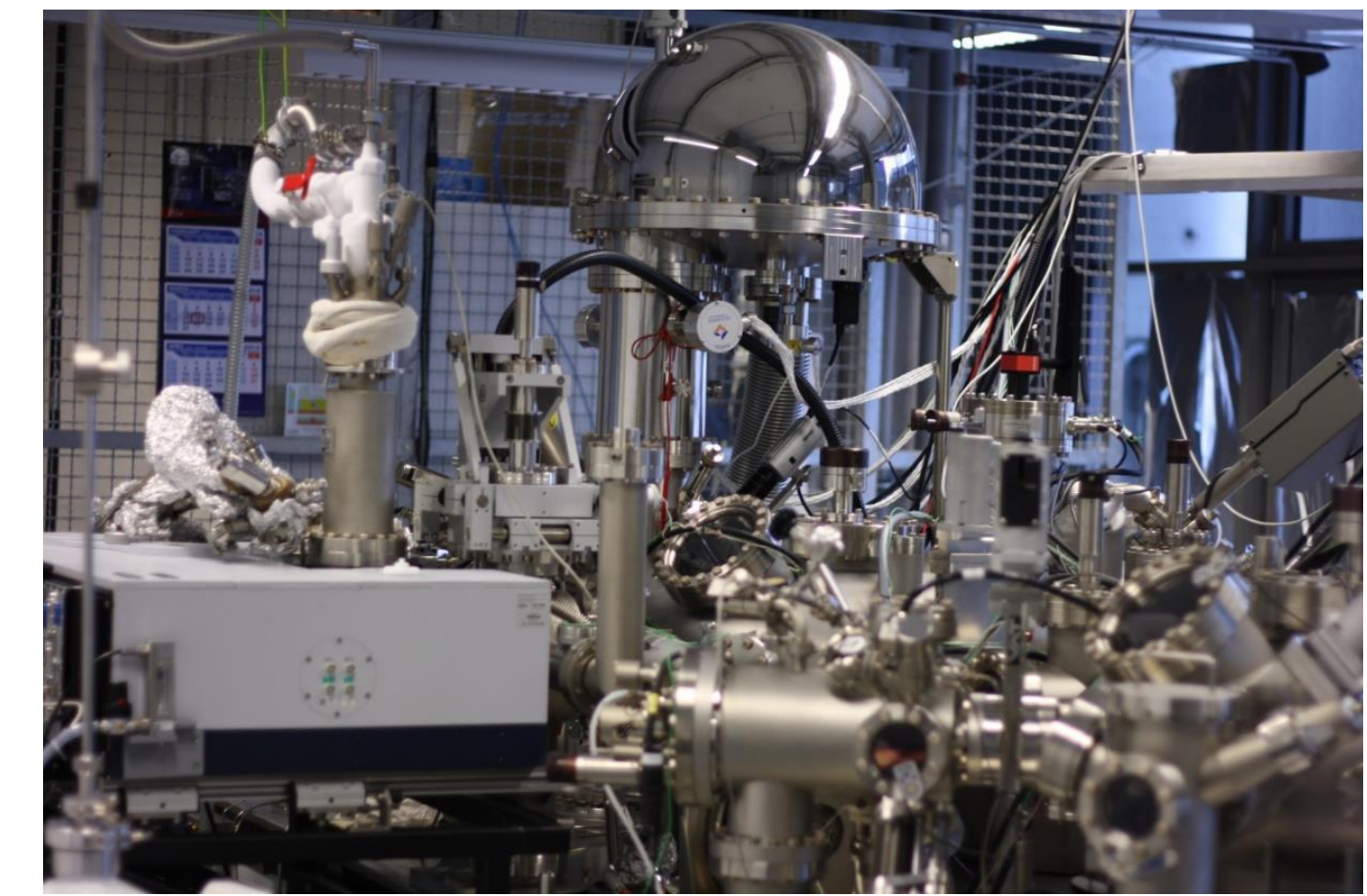
NEXAFS and PES measurements were carried out on the HE-SGM beamline at BESSY II. NEXAFS measurements were performed at 120 K after desired Ce oxidation state as judged by PES. Exposure to 50 Langmuirs N₂O was achieved by backfilling the analysis chamber up to 2.6×10⁻⁷ mbar for 250 seconds. Due to severe charging problems, PES measurements cannot be performed at temperature for N₂O dosing (120 K), but the valence band (VB) spectra were recorded at 150 K to check the change of cerium oxidation state of samples before and after interaction with N₂O.

IRRAS measurements were conducted at ~120K on the other UHV apparatus at KIT. N₂O dosing was achieved by backfilling the IR chamber. The lamp N-8 L (Herolab) with power of 8 W @ λ=365 nm was used for UV-irradiation, which was shed directly on the samples through a quartz-window on IR chamber.

NEXAFS/PES Endstation at HE-SGM Beamline

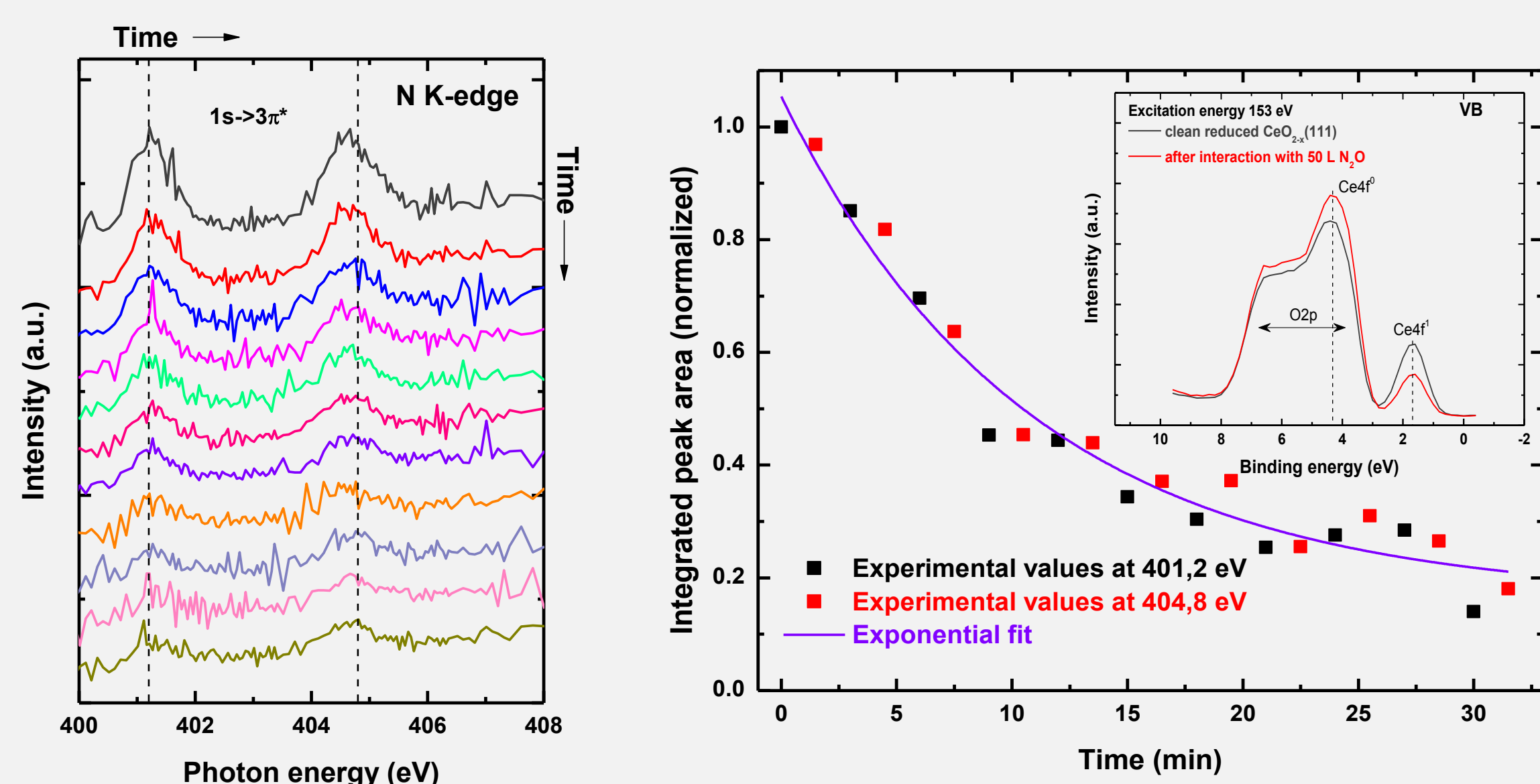


UHV-IR/PES System "Theo"



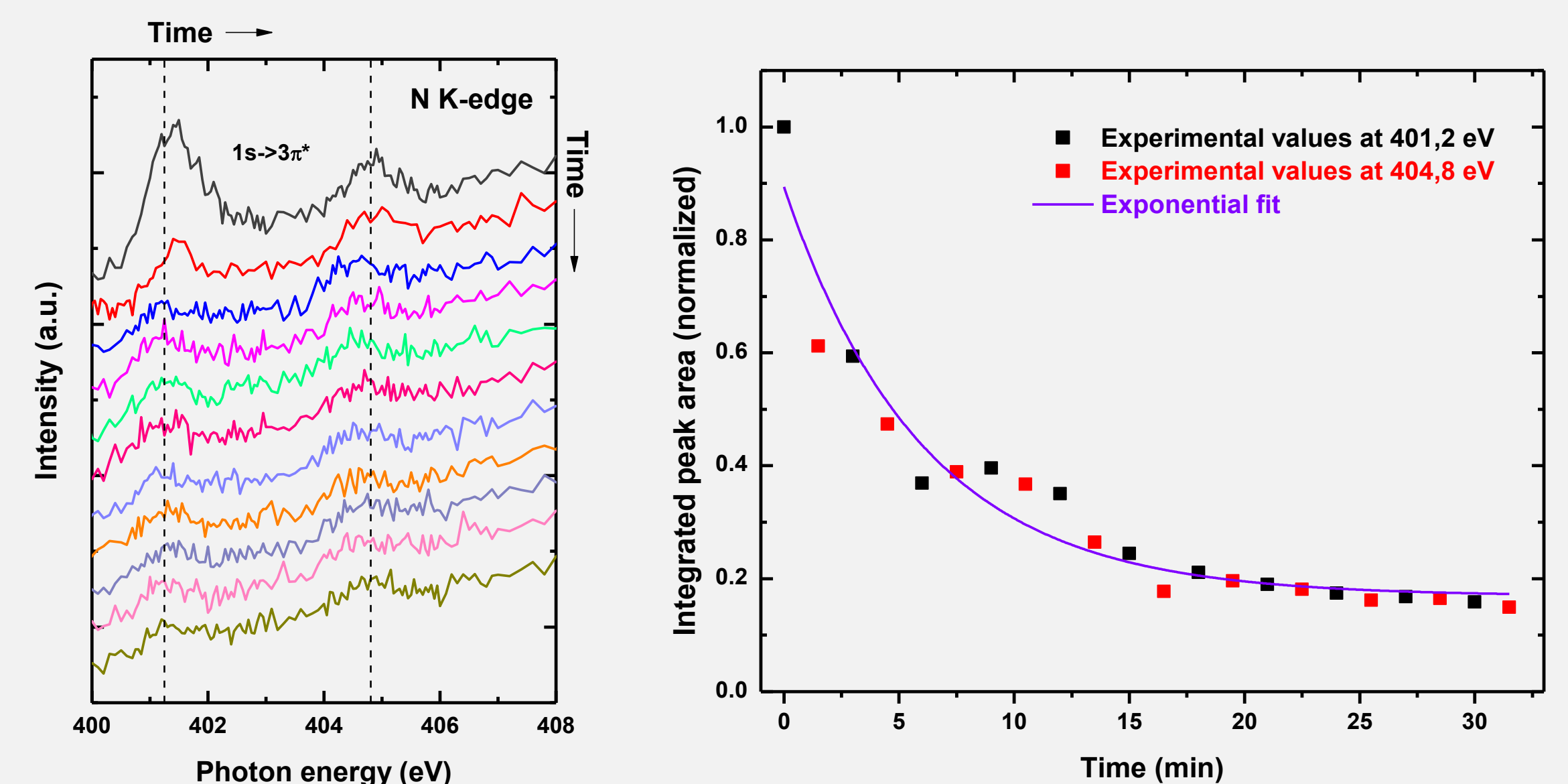
NEXAFS/PES Results

CeO_{2-x}(111)



N K-edge NEXAFS spectra of the reduced CeO_{2-x}(111) surface after exposure to 50 Langmuirs N₂O at 120 K are depicted (left). Two X-ray resonances at 401.2 eV (Ce-O-N-N) and 404.8 eV (Ce-O-N-N) were observed. The signal decay at both photon energies is given in a time dependent plot (right). The measurement time between both signals in one spectrum was estimated to 1.5 min, while between two stacked spectra it was 3 min. Kinetic predictions should be valid under the consideration that both signals have equal peak intensities on a simultaneous time recording scale. **Inset:** VB spectra of partially reduced CeO_{2-x}(111) and the CeO₂(111) reoxidized by N₂O photo-decomposition.

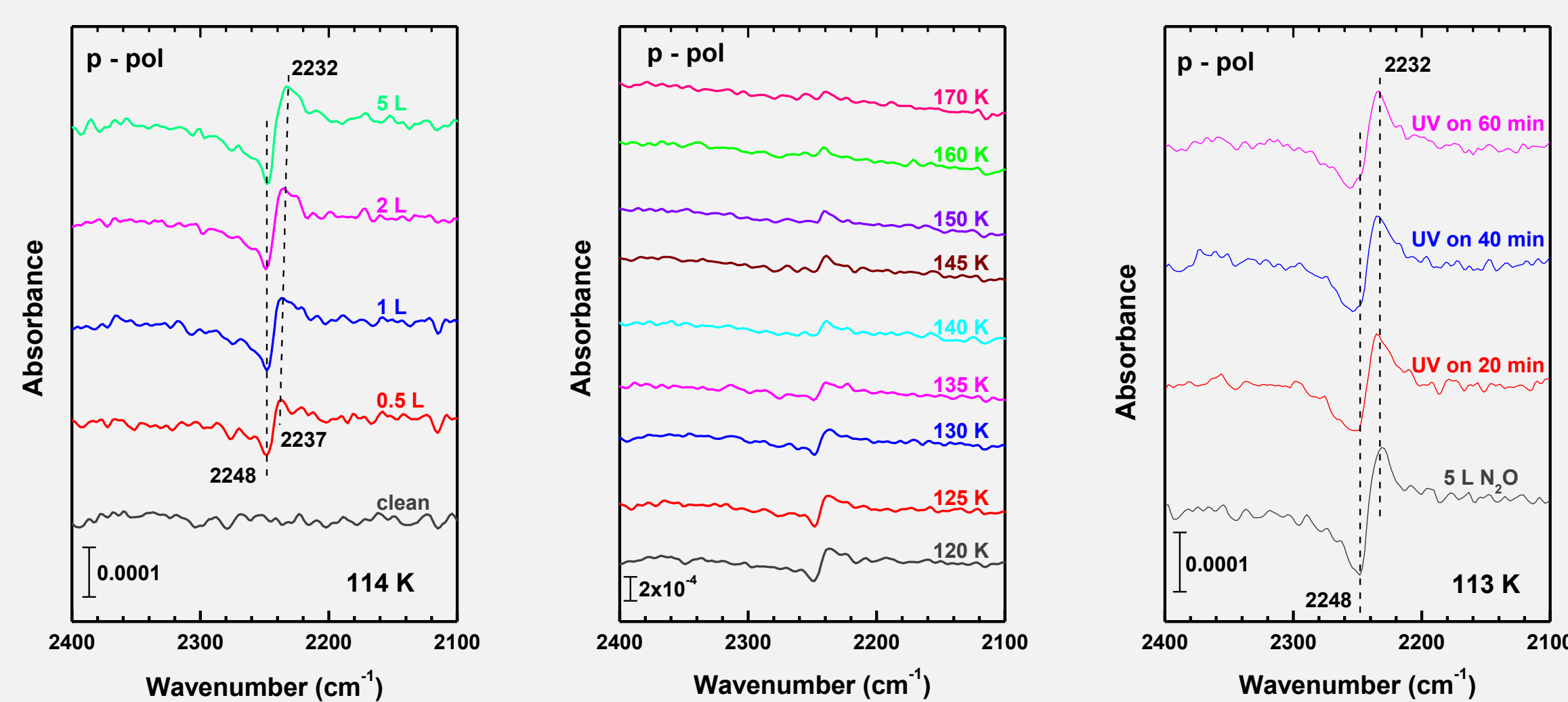
CeO_{2-x} powders



N K-edge NEXAFS spectra of reduced ceria powders were recorded after exposure to 50 Langmuirs N₂O at 120 K (left). The corresponding kinetic profile illustrates the signal decay over time (right). Exponential fitting reveals a first order kinetics for N₂O decomposition over reduced ceria powders.

IRRAS Results

CeO_{2-x}(111)

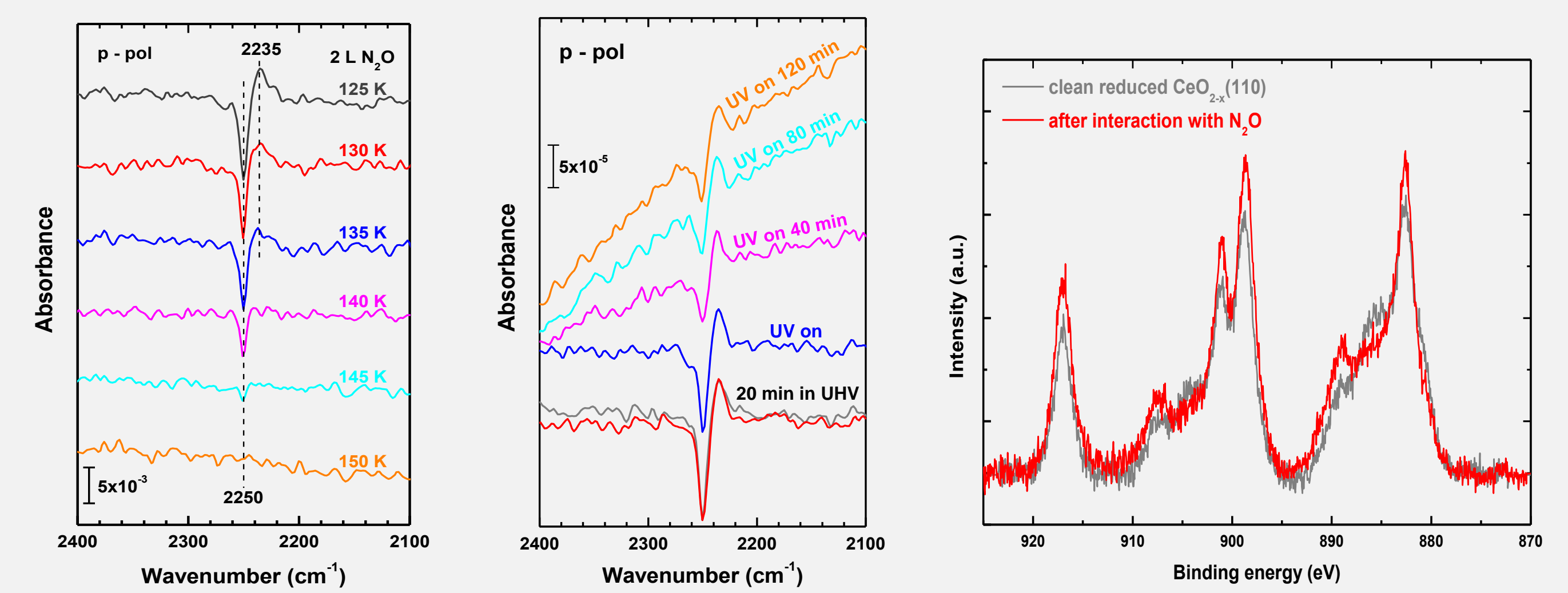


N₂O on reduced CeO₂(111)

IRRAS thermal desorption of N₂O on reduced CeO_{2-x}(111)

Photochemical depletion of N₂O on reduced CeO_{2-x}(111)

CeO_{2-x}(110)



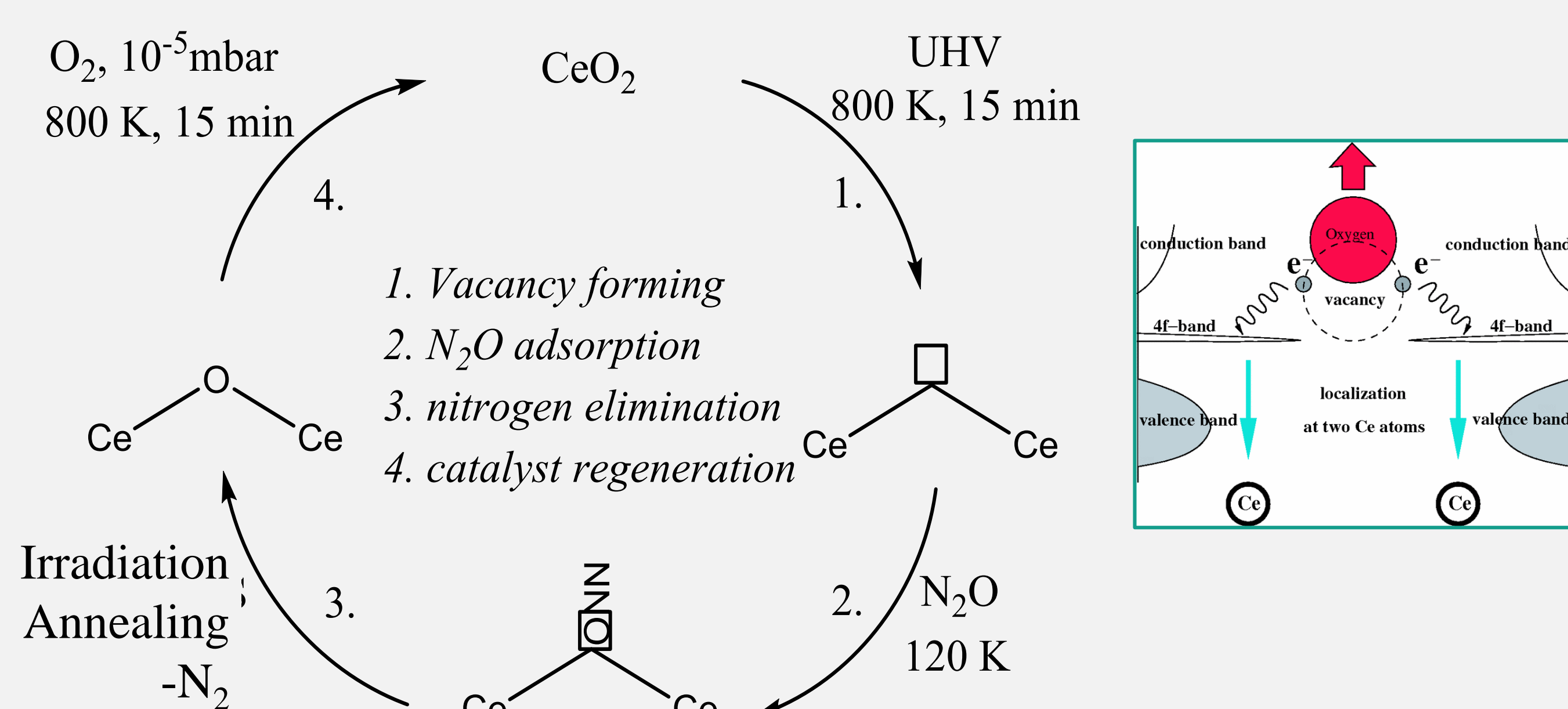
IRRAS thermal desorption of N₂O on reduced CeO_{2-x}(110)

Photochemical depletion of N₂O on reduced CeO_{2-x}(110)

Comparison of grazing emission XP spectra of reduced CeO_{2-x}(110) before and after N₂O treatment indicates N₂O donated oxygen atom to the oxygen vacancy and re-oxidized the reduced CeO_{2-x}(110).

Mechanisms

Schematic view on N₂O decomposition over nonstoichiometric ceria.



Conclusions

In this work we present NEXAFS and IRRAS results of thermal and photo decomposition of the most inert nitrogen oxide, N₂O, to N₂ over reduced ceria substrates and powders. After exposure of N₂O to reduced CeO_{2-x}(111) and CeO_{2-x} powders at 120 K, two apparent resonances were observed at photon energies of 401.2 eV and 404.8 eV in N K-edge NEXAFS spectra. The tunable excitation energy of X-ray source at synchrotron enabled us to monitor the re-oxidation of reduced ceria samples indicated by the shrink of the Ce4f states signal in valence band (VB) photoemission spectra, which is a direct evidence for replenishing the voids on reduced ceria surfaces with oxygen atoms probably left behind by the decomposition of N₂O to N₂.

IRRAS data corroborate the observations by NEXAFS. After N₂O adsorption on reduced ceria (111) and (110) single crystal surfaces, two IR bands at ~2250 and 2235 cm⁻¹ with different signs are observed, which can be ascribed to asymmetric stretching vibration of N₂O adsorbed at O-defect sites and perfect sites, respectively. Both bands shrink with temperature increasing or UV irradiation. Comparison of grazing emission XP spectra of reduced ceria substrates before and after N₂O treatment indicates N₂O donated oxygen atom to the oxygen vacancy and thereby re-oxidized reduced ceria surfaces. This is the first report revealing nonstoichiometric ceria has extraordinary photochemical reactivity for the DeNO_x process.

References

- [1] A. R. Ravishankara, J. S. Daniel, R. W. Portmann, *Science*, **2009**, 326, 123.
- [2] D. R. Mullins, *Surface Science Reports*, **2015**, 70, 42.
- [3] J. A. Rodriguez, *Environmental Catalysis*, **2005**, 211, Taylor & Francis Group.
- [4] G. Ceballos, H. Wende, K. Baberschke, D. Arvanitis, *Surface Science*, **2001**, 482-485, 15.
- [5] C. N. Rusu, J. T. Yates Jr., *Journal of Physical Chemistry B*, **2001**, 105, 2596.
- [6] 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.