N_2O-N_2 conversion on reduced ceria surface

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Motivation

N_2O together with other nitrogen oxide species (NO, NO_2) is formed in the engine and also in the catalytic converter by the reaction of N_2 with adsorbed oxygen atoms. The destruction of these gases (DeNOx process) via reduction of NO_x to N_2 is of great significance due to their environment and health impact. Especially for nitrous oxide (N_2O) 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 NO_2 have to be firstly converted into N_2O characterized by the high inertness, and then N_2O further liberates oxygen to finally generate environmentally benign N_2, where the latter is the rate determining step of DeNOx process. Reducible oxides, such as TiO_2, CeO_2 and Fe_2O_3, have shown the reactivity to convert N_2O to N_2 presumably at oxygen vacancy sites.

In this study, we monitor the conversion of N_2O to N_2 over the model catalyst oxide support, namely CeO_2 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.
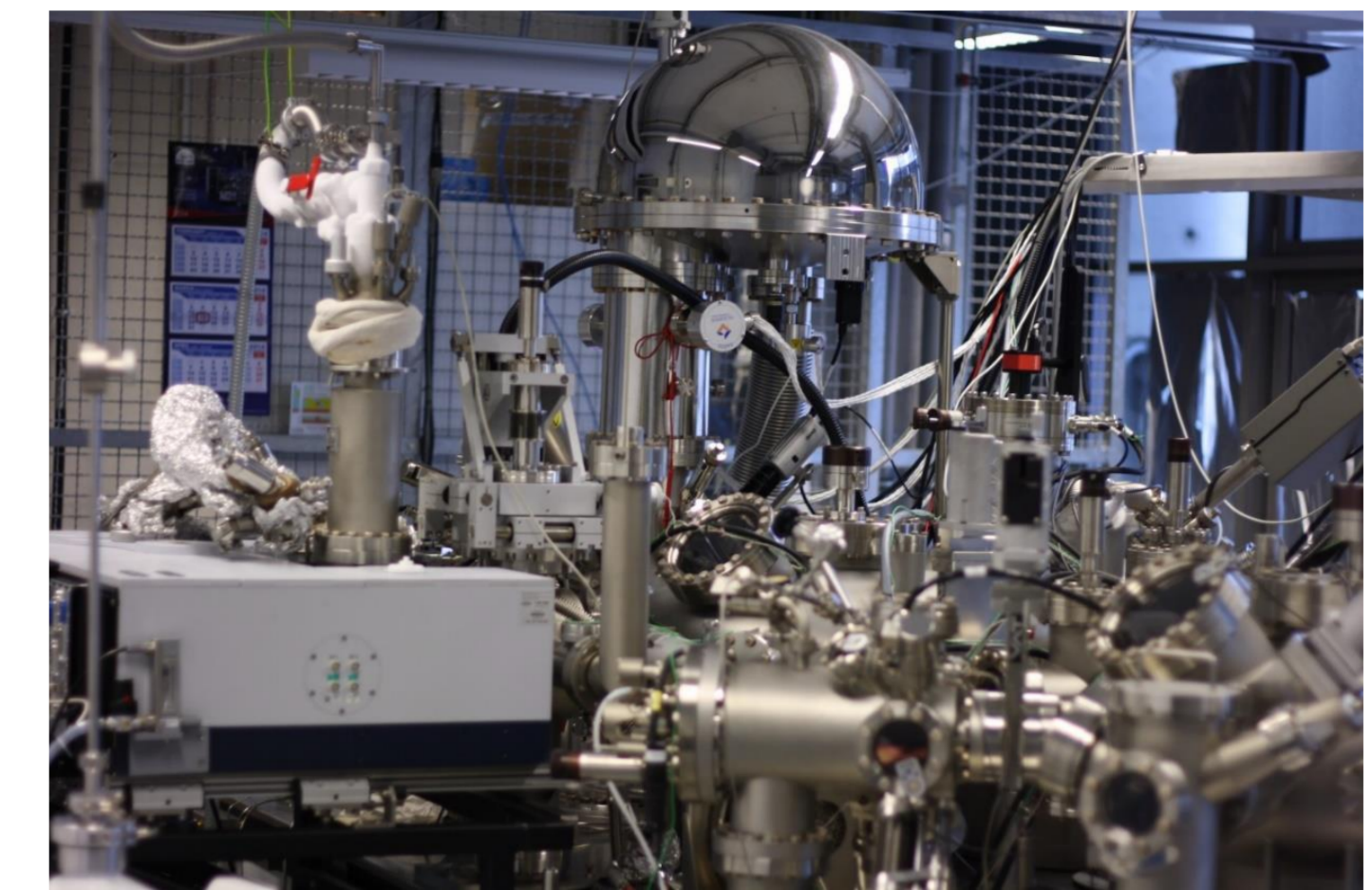
Experimental

The NEXAFS and PES measurements were carried out at the HE-SGM beamline at BESSY II. The CeO_2 single crystal surface was prepared by repeated cycles of sputtering with 1 keV Ar+ and annealing at 800 K for 15 min in an O_2 atmosphere of 1×10^{-5} mbar for forming a stoichiometric surface, or alternately without O_2 to create a reduced one. For preparation of ceria powders, the sample was annealed stepwise from 800 K to 1000 K for 30 min.
NEXAFS measurements were performed at 120 K after desired Ce oxidation state as judged by PES. Exposure to 50 Langmuir N_2O was achieved by backfilling the analysis chamber up to 2.6×10^{-7} mbar for 250 seconds. Due to strong grounding effects, PES measurements cannot be performed at that low temperature. For that reason the temperature was elevated to a given set of temperatures. The VB data were gathered for evaluation of the ceria oxidation state.
IRRAS measurements were performed at 115-170K. Exposure of N_2O was achieved by backfilling the IR chamber up to 2.6×10^{-9} mbar with corresponding time to obtain necessary coverage. For UV-irradiation the lamp N-8 L (Herolab) with power of 8 W @ λ=365 nm was used. The irradiation takes place in IR chamber through quartz-window (directly at measurement position).
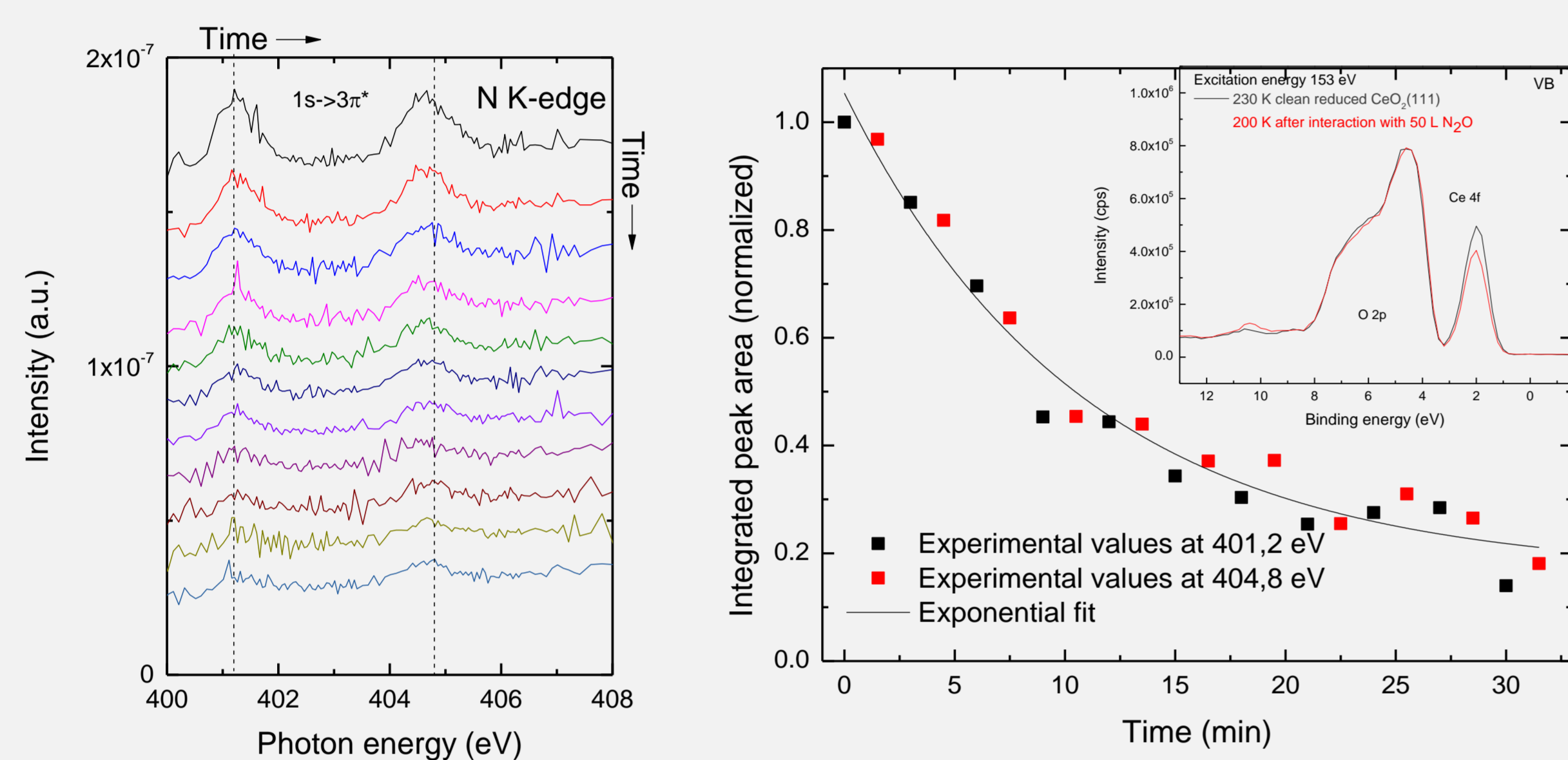
NEXAFS/PES Endstation at HE-SGM Beamline
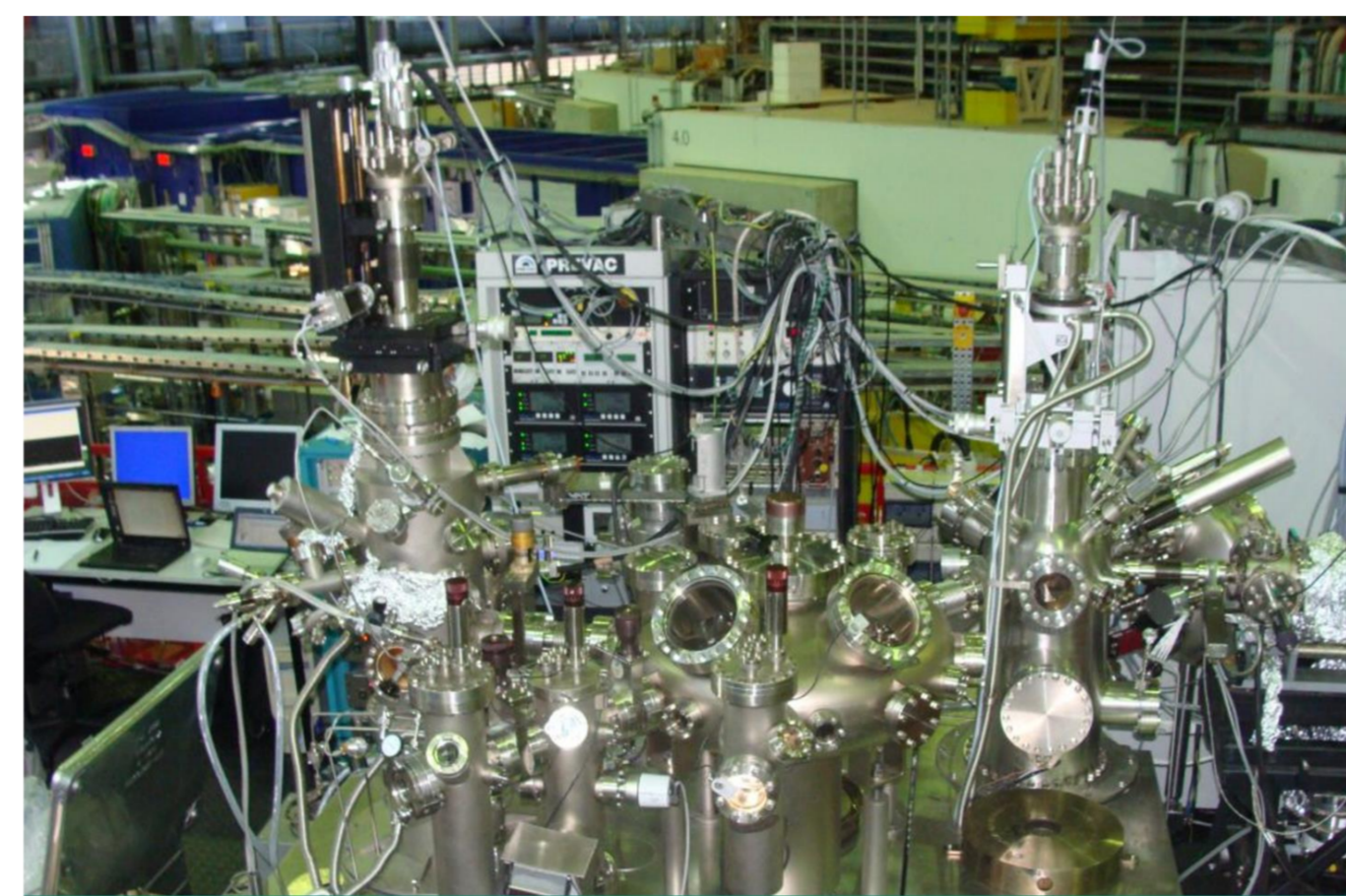
UHV-IR/PES System "Theo"


NEXAFS/PES experiments

CeO_{2-x}(111)

N K-edge NEXAFS spectra after dosing 50 Langmuir N_2O on a reduced CeO_2(111) surface (left) at 120 K are depicted. 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 for both photon energies is given in a time dependent plot (right). The measuring time between both signals in one spectrum was estimated to 1.5 min, between stacked spectra it was set to 3 min. Kinetic predictions should be valid under the consideration that both signals have equal peak areas on a simultaneous time recording scale.
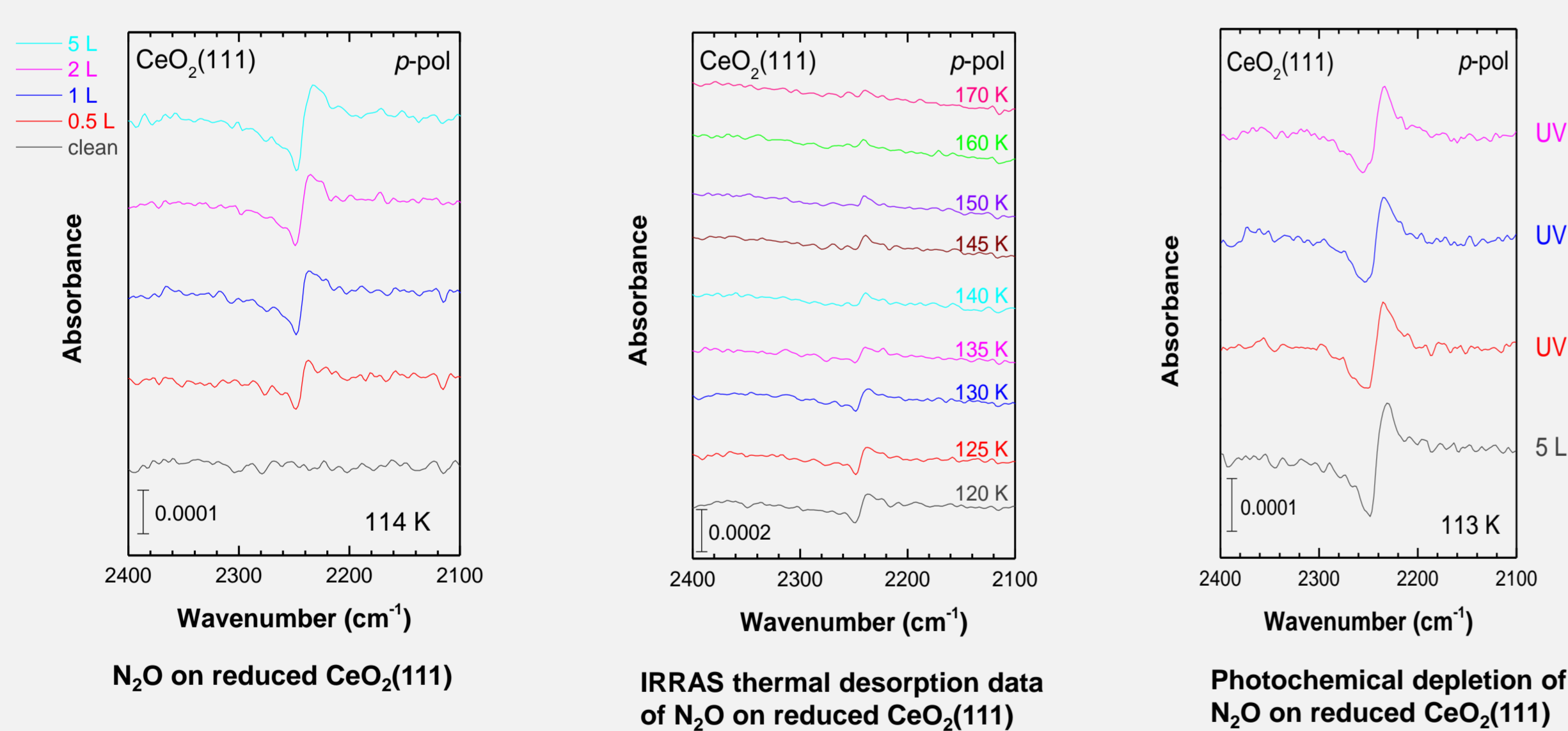**Inset:** Valence band spectra on partial reduced ceria and photorelated ceria reoxidation by N_2O.
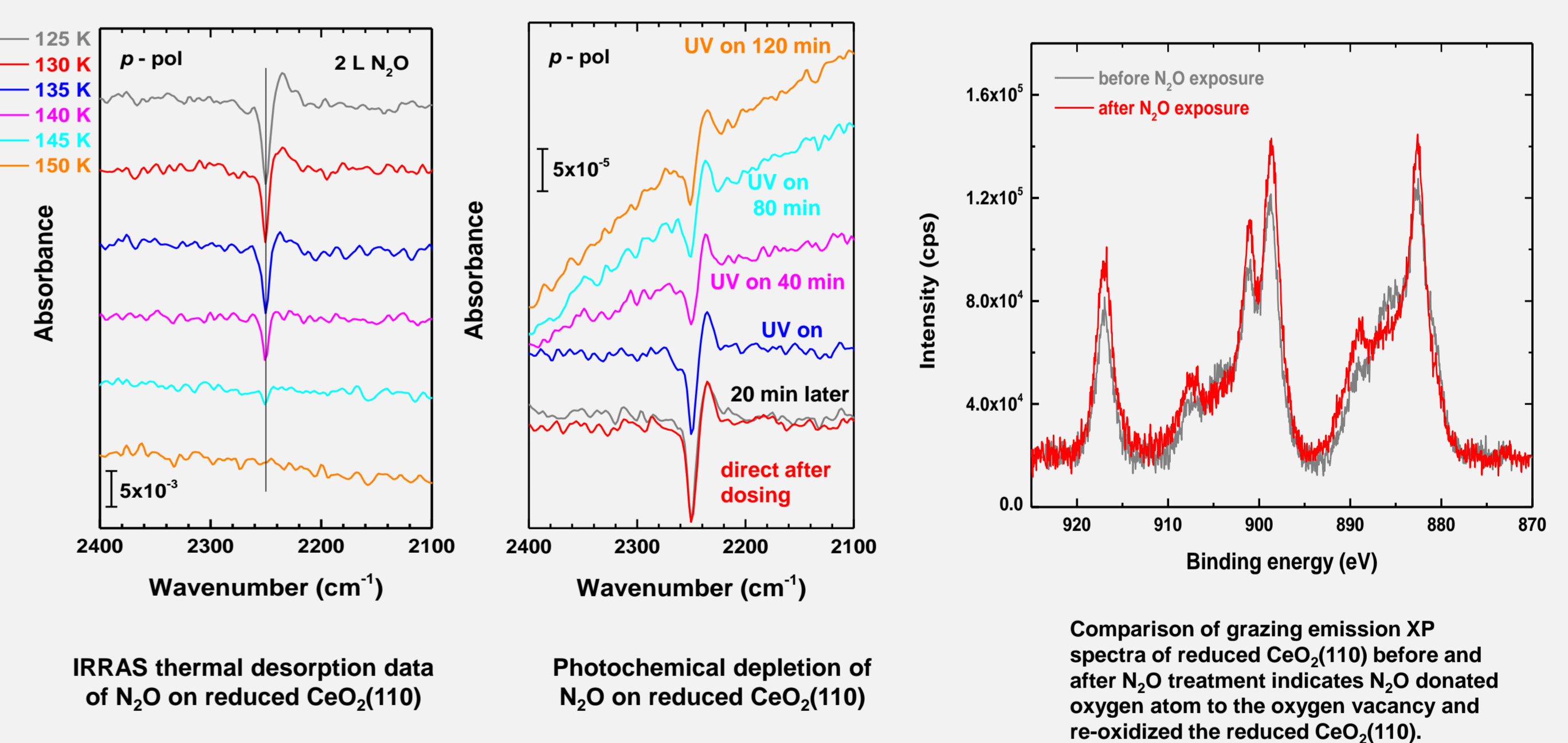
CeO_{2-x} powder
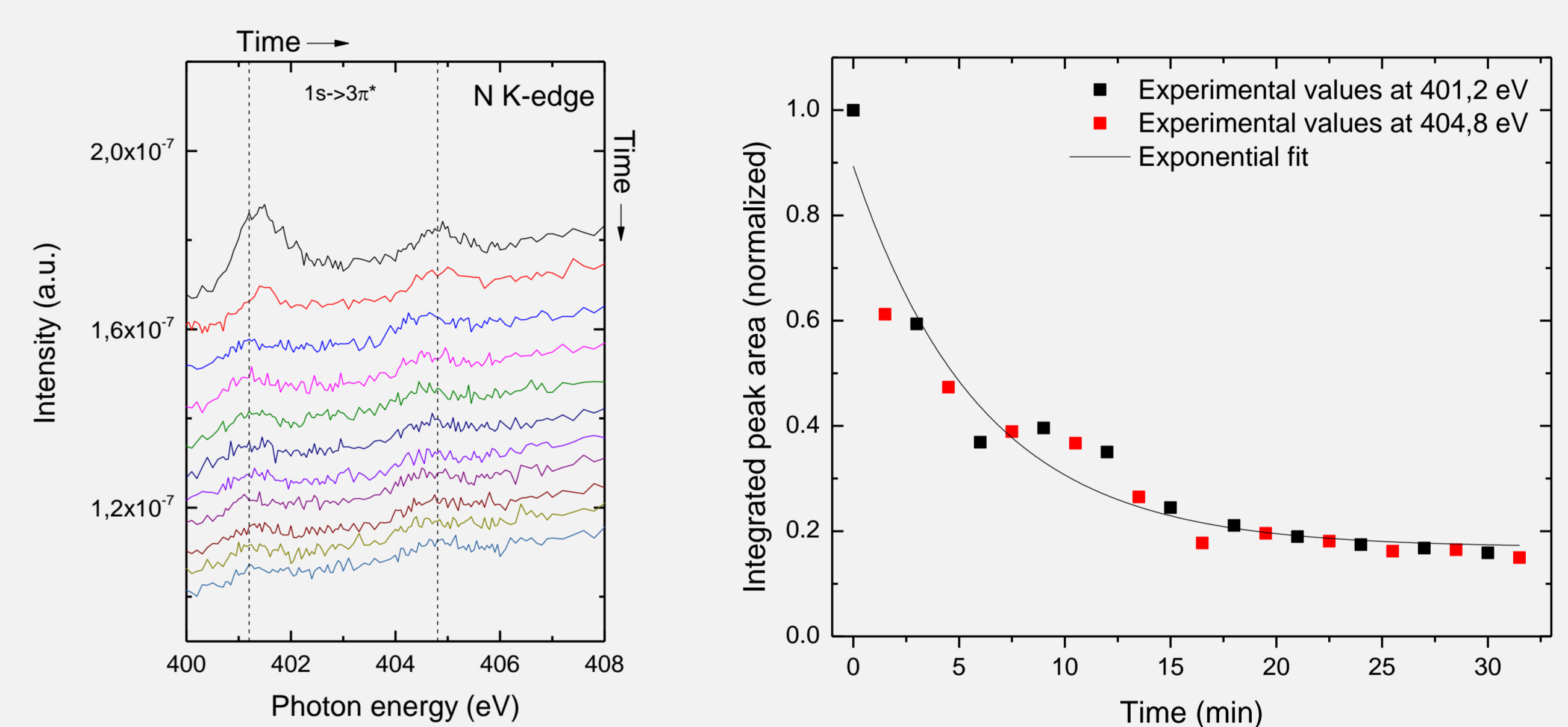
NEXAFS spectra were recorded in the N K-edge region after interaction with 50 L N_2O on reduced ceria powder at an ambient temperature of 120 K. The corresponding kinetic profile is illustrating the signal decay over time (right). Exponential fitting reveals a first order kinetic for N_2O splitting on reduced ceria.

IRRAS Experiments
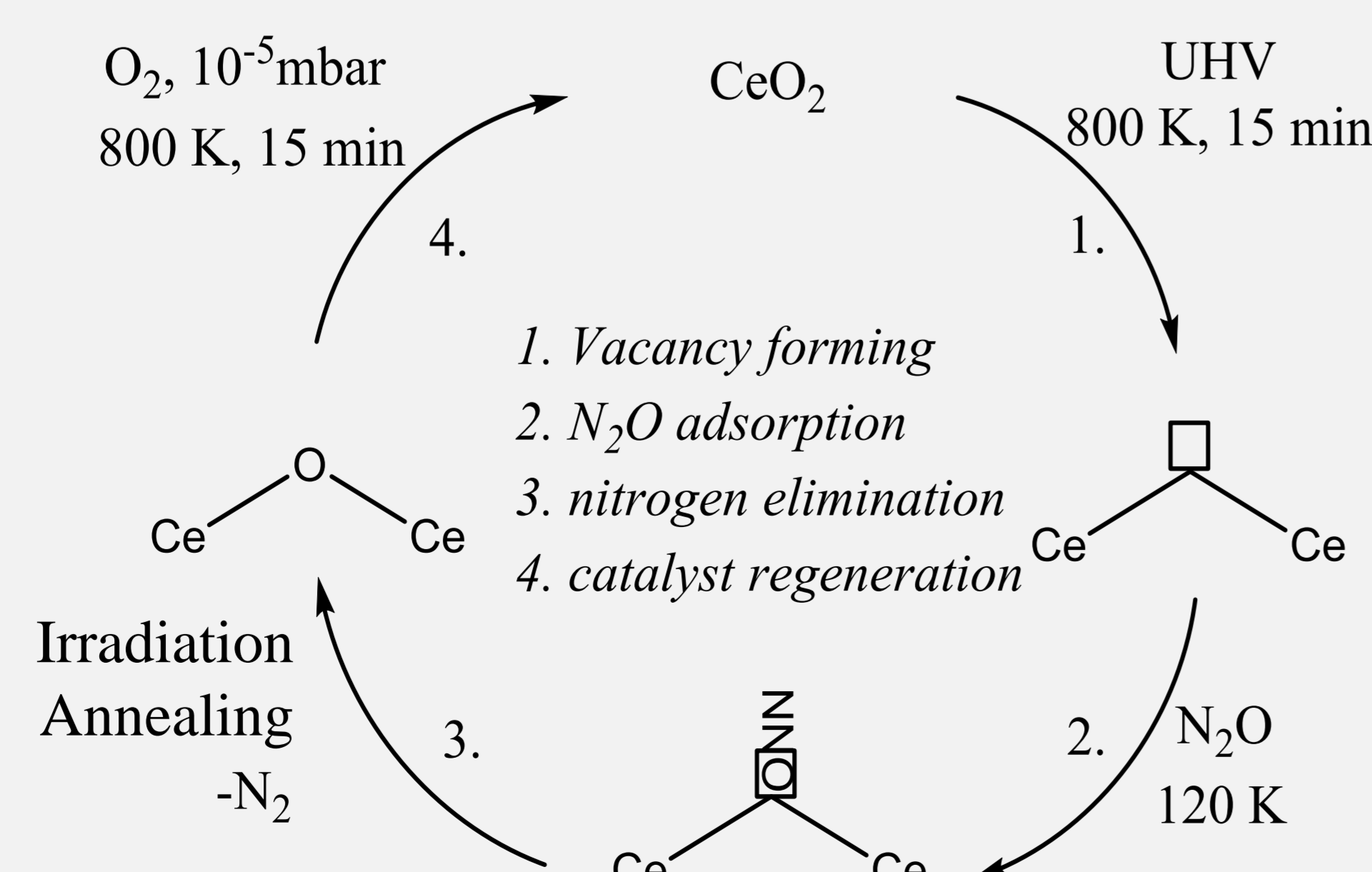
N_2O on reduced CeO_{2-x}(111)

N_2O on reduced CeO_2(111)

IRRAS thermal desorption data of N_2O on reduced CeO_2(111)

Photochemical depletion of N_2O on reduced CeO_2(111)

N_2O on reduced CeO_{2-x}(110)

IRRAS thermal desorption data of N_2O on reduced CeO_x(110)

Photochemical depletion of N_2O on reduced CeO_x(110)

Comparison of grazing emission XP spectra of reduced CeO_2(110) before and after N_2O treatment indicates N_2O donated oxygen atom to the oxygen vacancy and re-oxidized the reduced CeO_x(110).

Proposed mechanism

Schematic view on N_2O conversion for ceria and preparation conditions.

O_2, 10^{-5}mbar
800 K, 15 min

CeO_2

UHV
800 K, 15 min

4.

1.

1. *Vacancy forming*
2. *N_2O adsorption*
3. *nitrogen elimination*
4. *catalyst regeneration*

Irradiation
Annealing
-N_2

3.

2. N_2O
120 K

Conclusions

In this work we presented the *in-situ* reaction monitoring of laughing gas (N_2O) to N_2 on reduced ceria substrates by NEXAFS and IRRAS experiments. After deposition of 50 L N_2O at 120 K, two apparent signals were observed for photon energies of 401,2 eV and 404,8 eV in NEXAFS spectra inside the N K-edge region on CeO_{2-x}(111) and CeO_{2-x} powder, respectively. For the single crystal surface the oxidation process could be directly followed by the shrink of the Ce4f shell signal in valence band photoemission spectra, which is a clear indication for replenishing the voids on reduced surfaces with atomar oxygen. Hence the chemical conversion from N_2O to molecular nitrogen can be assumed. The nitrogen signal decay in NEXAFS occurs much more rapid than for single crystals, so the conversion seems to be more effective on powders for multilayer dosages due to much higher surface area.
IRRAS data confirm NEXAFS results. After N_2O adsorption on reduced CeO_2 surface, only one band at 2250 cm^{-1} is observed, which can be described as a nitrogen-nitrogen asymmetric stretching vibration. After the temperature increase as well as after the UV irradiation the band intensity goes down. Comparison of grazing emission XP spectra of reduced CeO_x(110) before and after N_2O treatment indicates N_2O donated oxygen atom to the oxygen vacancy and re-oxidized the reduced CeO_x(110).

References

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