N_2O to N_2 conversion on reduced ceria surface: NEXAFS and IRRAS studies

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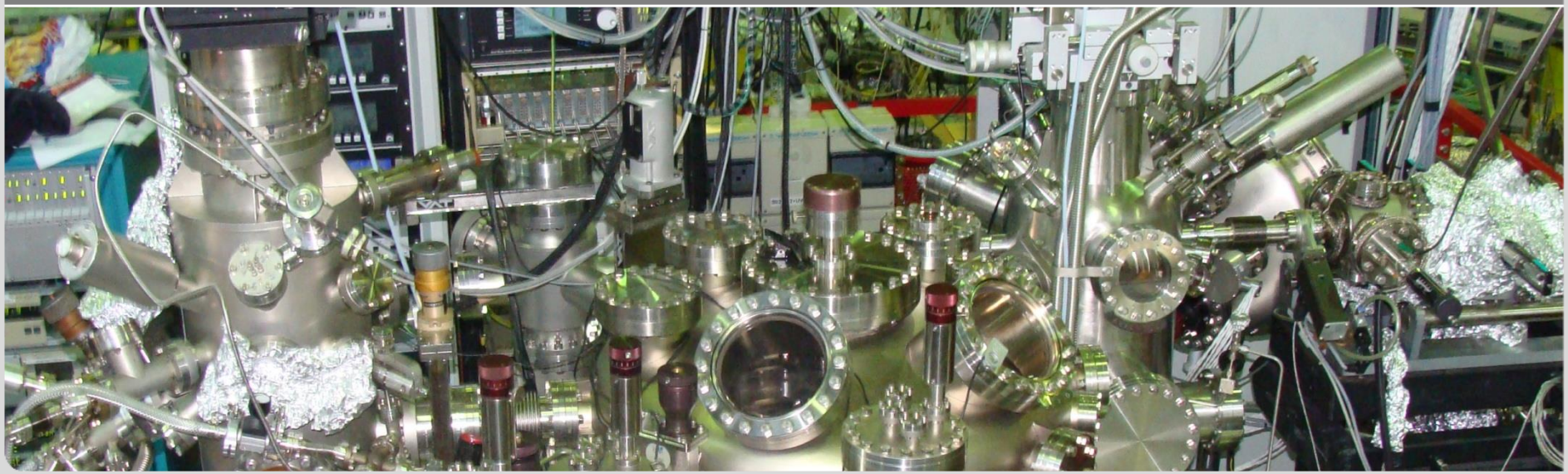
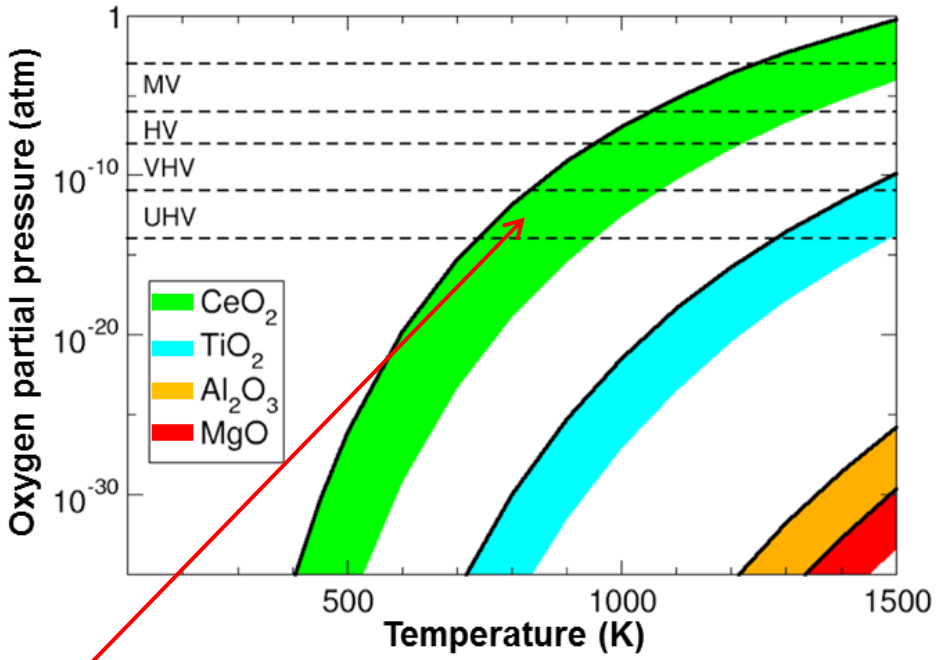


Motivation

- Nitrous Oxide (N_2O) has a global warming potential of 298, indicating emission of one gram of N_2O is equivalent to 298 grams of CO_2.
- Annually, about 1.2 mio. tonnes of N_2O are emitted by the nitric acid industry, which is equivalent to the CO_2 emissions of 80 mio. passenger cars
- In 2013, nitrous oxide (N_2O) accounted for about 5% of all U.S. greenhouse gas emissions from human activities.
- The reduction of NO_x to N_2 ($DeNO_x$ process) is of great significance due to their environment and health impact.

Reducible oxides as model catalyst

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.

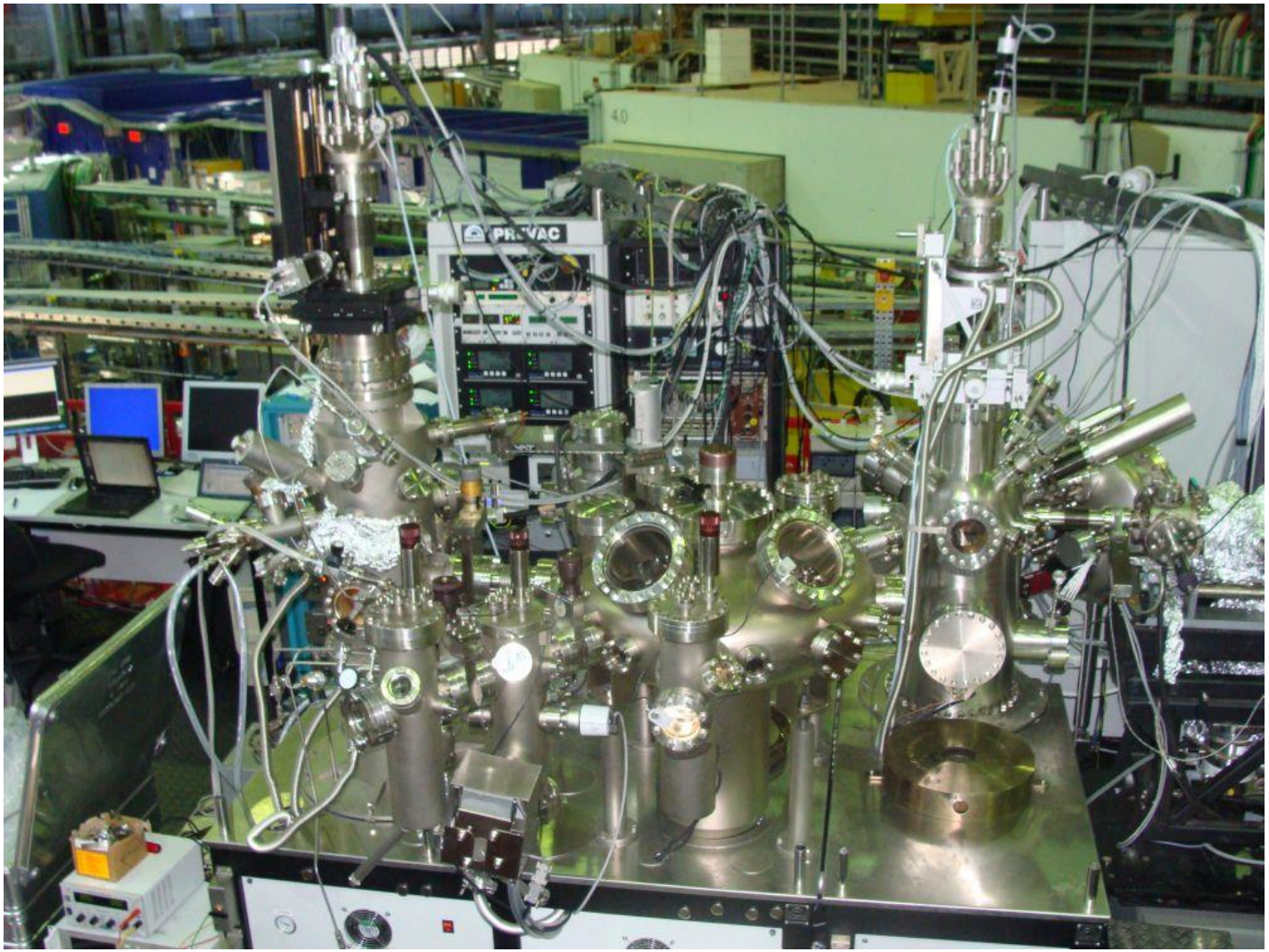


The best choice: CeO_2

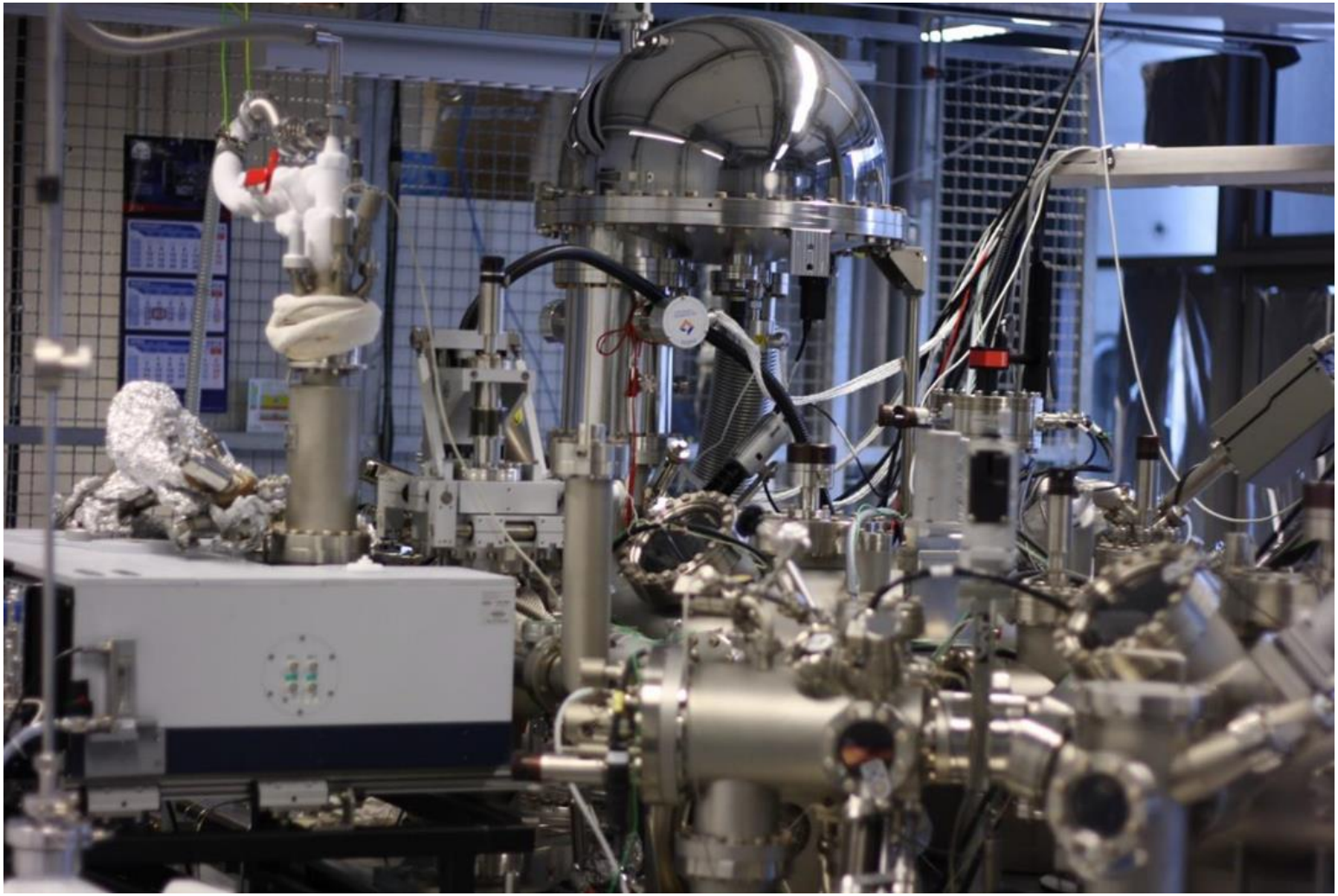
J. Paier, C. Penschke, J. Sauer, *Chem. Rev.*, 2013, 113, 3949.

In this study, we monitor the conversion of N_2O to N_2 over the model catalyst oxide support, namely CeO_2 by near edge x-ray absorption fine structure spectroscopy (NEXAFS) and ultra-high-vacuum infra-red reflection absorption spectroscopy (UHV-IRRAS).

XPS/NEXAFS endstation @ HESGM (BESSY II)



UHV-FTIR Apparatus



Sample preparation

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.

No N_2O adsorption @ oxidized ceria at least above 100K!

Layout of the experiment

Experiments @ BESSY II

- Exposure to 50 Langmuir N_2O was achieved by backfilling the analysis chamber up to 2.6×10^{-7} mbar for 250 seconds.
- NEXAFS measurements @ 120K

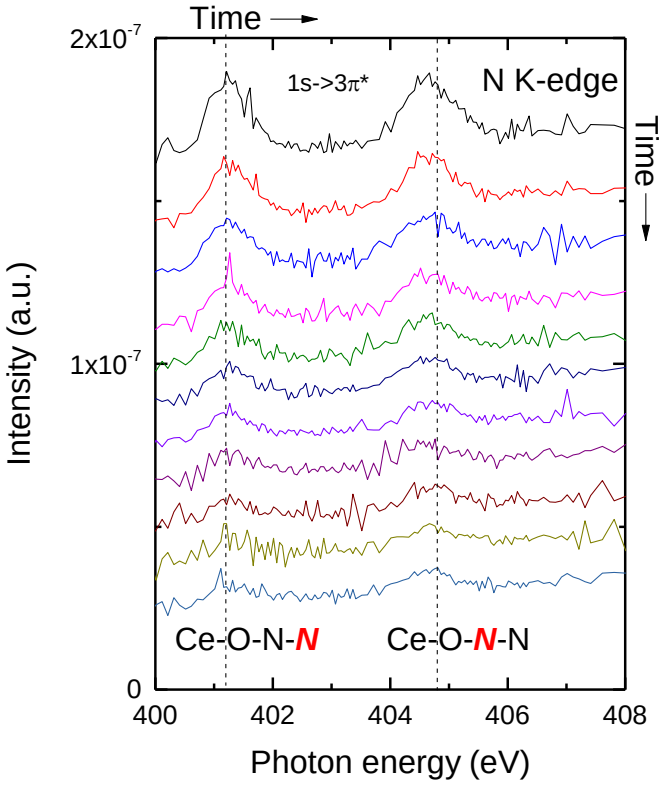
Strong charging @ LT – XPS measurements aren‘t possible!

XPS experiments were carried out at elevated temperatures.

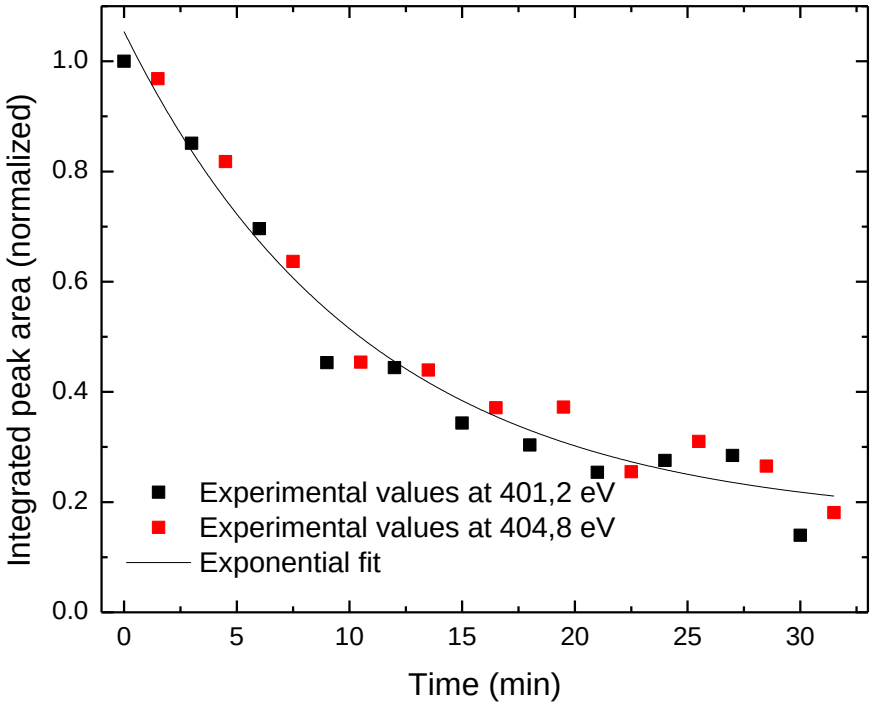
IRRAS measurements:

- 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.
- Temperature range: 115-170K.
- For UV-irradiation the lamp N-8 L (Herolab) with power of 8 W @ λ=365 nm was used. The irradiation takes place directly in IR chamber through quartz-window.

N K-edge NEXAFS experiments: CeO_{2-x}(111) single crystal

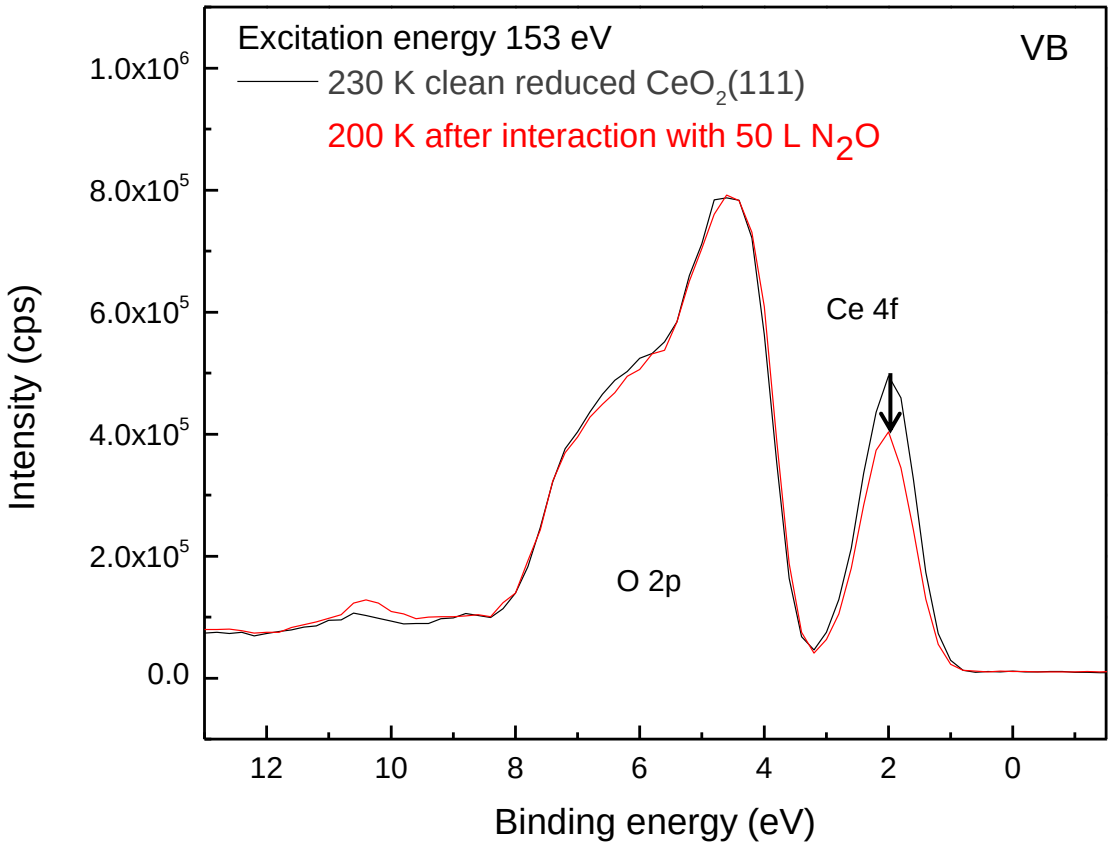


The measuring time between both signals in one spectrum was estimated to 1.5 min, between stacked spectra it was set to 3 min..



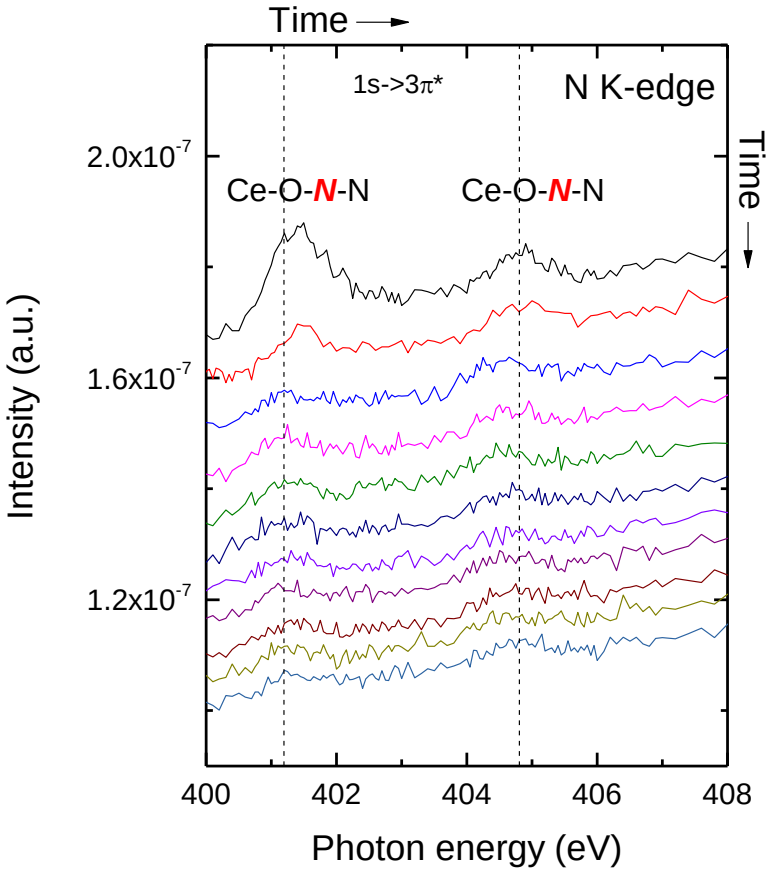
The signal decay for both photon energies is given in a time dependent plot

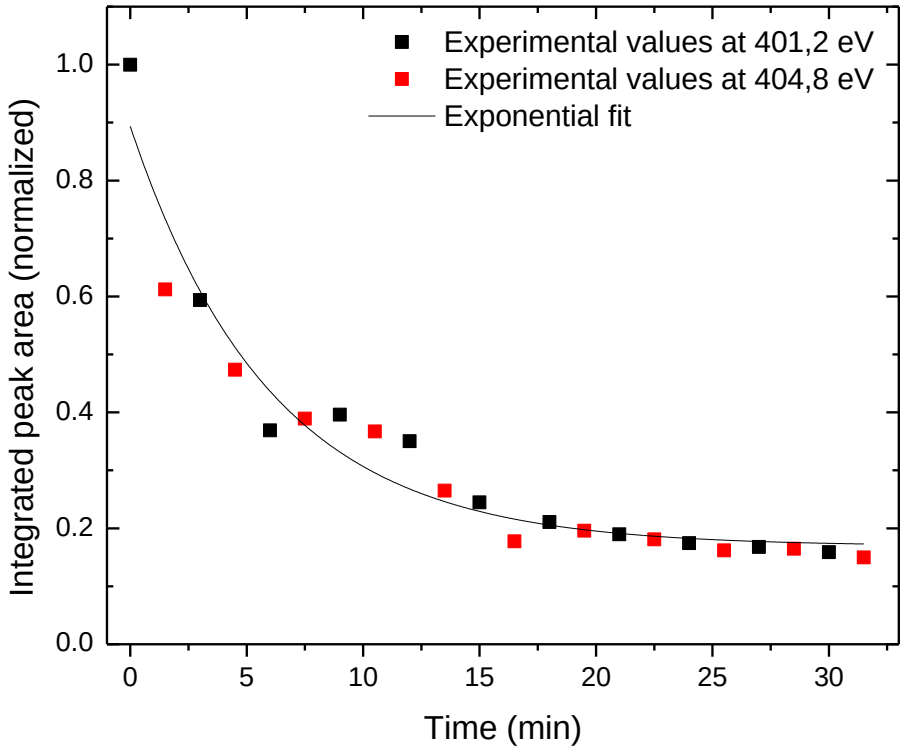
PES experiments: CeO_{2-x}(111) single crystal



Valence band spectra on partial reduced ceria and photorelated ceria reoxidation by N_2O. The Ce4f shell signal in VB PE spectra is decreased, which is a clear indication for replenishing the voids on reduced surfaces with atomar oxygen.

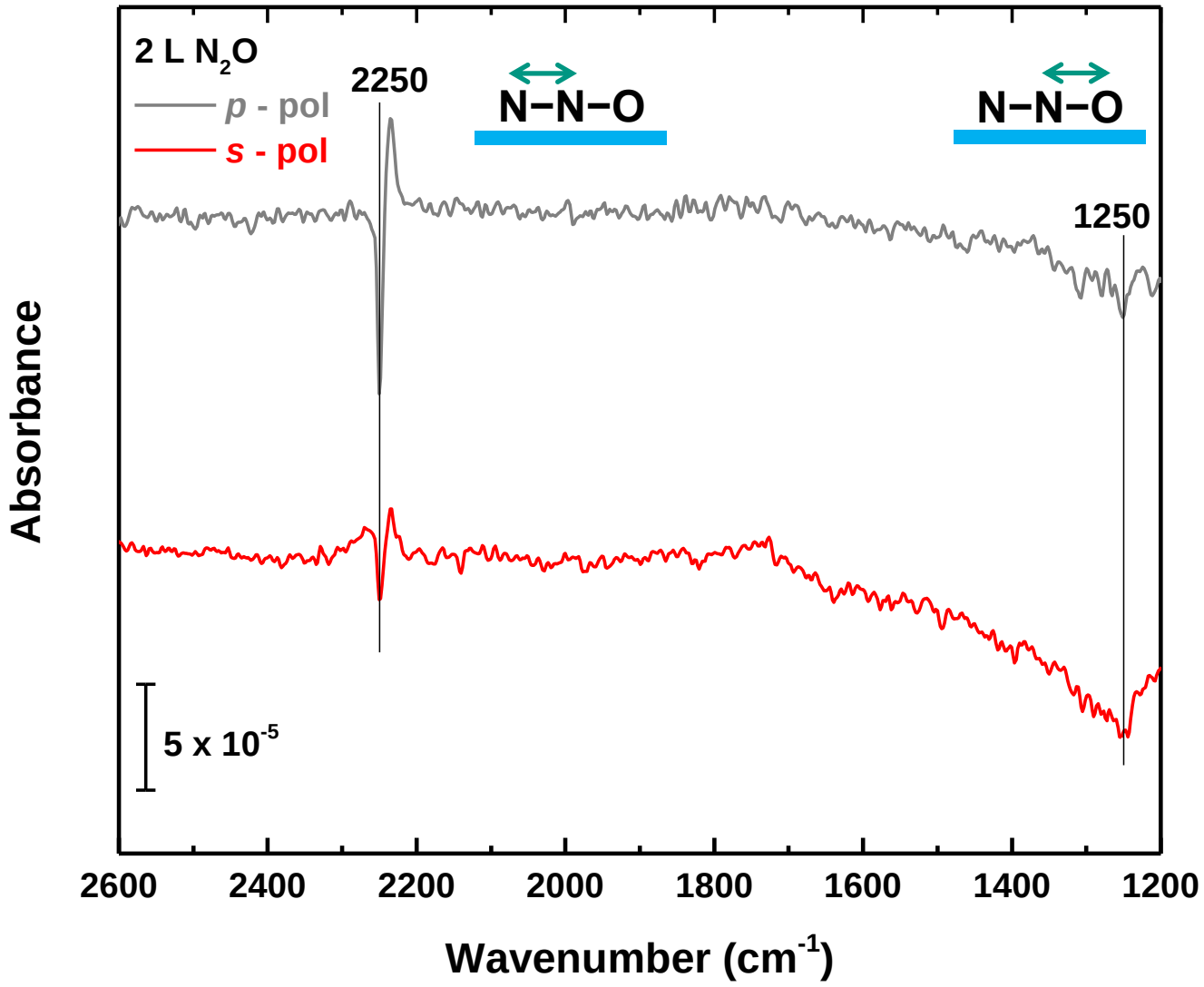
N K-edge NEXAFS experiments: CeO_{2-x} powder



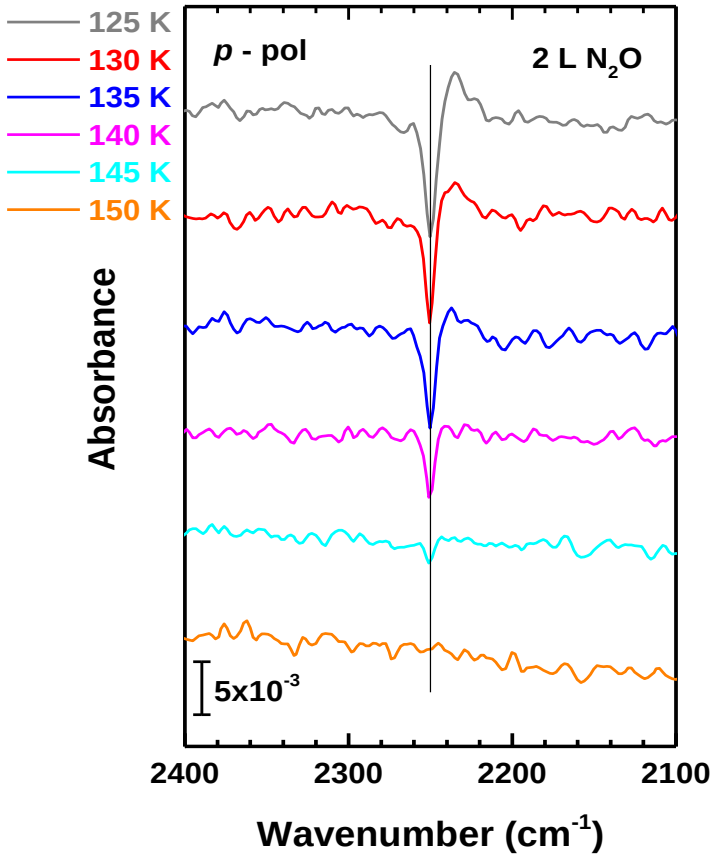


The kinetic profile is illustrating the signal decay over time (right). Expontential fitting reveals a first order kinetic for N_2O splitting on reduced ceria.

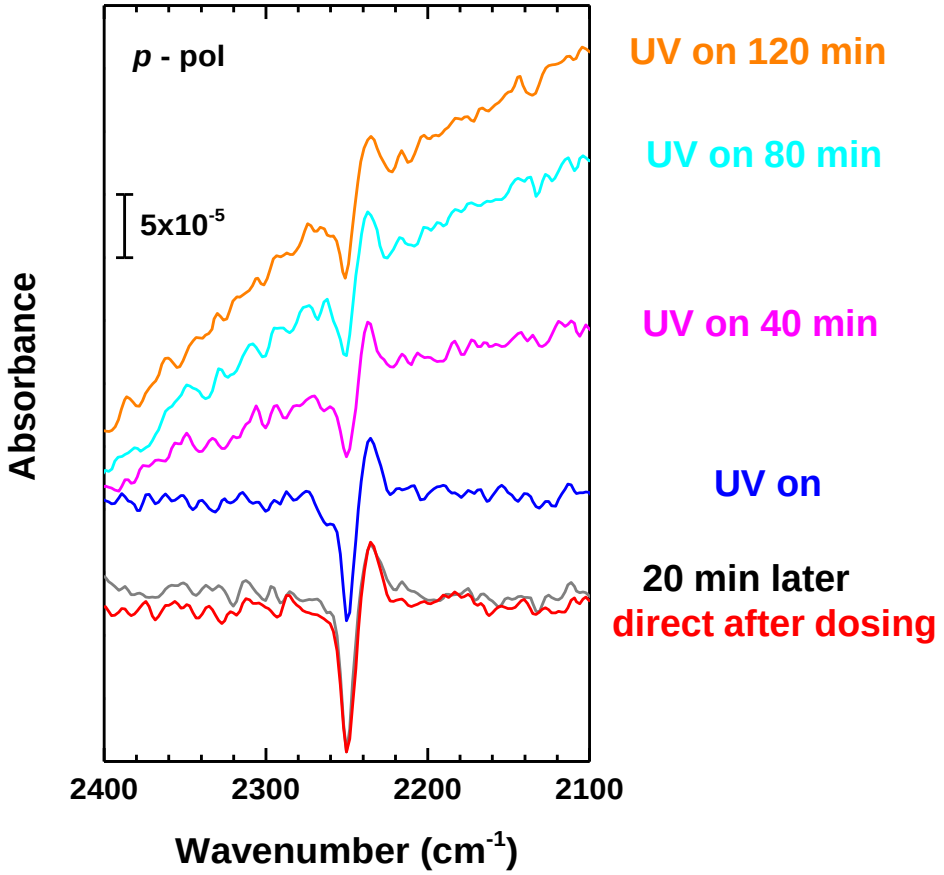
IRRAS Experiments:CeO_{2-x}(110) single crystal



IRRAS Experiments: CeO_{2-x}(110) single crystal

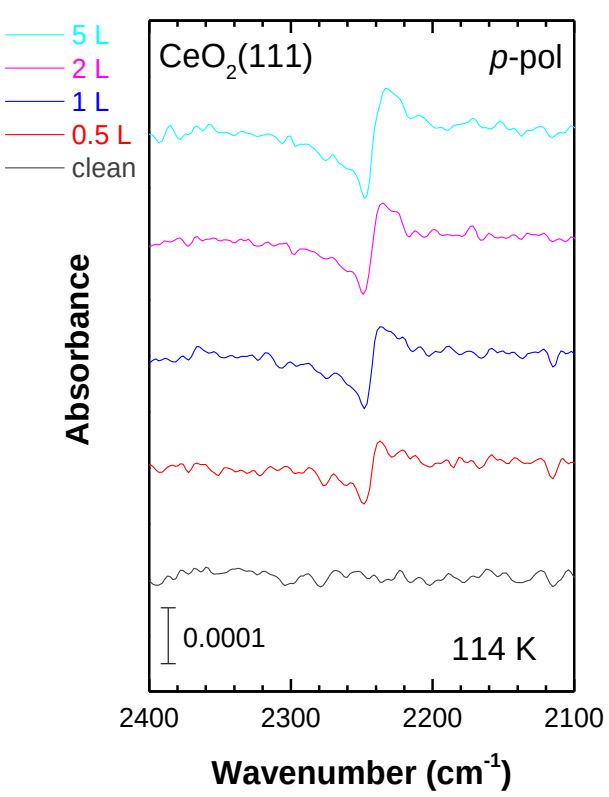


IRRAS thermal desorption data of N_2O on reduced CeO_2(110)

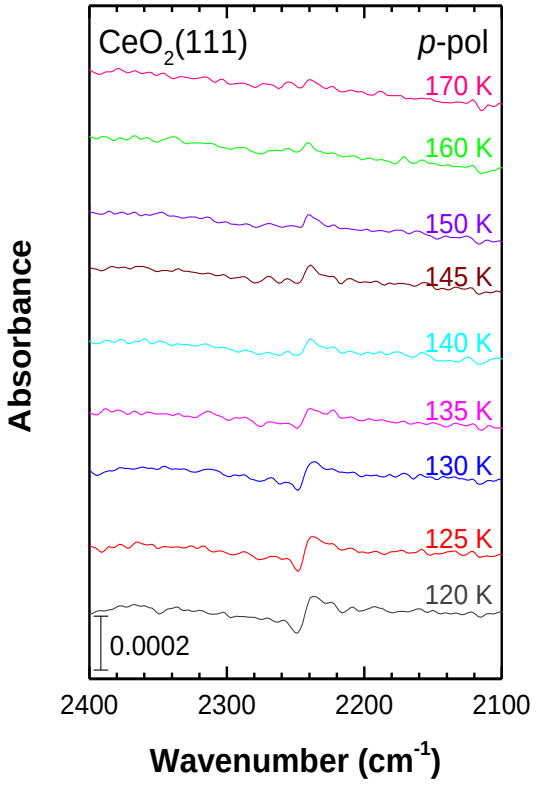


Photochemical depletion of N_2O on reduced CeO_2(110)

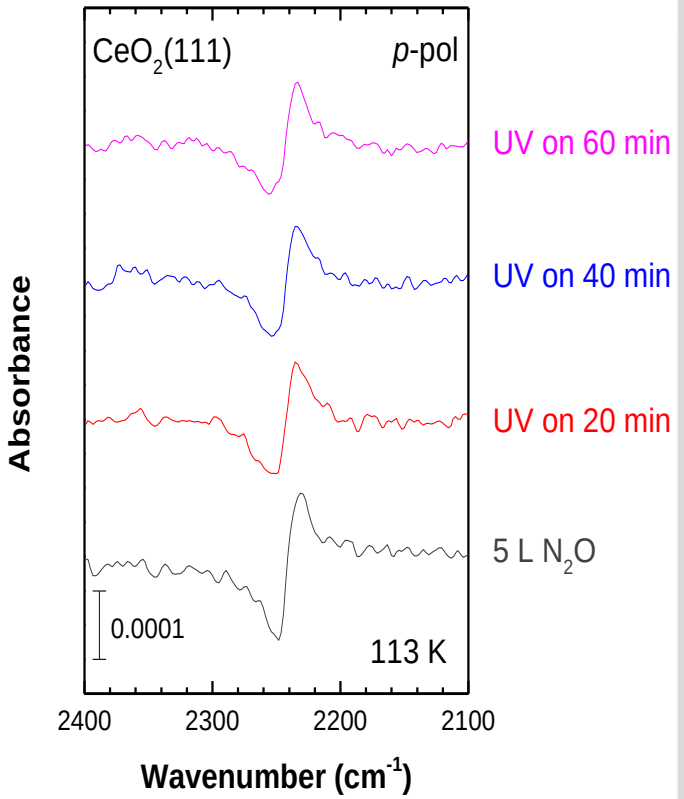
IRRAS Experiments: CeO_{2-x}(111) single crystal



N_2O on reduced CeO_2(111)

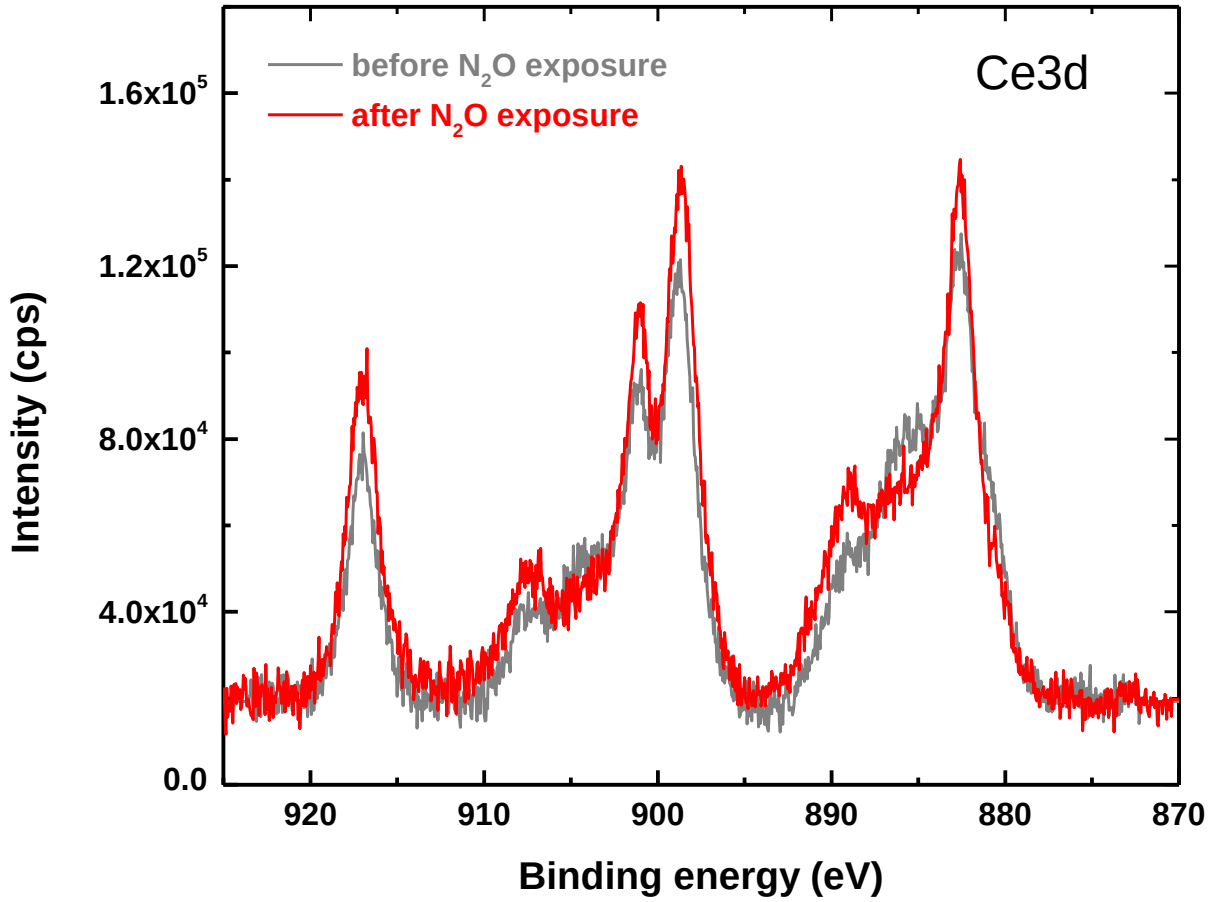


IRRAS thermal desorption data of N_2O on reduced CeO_2(111)



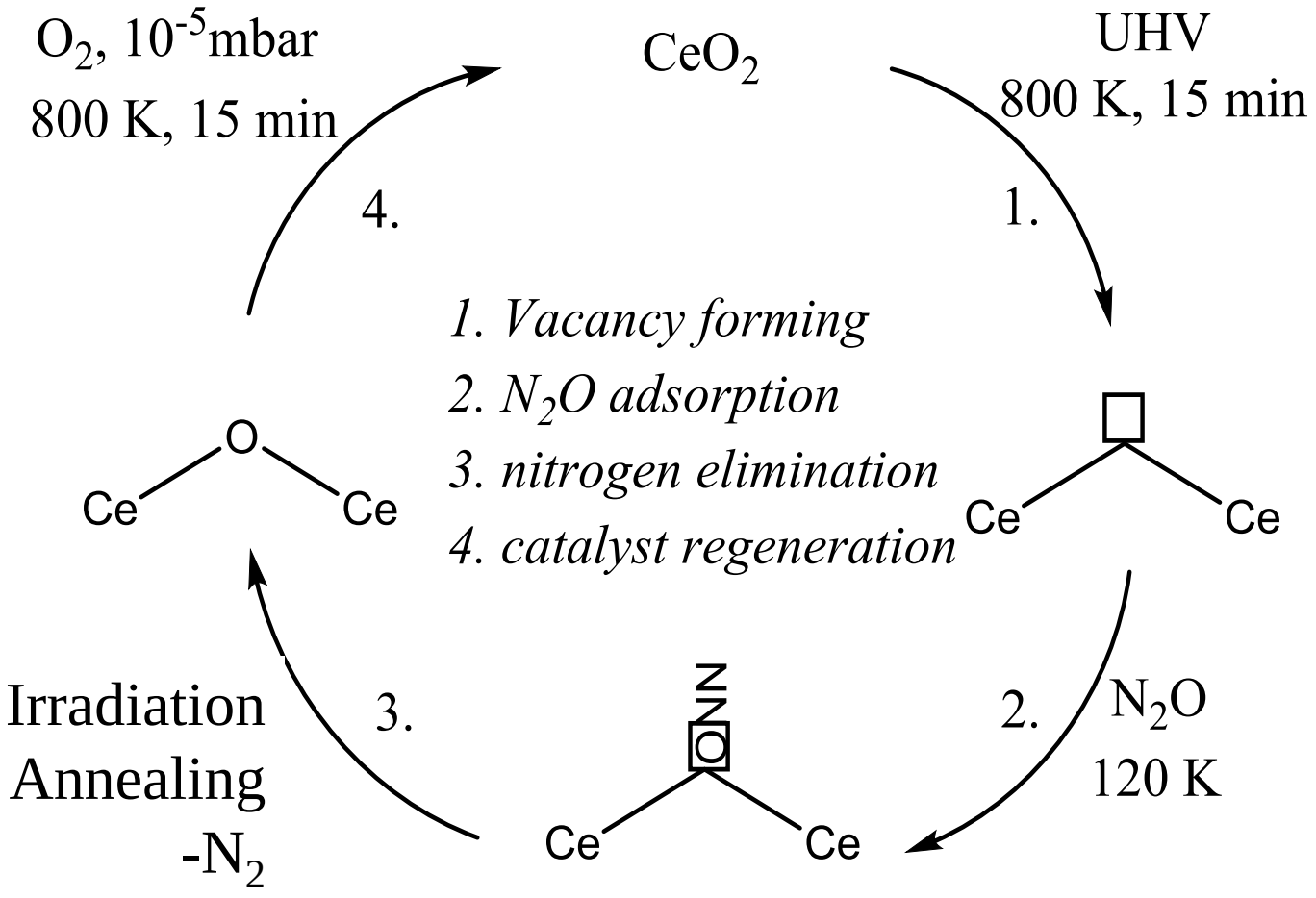
Photochemical depletion of N_2O on reduced CeO_2(111)

XPS experiments



Comparison of grazing emission (take-off angle 70°) 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_2(110).

Schematic view on ceria preparation conditions and N_2O conversion



Summary

- In this work we presented the *in-situ* reaction monitoring of N_2O to N_2 on reduced ceria substrates by NEXAFS and IRRAS experiments.
- After deposition of N_2O, two resonanses 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.
- 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, the 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_2(110) before and after N_2O treatment indicates N_2O donated oxygen atom to the oxygen vacancy and re-oxidized the reduced CeO_2(110).

Thank you for attention!

Ceria: comparison