

# New insights into the gas-phase oxidation of isoprene by the nitrate radical from experiments in the atmospheric simulation chamber SAPHIR

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Philip Carlsson<sup>1</sup>, Patrick Dewald<sup>2</sup>, Justin Shenolikar<sup>2</sup>, Nils Friedrich<sup>2</sup>, John Crowley<sup>2</sup>, Steven Brown<sup>3</sup>, François Bernard<sup>4</sup>, Li Zhou<sup>4</sup>, Juliane Fry<sup>5</sup>, Bellamy Brownwood<sup>5</sup>, Mattias Hallquist<sup>6</sup>, Epameinondas Tsiligiannis<sup>6</sup>, Xu Kangmin<sup>7</sup>, Rupert Holzinger<sup>7</sup>, Changmin Cho<sup>1</sup>, Luisa Hantschke<sup>1</sup>, Sungah Kang<sup>1</sup>, David Reimer<sup>1</sup>, Ralf Tillmann<sup>1</sup>, Sergej Wedel<sup>1</sup>, Rongrong Wu<sup>1</sup>, Hendrik Fuchs<sup>1</sup>, Luc Vereecken<sup>1</sup>, Anna Novelli<sup>1</sup>, Birger Bohn<sup>1</sup>, Franz Rohrer<sup>1</sup>, Thomas Mentel<sup>1</sup>

1:IEK 8, Forschungszentrum Jülich GmbH, Jülich, Germany

2:Max-Planck Institute for Chemistry, Mainz, Germany

3:NOAA Earth System Research Laboratory, Boulder, CO, United States

4:CNRS, Orleans, France

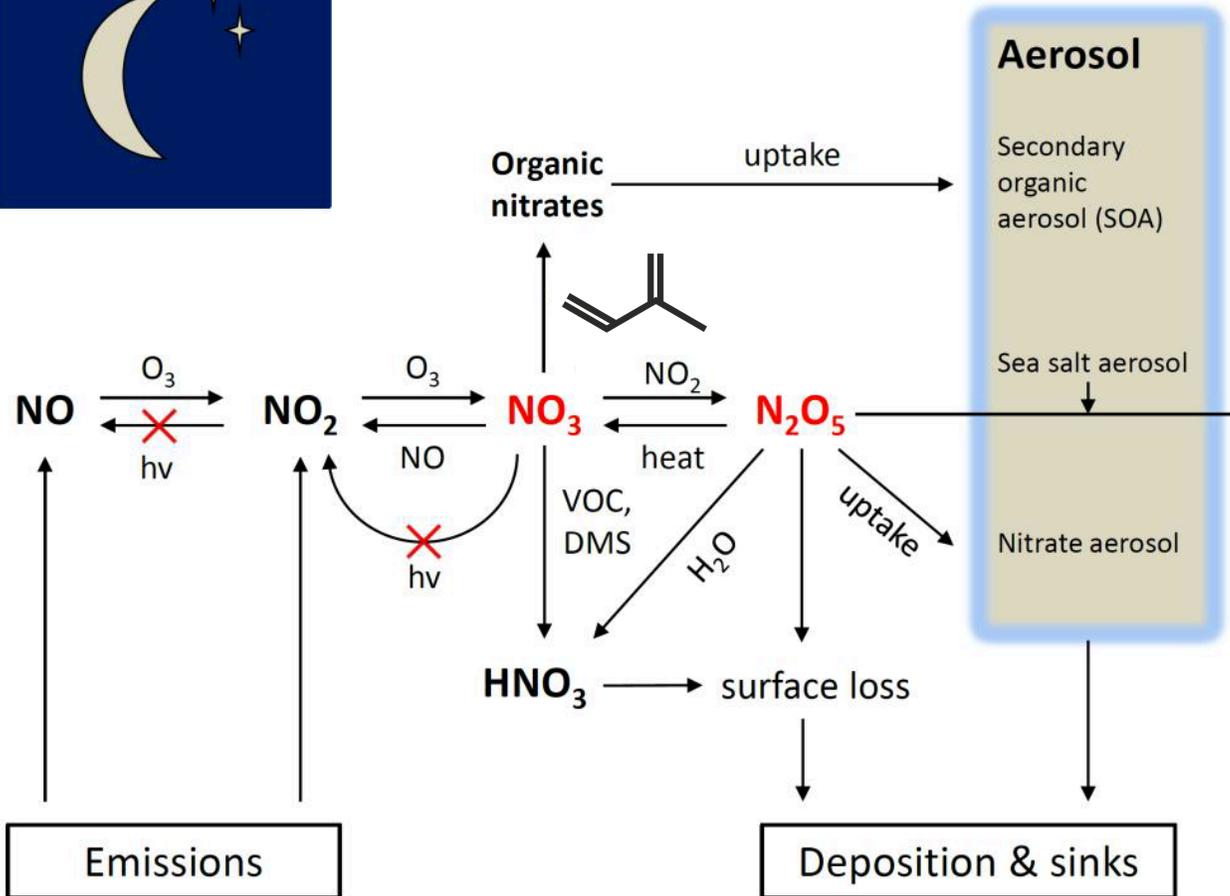
5:Reed College, Chemistry and Environmental Studies, Portland, United States

6:University of Gothenburg, Department of Chemistry, Atmospheric Sciences, Gothenburg, Sweden

7:Institute for Marine and Atmospheric Research Utrecht, Utrecht, Netherlands

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# MOTIVATION



- Isoprene is a highly abundant BVOC with about 500 Tg/a
- NO<sub>3</sub> is responsible for most night-time oxidation where anthropogenic influences are present
- Yields low volatility nitrates, interesting for (new) particle and aerosol formation
- Sink for NO<sub>2</sub>, changes O<sub>3</sub> production

S. Ball, ECG Environmental Brief No. 3

# INSTRUMENTATION

Nitrogen inorganic:

- NO / NO<sub>2</sub> / NO<sub>3</sub> / N<sub>2</sub>O<sub>5</sub> / NO<sub>3</sub> reactivity (CLD, CRDS)
- HNO<sub>3</sub> (CIMS CO<sub>3</sub><sup>-</sup>, TD-NO<sub>2</sub>-CRDS)
- HONO (LOPAP)

Nitrogen organic:

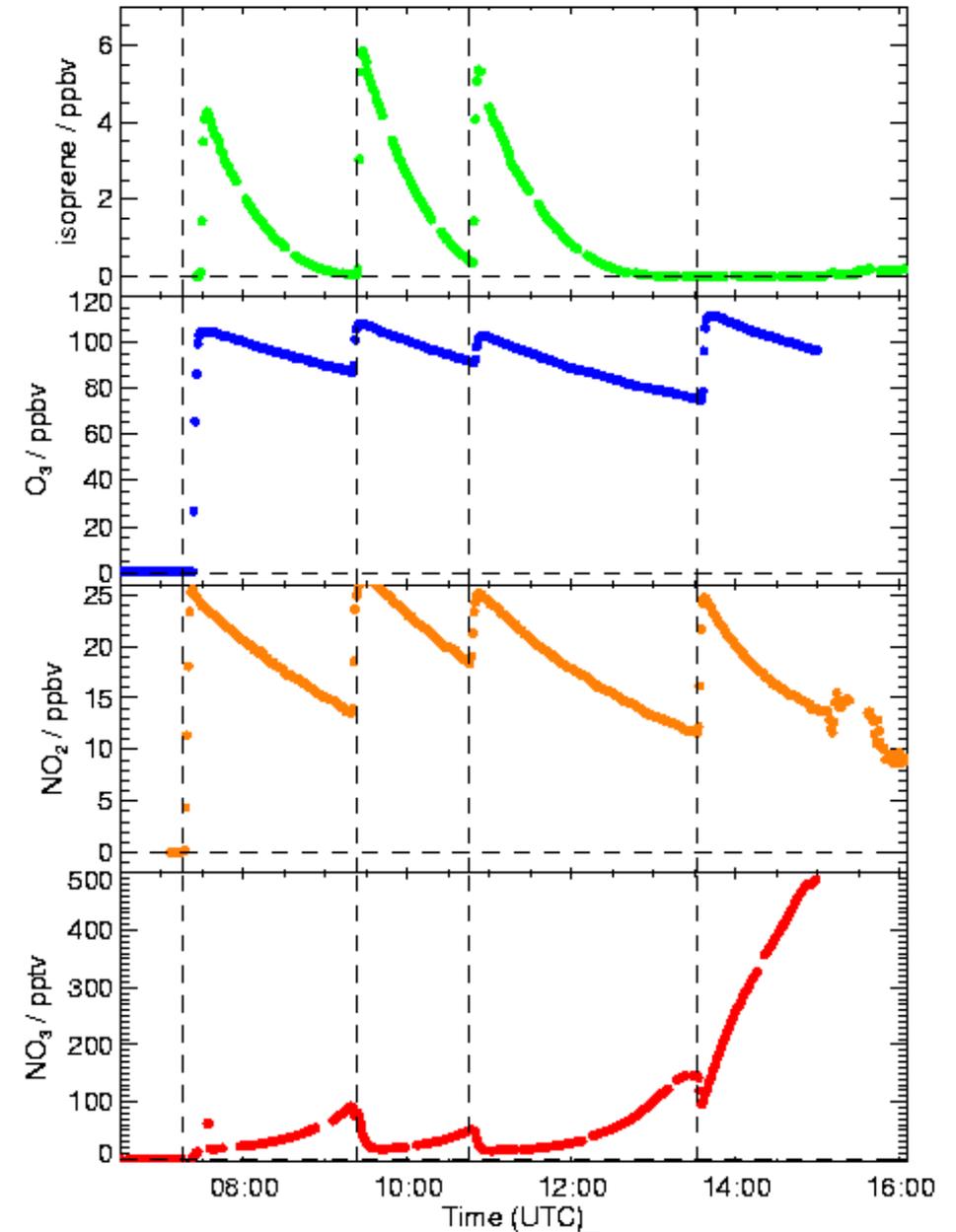
- Thermal decomposition of organic nitrogen family species (TD-NO<sub>2</sub>-CRDS)
- Speciated nitrogen organic compounds (several CIMS, several PTR)

ROx:

- OH, RO<sub>2</sub>, OH reactivity (LIF)
- HO<sub>2</sub> (LIF, CIMS)

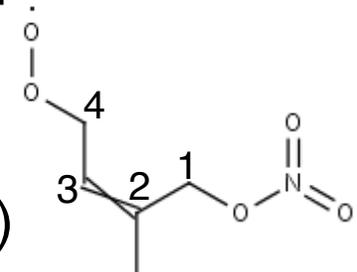
# TYPICAL EXPERIMENT RUN

- During the month long campaign, experiments on:
  - high RO<sub>2</sub> concentrations for RO<sub>2</sub> + RO<sub>2</sub> reactions
  - isomerisation of RO<sub>2</sub>
  - photooxidation of the products
  - forcing HO<sub>2</sub> + RO<sub>2</sub> by increased [HO<sub>2</sub>]
  - Influence of aerosol load with seeds
  - photooxidation of isoprene, followed by NO<sub>3</sub> addition
- Four injections of O<sub>3</sub> and NO<sub>2</sub> at the same time, respectively
- Injection of isoprene at the first three O<sub>3</sub>/NO<sub>2</sub> injections
- The last O<sub>3</sub>/NO<sub>2</sub> injection is to allow for further oxidation of reaction products with NO<sub>3</sub> in this specific experiment



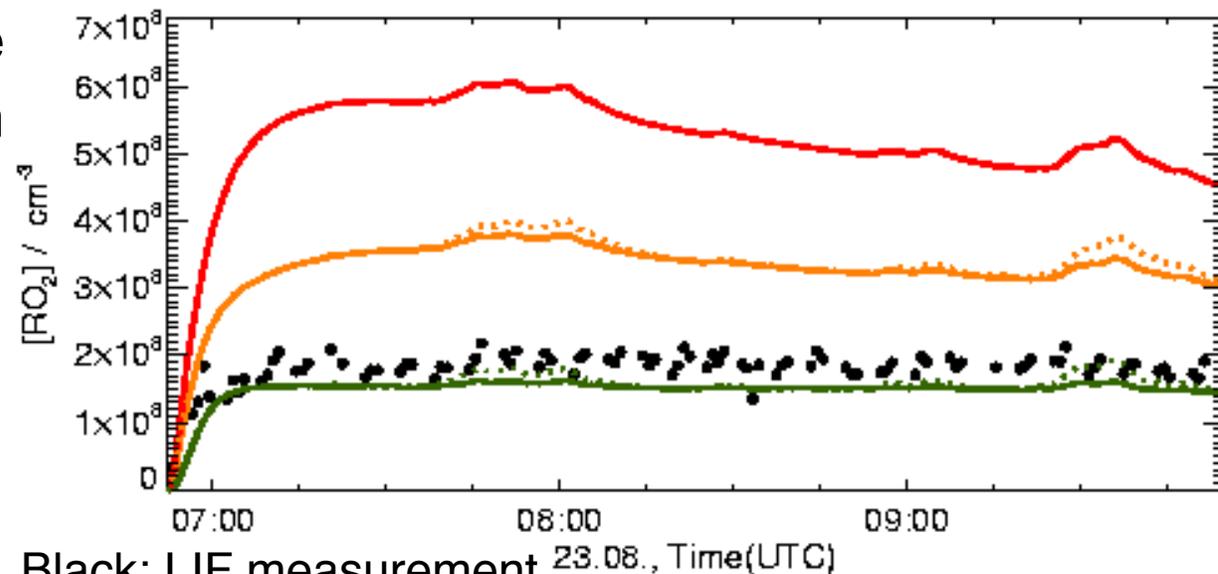
# KINETIC MODELLING

- We compare three models:
  - master chemical mechanism (MCM, current version: 3.3.1)
  - CalTech mechanism (Wennberg et. al, *Chem. Rev.* **2018**, 118, 3337–3390), with fill ins from the MCM where no description is given
  - a modified mechanism, based on the OH and O<sub>3</sub> chemistry from MCM, the NO<sub>3</sub> chemistry from CalTech with further adaptations to better fit to the experiments.
- Regarding the NO<sub>3</sub> chemistry, there is a fundamental difference in the approach to the RO<sub>2</sub> description:
  - MCM only has one RO<sub>2</sub> species ISOP1N4OO (see image)
  - CalTech includes three additional RO<sub>2</sub> (1N2OO, 1OO4N and 3OO4N)
  - The new modification in this work introduces O<sub>2</sub> equilibration similar to the OH RO<sub>2</sub>, with the equilibrium distribution given by the Boltzmann distribution. Also explicit *cis* species (Z1N4OO and Z4N1OO) as well as isomerisation reactions are added.



# MODEL PERFORMANCE - RO<sub>2</sub>

- Already the RO<sub>2</sub>-yields from pure isoprene ozonolysis show a need for modification.
- Drastic improvement by changing the branching ratios according to Zhang et. al, *Chem. Phys. Lett.* **2002**, 358, 171–179. This includes 95% instead of 56% stabilisation of the formed C1-Criegee Intermediate, halved stabilisation of the “MACROO” CI with increased propene formation and no propene formation from the “MVKOO” CI.
- Theory predicts that not all RO<sub>2</sub> are detectable with our setup, since it relies on HO<sub>2</sub> formation from the alkoxy radical: from the main RO<sub>2</sub> isomer (ISOP1N2OO) decomposition to NO<sub>2</sub>+CH<sub>2</sub>O+1-butene-3-one takes place instead. CalTech and Modification include corrections for this; uncorrected values are shown as dotted lines, corrected as solid.



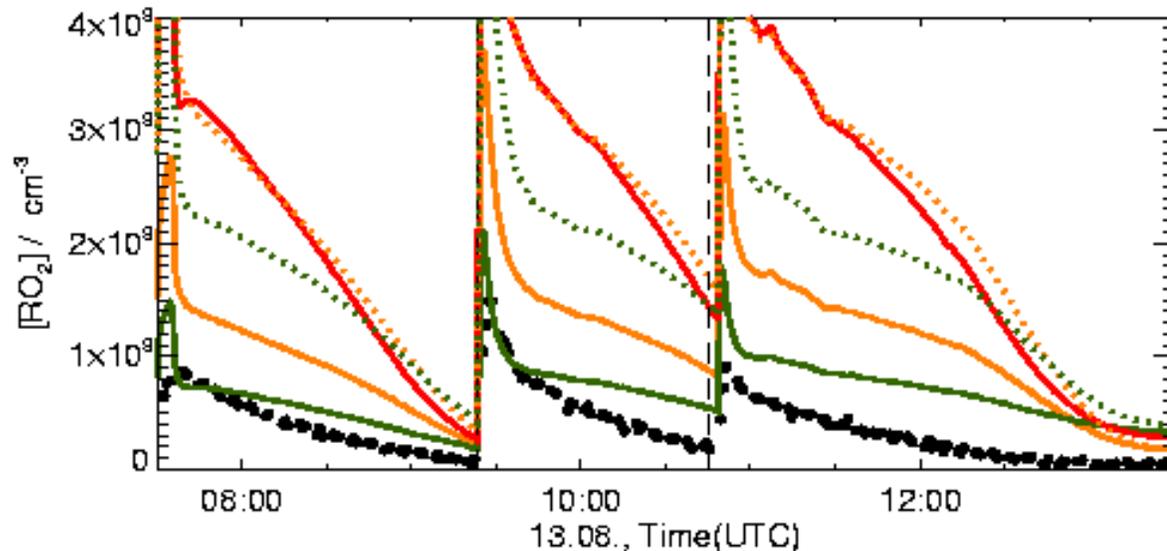
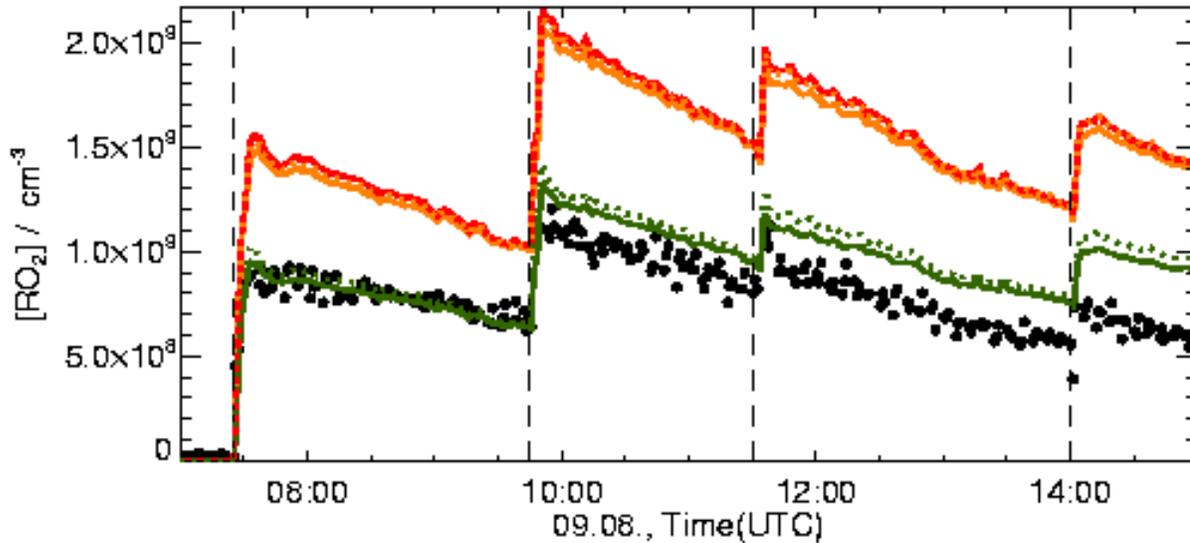
Black: LIF measurement 23.08., Time(UTC)

Red: MCM

Orange: CalTech

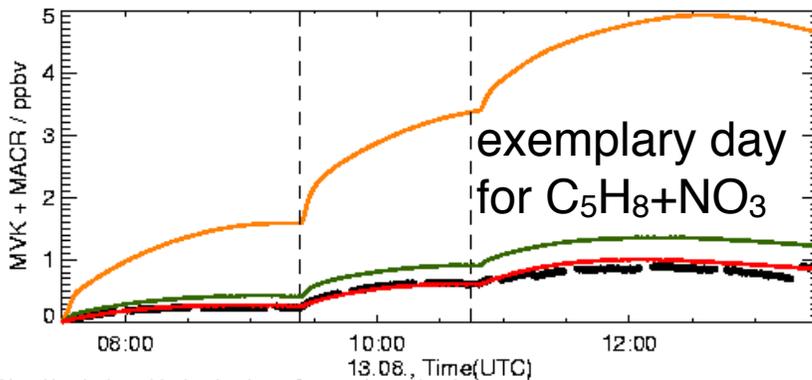
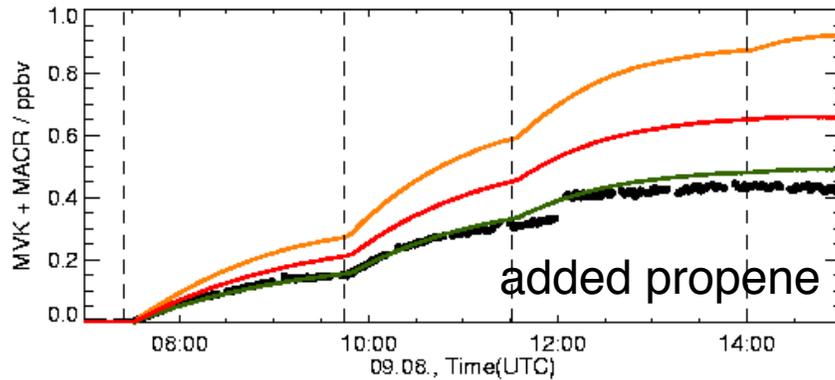
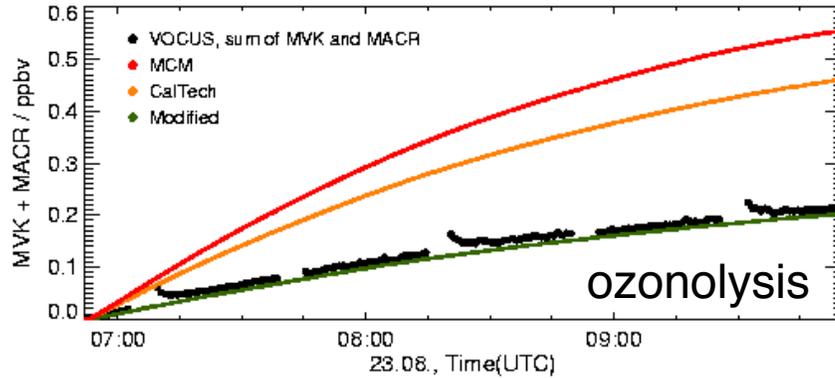
Green: Modification

# MODEL PERFORMANCE - RO<sub>2</sub> (CONTINUED)



- Top shows an experiment with large amounts of propene added (70 and 50 ppb, at 7:30 and 9:45) to provide an additional HO<sub>2</sub> source.
- Here also a discrepancy in the propene ozonolysis was found and largely mitigated by applying branching ratios from Horie and Moortgat, *Atmos. Env.* **1990**, 25A, 1881–1896, increasing CI stabilisation.
- All modifications together are then able to reproduce the isoprene + NO<sub>3</sub> focussed experiments much more satisfactorily, exemplarily shown here for one day.

# MODEL PERFORMANCE - MVK



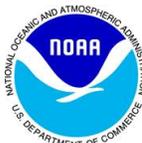
- MVK as a typical product from isoprene degradation is generally well predicted by MCM, but severely overestimated by CalTech
- The changes to the ozonolysis mechanism also change MVK yields, both directly and by reducing OH concentrations
- Further modifications to the CalTech NO<sub>3</sub> chemistry:
  - change the product branching of the RO<sub>2</sub>+RO<sub>2</sub> reactions of the ISOP1N2OO isomer to no longer form MVK
  - change the product branching for ISOP1N2OO+HO<sub>2</sub> to no longer form MVK and correspondingly ISOP3OO4N+HO<sub>2</sub> to no longer form MACR

# SUMMARY

- Ozonolysis of both isoprene and propene are not described well enough in the current MCM to match radical measurements
- The new pathway to MVK *via* ISOP1N2OO + HO<sub>2</sub> in the CalTech mechanism adds to a severe overestimation of MVK from that model
- We actually see no evidence of the ISOP1N2OO RO<sub>2</sub> contributing to prompt formation of MVK
- Oxygen re-equilibration and resulting nascent and equilibrium concentrations of the different RO<sub>2</sub> are crucial for the resulting product distribution in the NO<sub>3</sub> initiated isoprene degradation, as was the case for the OH degradation

I will be available for discussion on Wed., 06.05.  
from 14:00-15:45!

Also: [p.carlsson@fz-juelich.de](mailto:p.carlsson@fz-juelich.de)



Utrecht University



מכון ויצמן למדע  
WEIZMANN INSTITUTE OF SCIENCE

