Vibrational spectroscopy and reactivity of ultra-small silica and silicate fragments in the gas-phase

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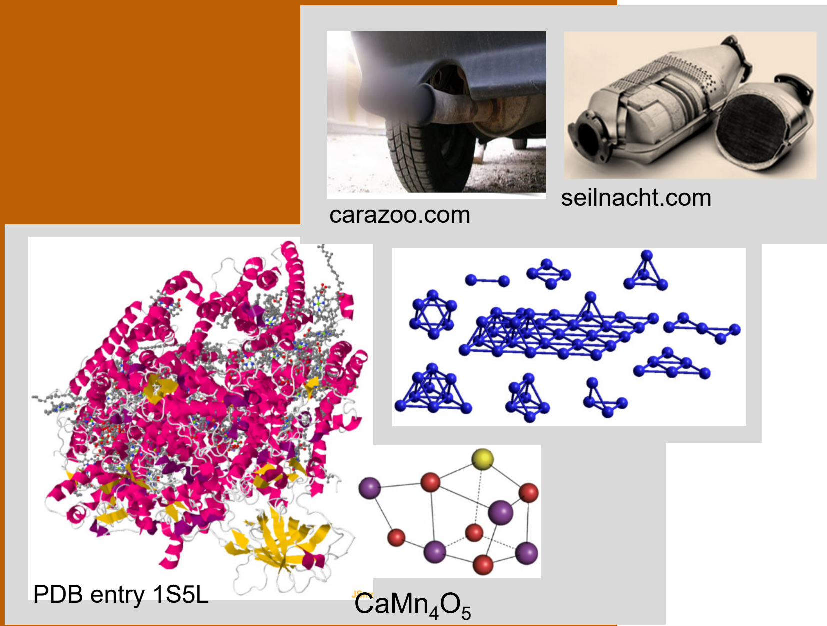
Modeling the Active Centers of Catalysts by Small Clusters in the Gas Phase



Biocatalysts

CaMnO
Water Oxidation

FeS
Nitrogen Fixation

Heterogeneous catalysts

Copper
CO_2 Conversion

Gold
Hydrocarbon Activation

Palladium
CO Oxidation

Ruthenium
CO Methanation

Astrochemically relevant materials

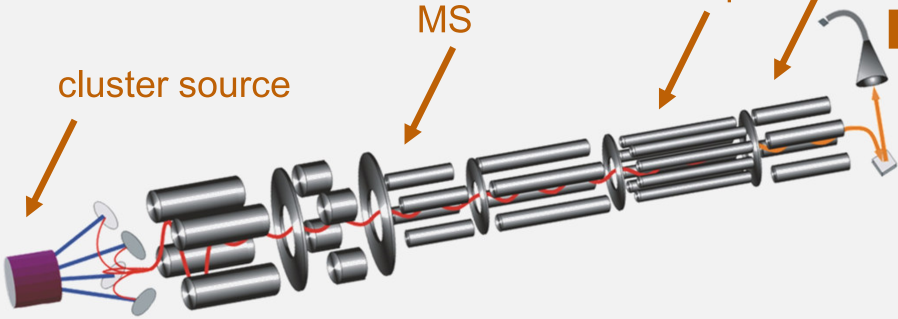
MgSiO

FeS

Methods

Experiments

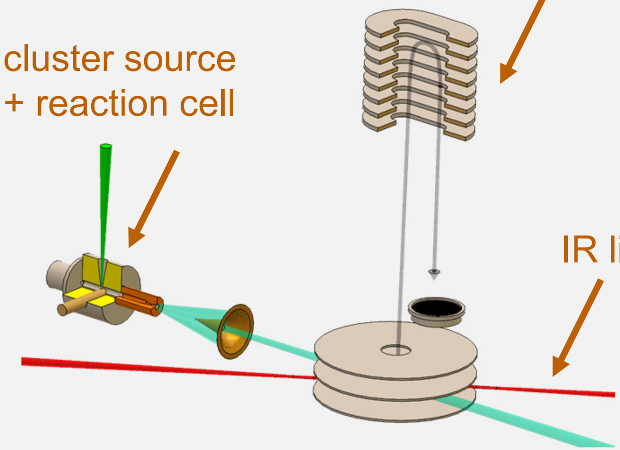
Ion Trap Reactivity
(Ulm)



IR-MPD Spectroscopy
(Nijmegen)

FELIX
Free Electron Lasers for
Infrared eXperiments

collaboration with J. Bakker



Theory

Theory

collaboration with
S. Bromley
U. Landman
T. Hölzl

Free Electron Lasers @ FELIX Laboratory Nijmegen

FELIX - **F**ree **El**ectron **L**aser for **I**nfrared **EX**periments

FELICE - **F**ree **El**ectron **L**aser for **I**ntra**C**avity **EX**periments

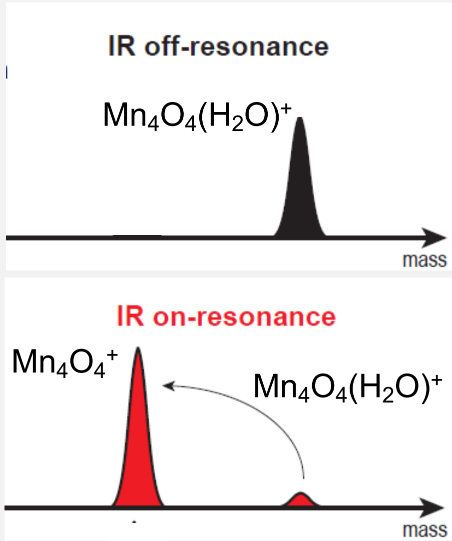
spectral range: 5-100 μm
2000-100 cm^{-1}

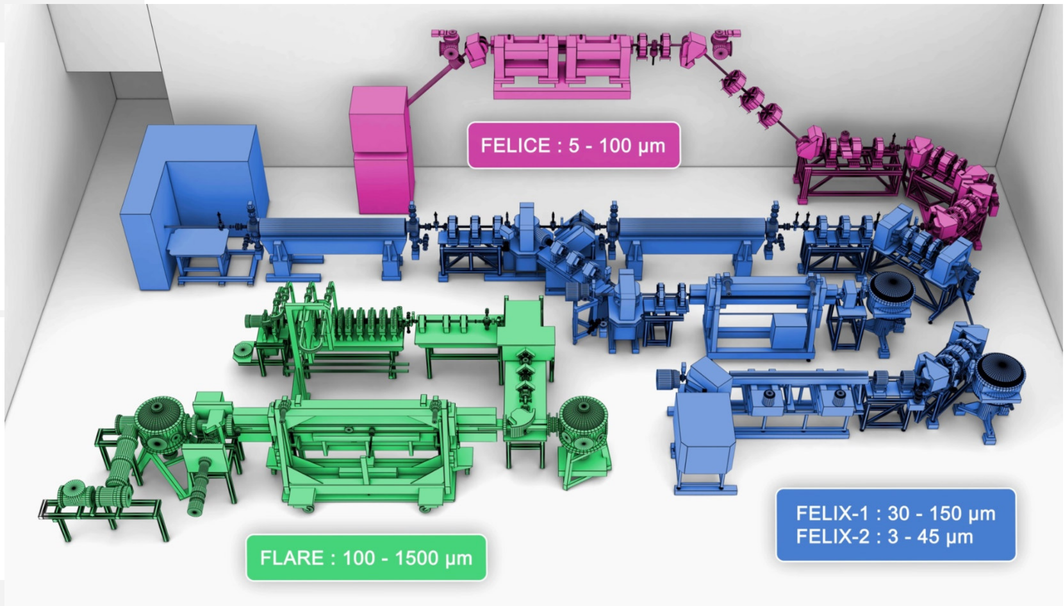
- molecule activation
- metal-metal
- metal-oxygen

pulse energy: 5J @ 1 GHz

- strongly bound species

Infrared **M**ulti-**P**hoton **D**issociation
= action spectrosocpy





Production of Magnesium Silicates

silicate dust:

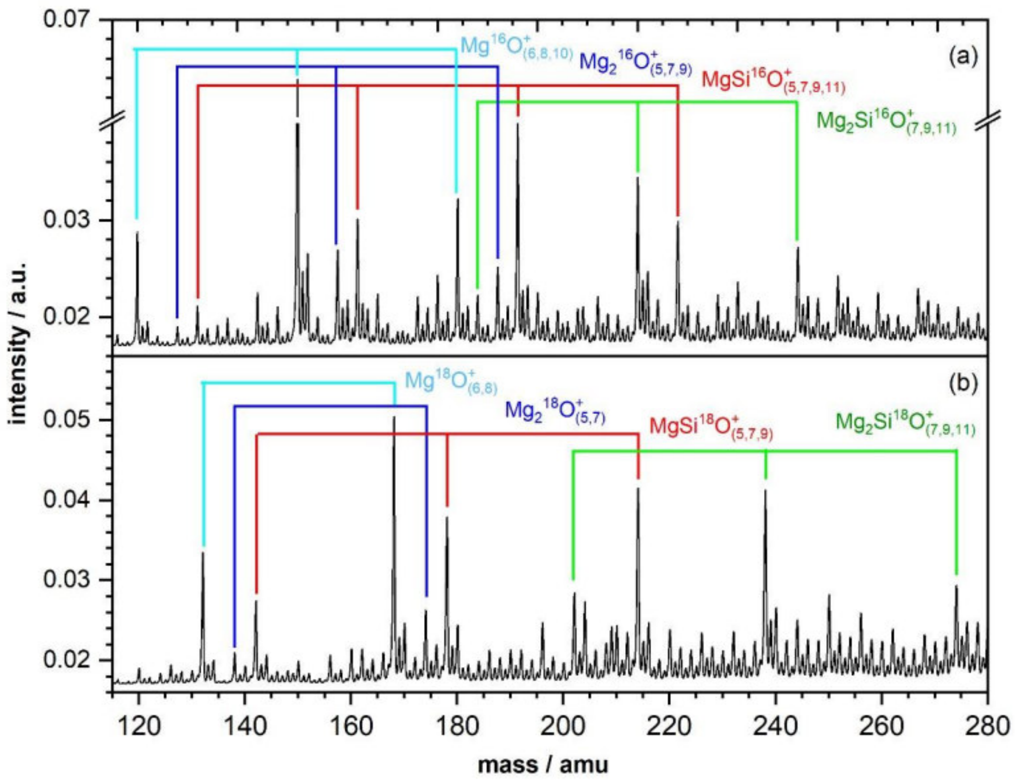
- pyroxene (enstatite) composition ($MgSiO_3$)
- olivine (forsterite) composition (Mg_2SiO_4)

identification of

- $MgO_{6,8,10}^+$ / $Mg_2O_{5,7,9}^+$
- $(MgSiO_3)(O_2)_{1,2,3,4}^+$ → pyroxene??
- $(Mg_2SiO_3)(O_2)_{2,3,4}^+$ → structure??

→ highly oxidized clusters

laser ablation of a Mg:Si = 2:1 target @ 1% O_2/He



Guiu et al., ACS Earth Space Chem. (2022) 6, 2465

Structure of Pyroxene $(MgSiO_3)^+$ Monomers

- $(MgSiO_3)^+$ are structurally robust
- cationic $(MgSiO_3)^+$ readily adsorb O_2
- rather strong binding of oxygen
  - 0.48−0.6 eV
  - $(MgSiO_3)^+(O_2)_3$: ozone like O_3: 4.3 eV
  - $(Mg_2SiO_3)^+(O_2)_3$: super-oxo like O_2: 1.47 eV
- amorphous silicates: ~0.08 eV

→ new oxygen reservoir??

- Mg atom binds to $(MgSiO_3)^+$ core

→ simple initial step in grain growth??

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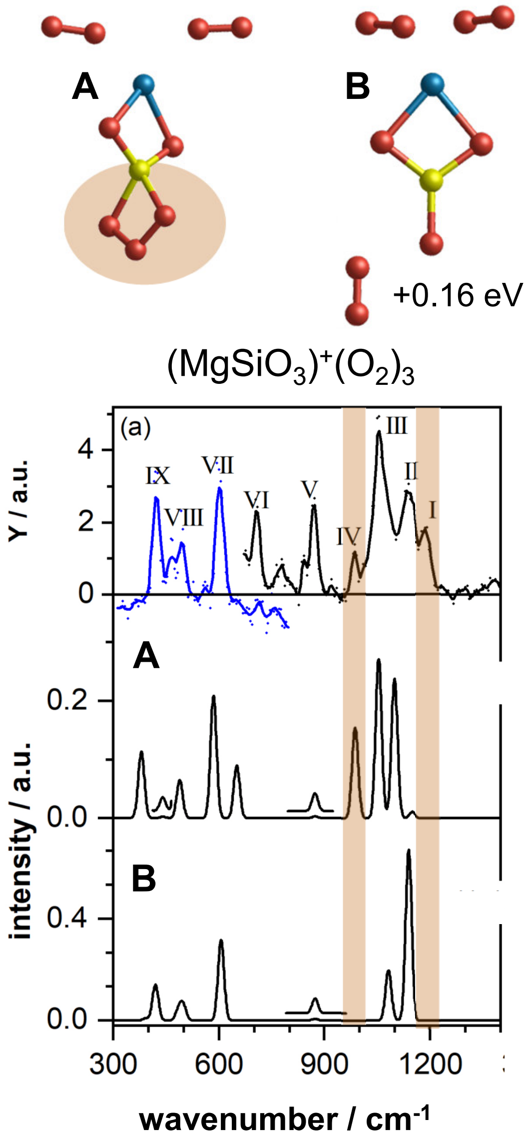
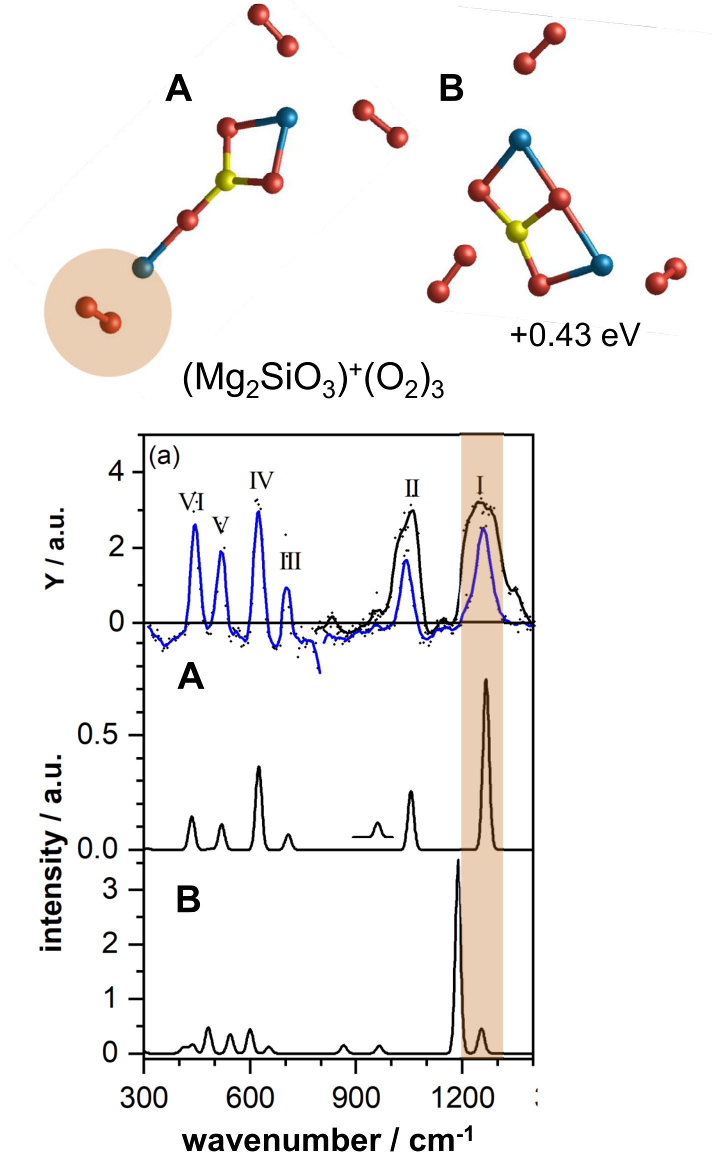




Summary

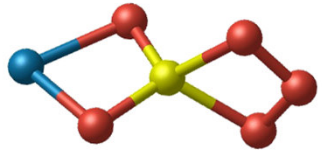
Combining Reaction Studies and IR Spectroscopy

- determination of cluster structures
- insight in cluster growth process
- insight into cluster chemistry

Ion Trap Reactivity

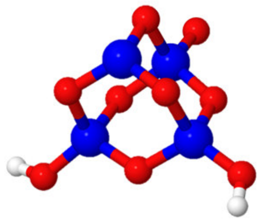
IR-MPD Spectroscopy

Pyroxene $(MgSiO_3)^+$ Monomers



- gas-phase formation of pyroxene $(MgSiO_3)^+$ monomers
- facile and strong adsorption of oxygen (ozone- and super-oxo-like)
- binding of Mg atom

Ultra-Small Silica Clusters



- dissociation of water
- stabilization of relaxed 3D structure through hydroxylation
- characteristic band at 1200-1150 cm^{-1}?
- dissociation of CO_2

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Prof. Dr. Joost M. Bakker
Felix Team

NWO
FELIX
Free Electron Lasers for Infrared eXperiments

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ISSPIC XXI Berlin 2023

International Symposium on Small Particles and Inorganic Clusters

September 3rd-8th, 2023

Berlin, Germany

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!!!!!! NEW !!!!!!

Graduate Student seminar

September 2nd-3rd 2023

All graduate student applicants can give an oral presentation. The best talks will be selected for Hot-Topic contributions at the ISSPIC.

abstract submission deadline: 30 June 2023!