

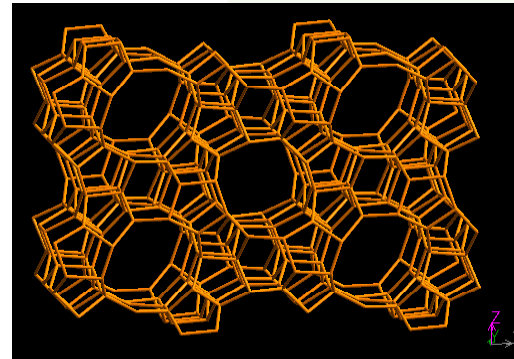
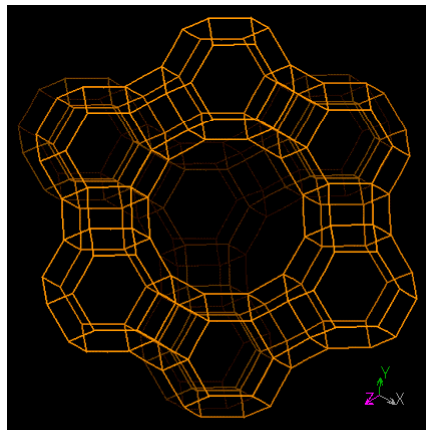
Synchrotron-based IR Reveals Heterogeneities in Zeolitic Catalysts

Javier Ruiz Martínez
Utrecht University

IR Workshop on Spectro-Microscopy, Basel
2nd February 2011

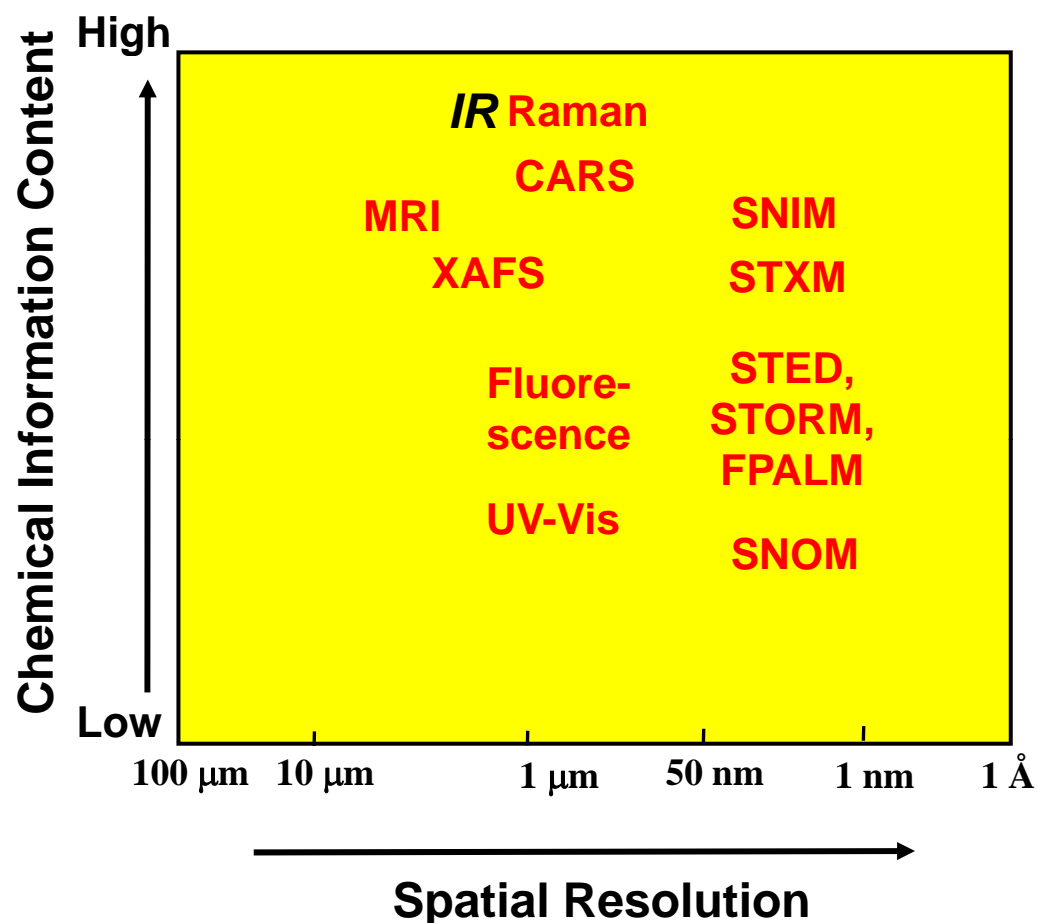
What are zeolites?

- Micropore aluminosilicate materials



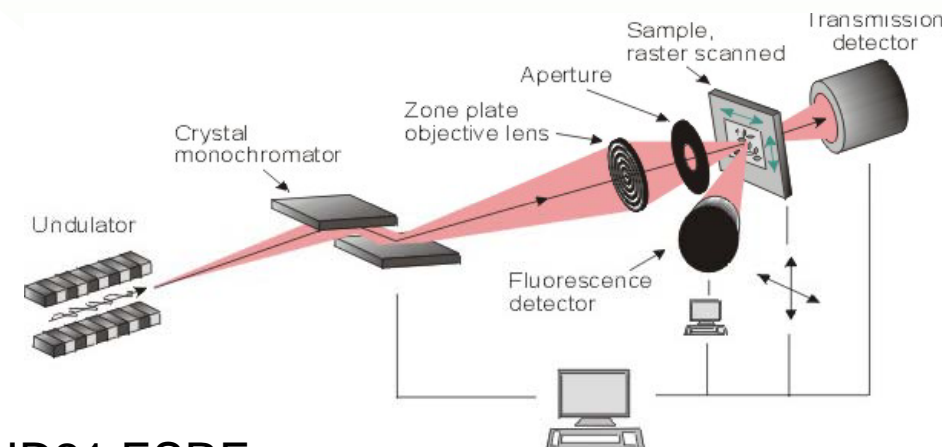
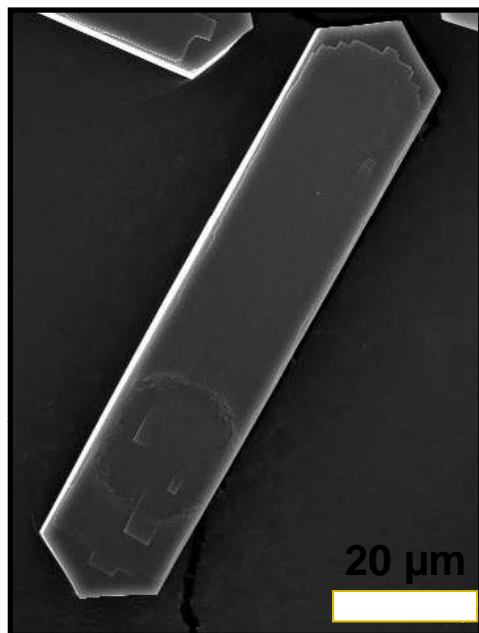
- Applications in catalysis
 - Fluid catalytic cracking
 - Oligomerization of light olefins
 - Methanol to hydrocarbons
 - ...

Chemical imaging of catalysts with photons: Techniques



Heterogeneous catalysts are truly heterogeneous
They are spatially and temporally non-uniform and very dynamic!

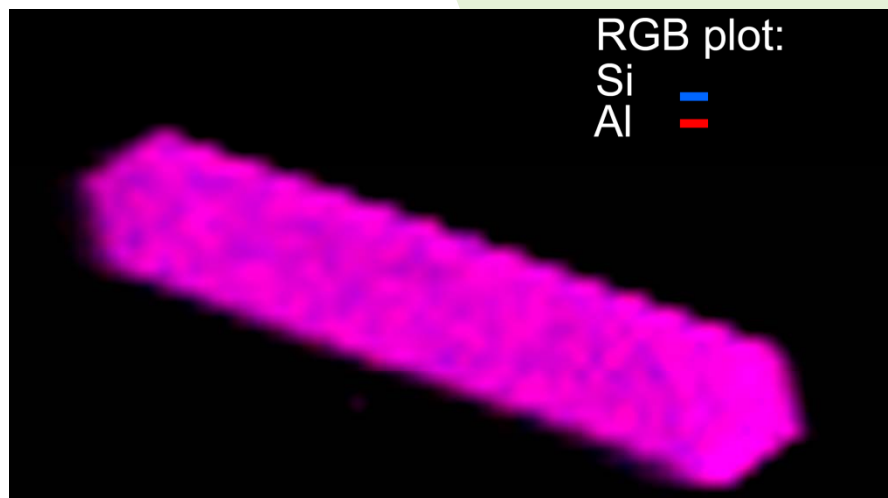
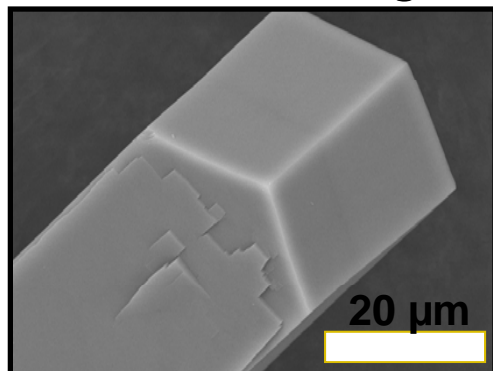
Showcase: large H-ZSM-5 crystals

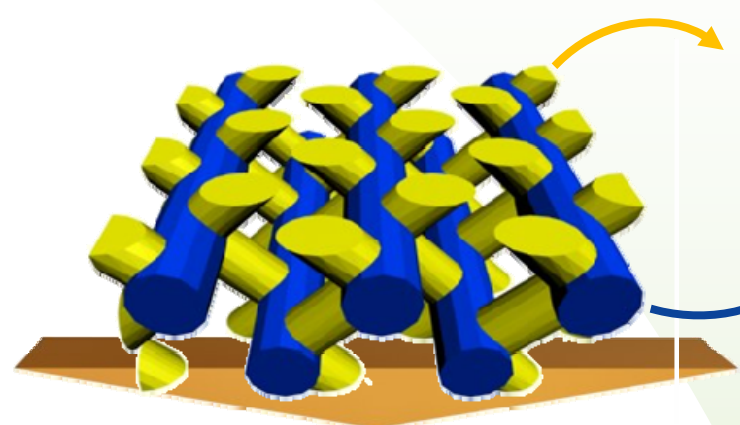
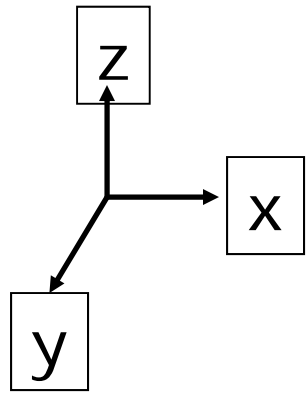


ID21 ESRF,
Grenoble, France
MicroXAS beamline

Si:Al ratio of 17

SEM images



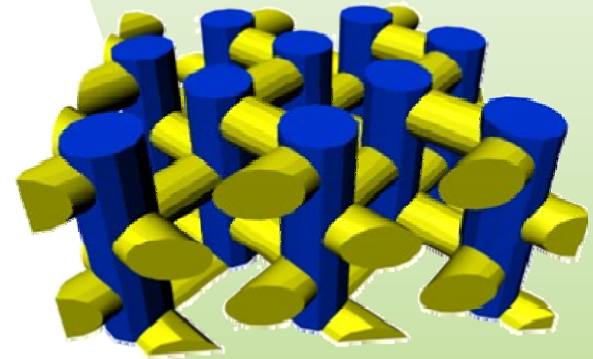
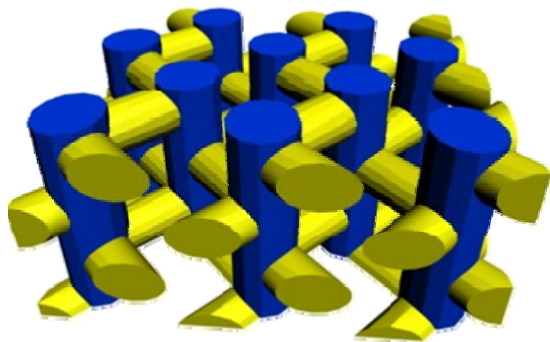


Sinusoidal pores

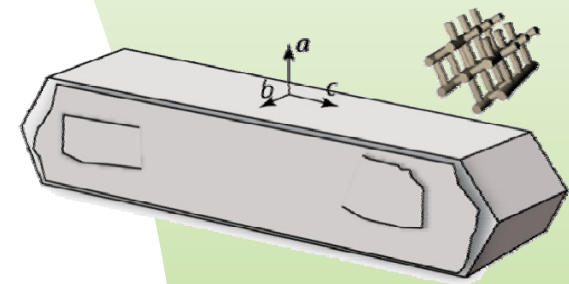
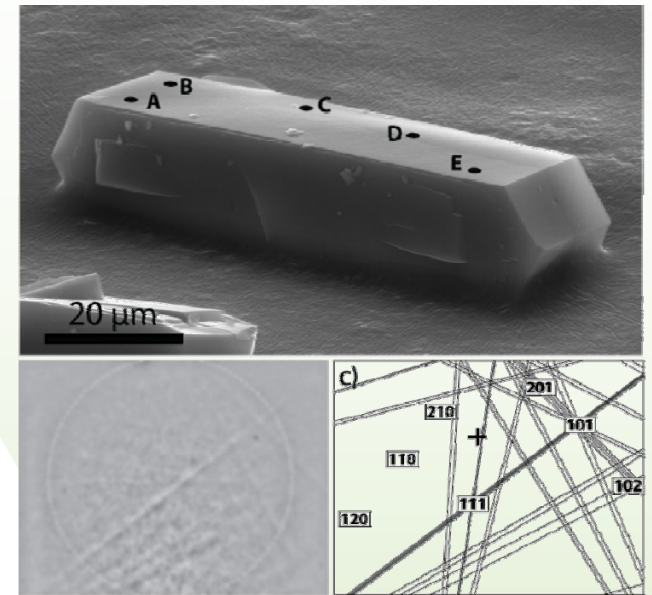
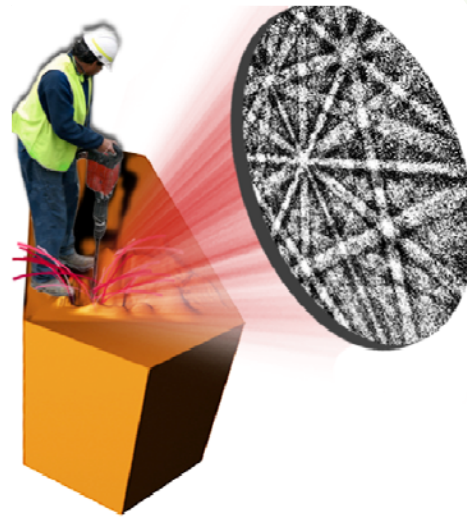
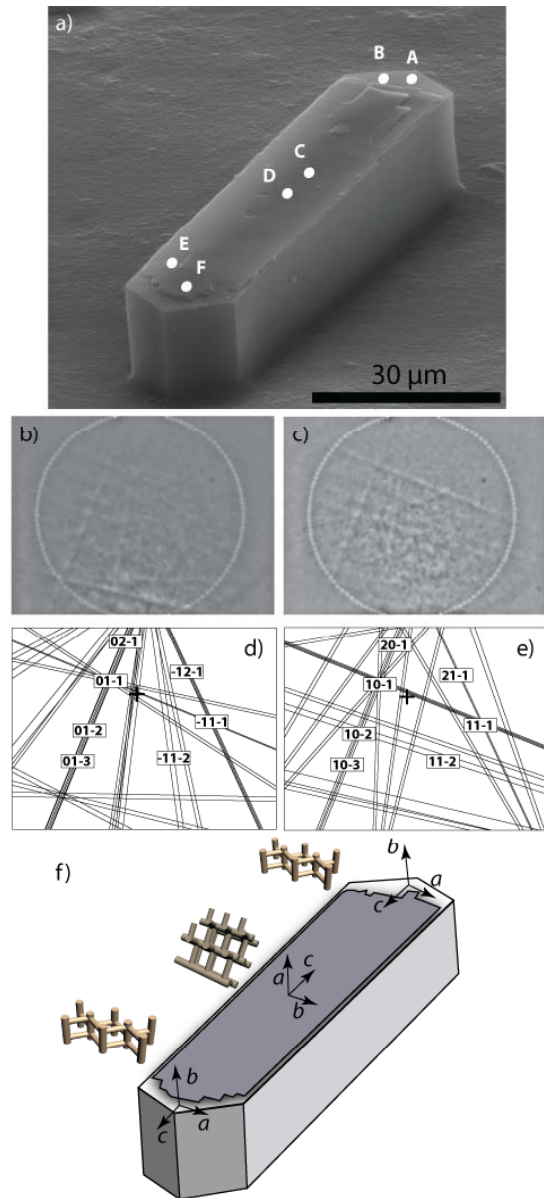
Straight pores

90° rotation

90° rotation

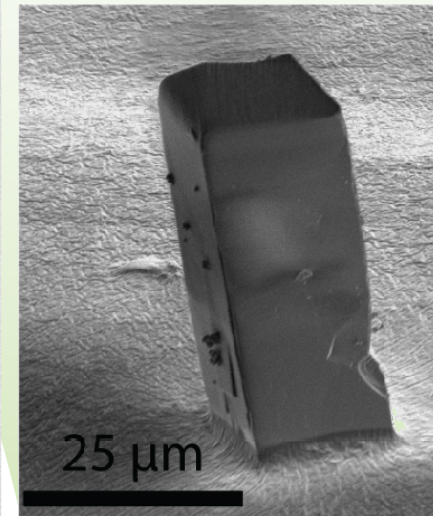
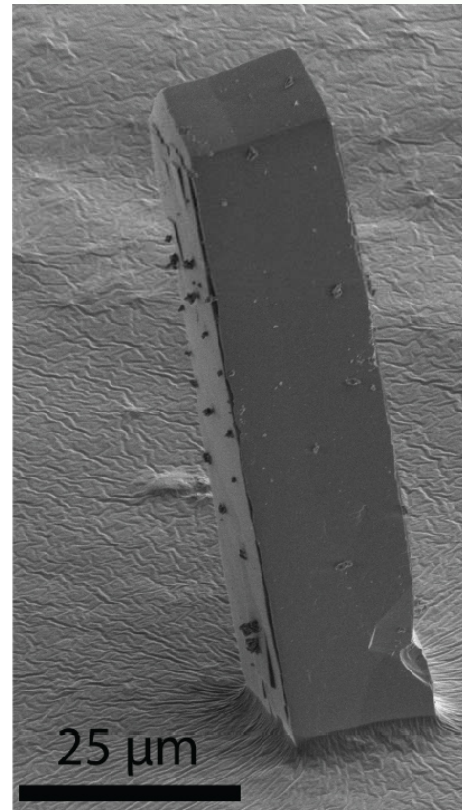
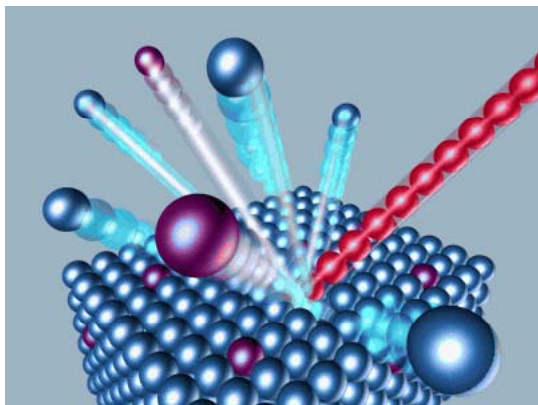
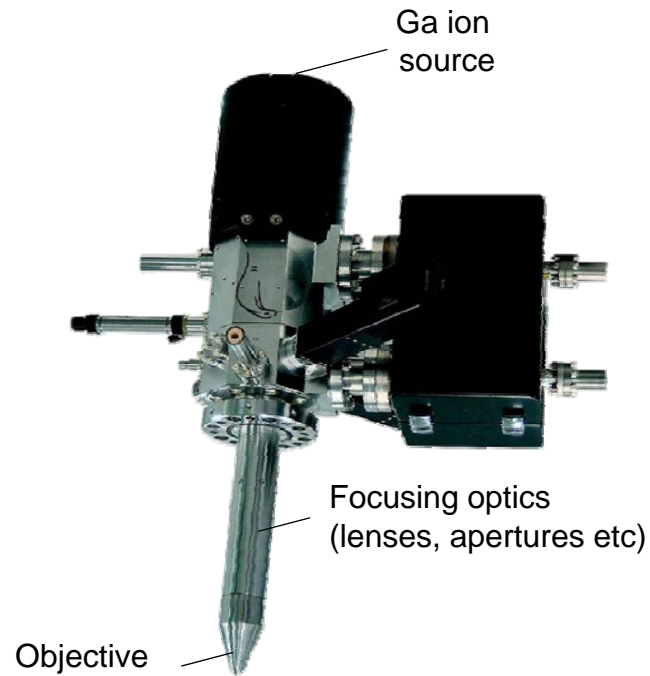


Electron backscattering diffraction studies

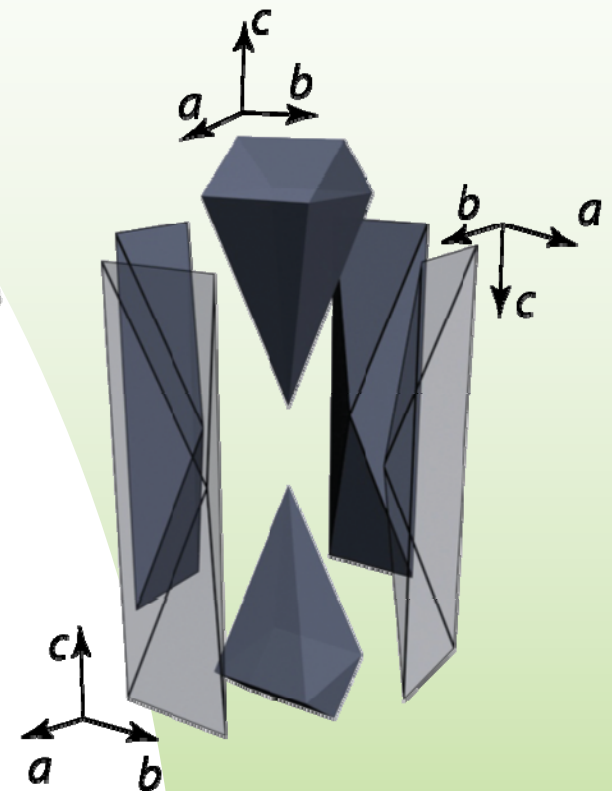
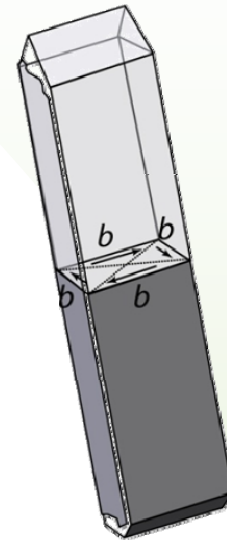
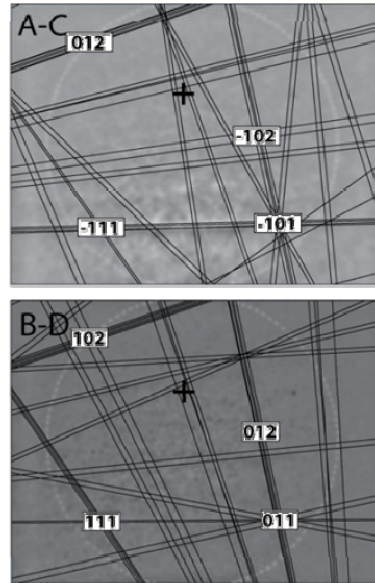
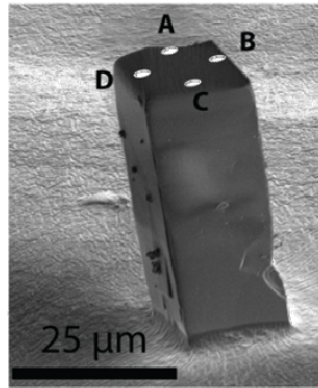




Focused ion beam milling experiments



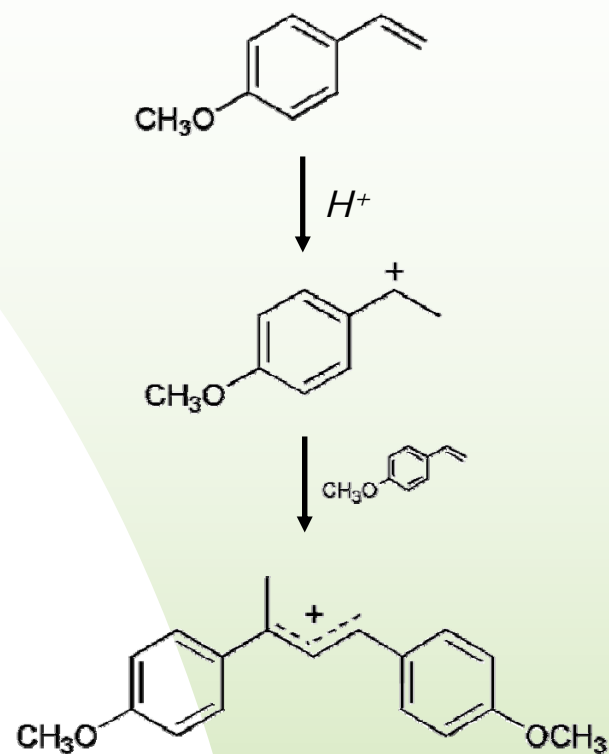
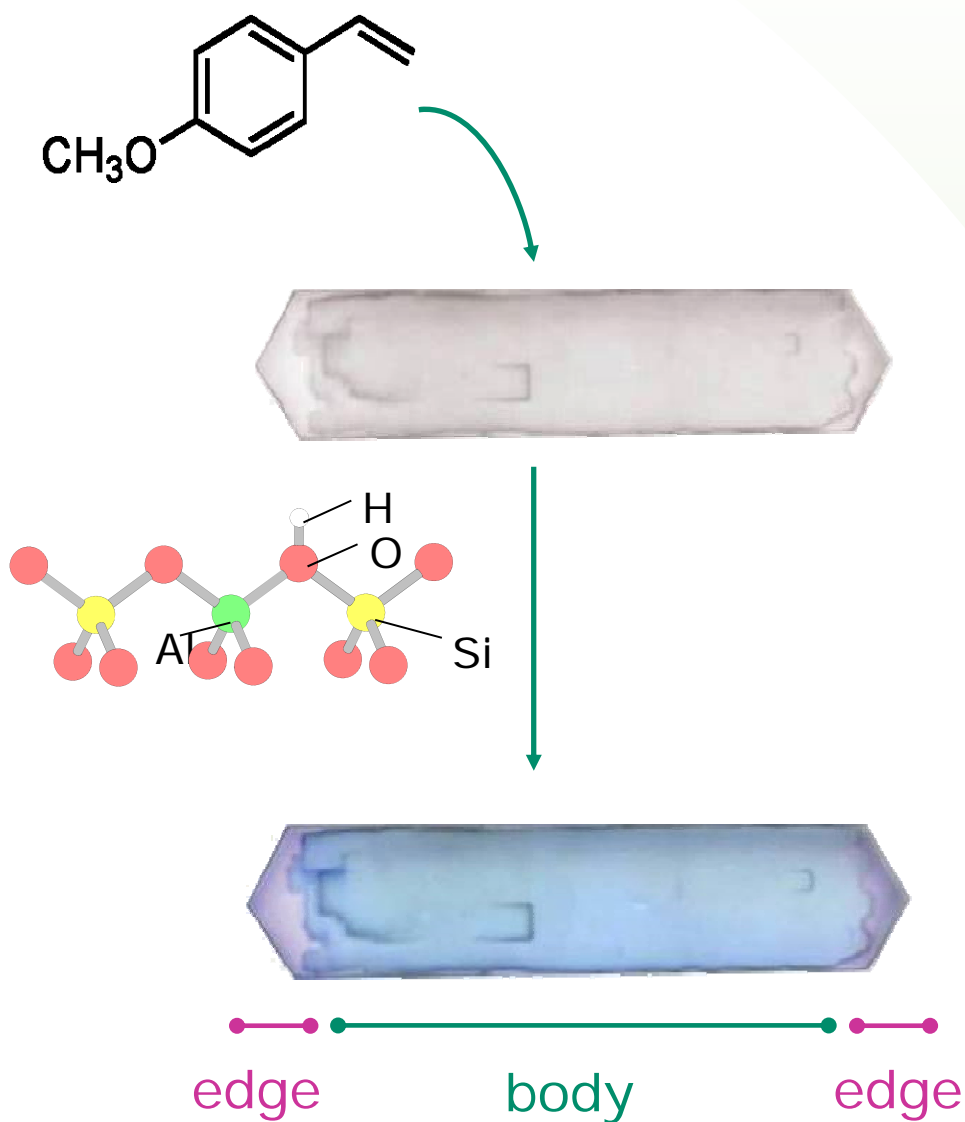
EBSD combined with focused ion beam milling



Stavitski, Weckhuysen et al., *Angew. Chem. Int. Ed.* 2008, 5637
 Karwacki, Weckhuysen et al., *Nature Materials* 2009, 8, 959

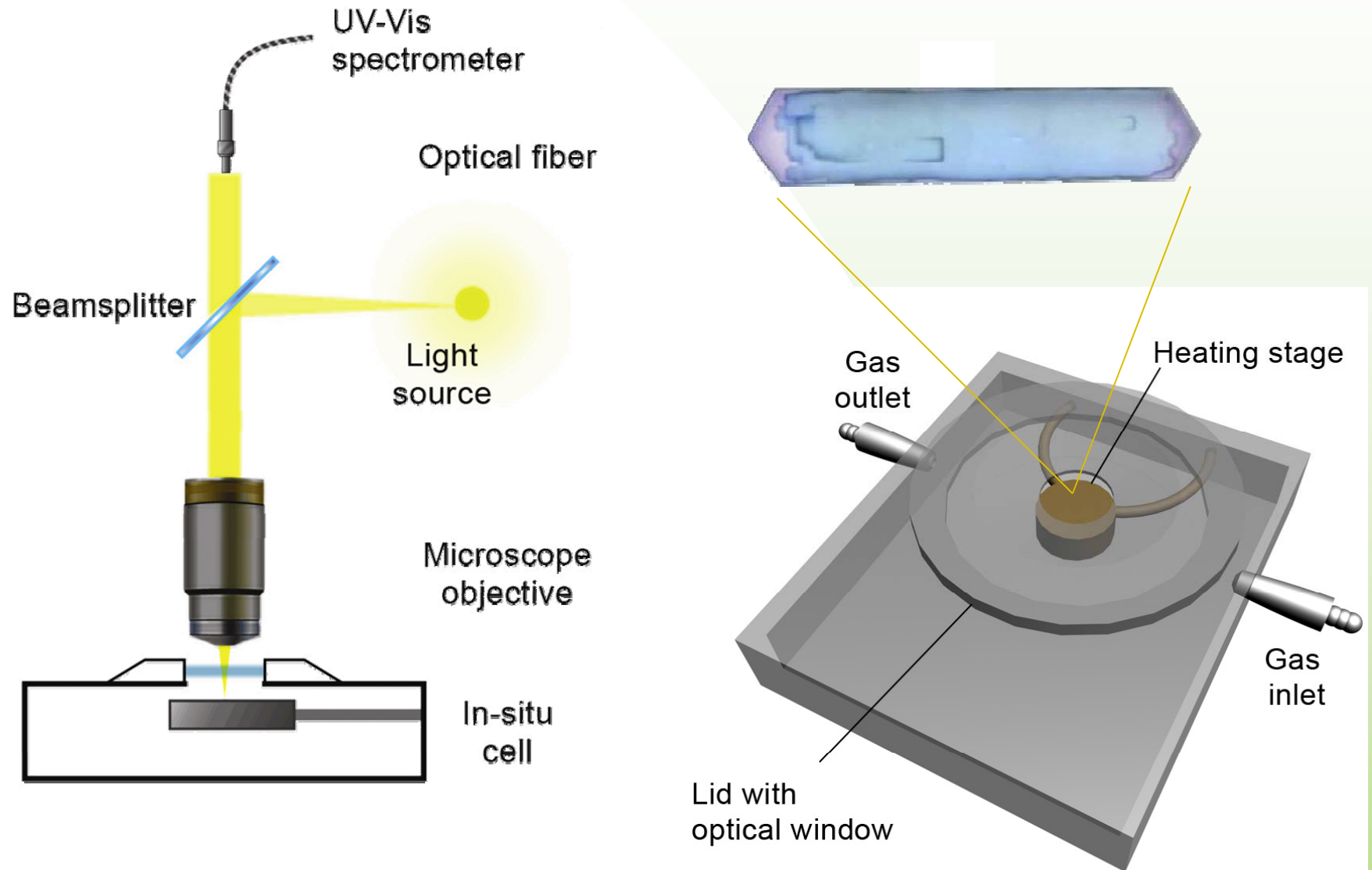


Styrene oligomerization over H-ZSM-5 zeolites

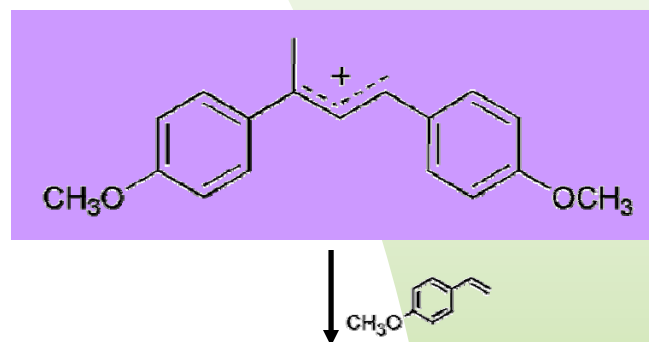
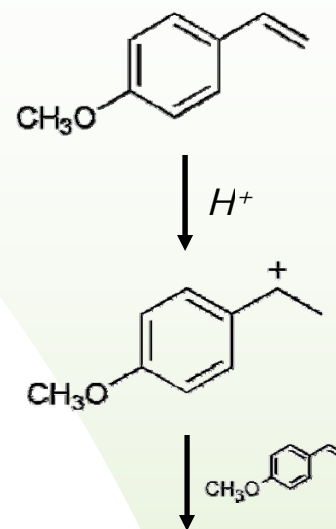
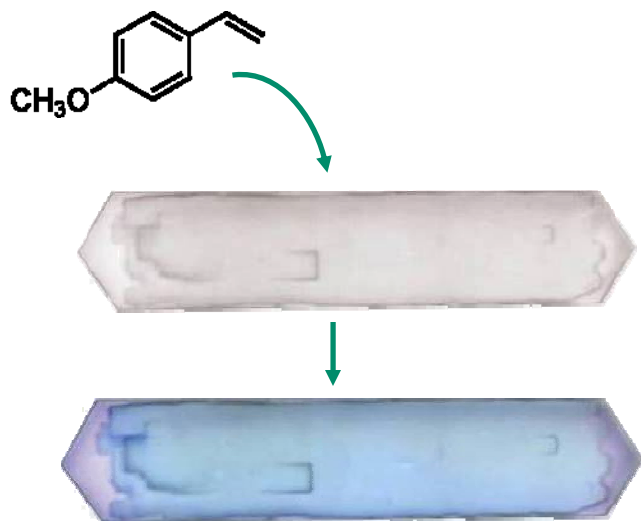


Formation of carbo-cation intermediates that can act as **reporter** molecules

In-situ UV-Vis micro-spectroscopy



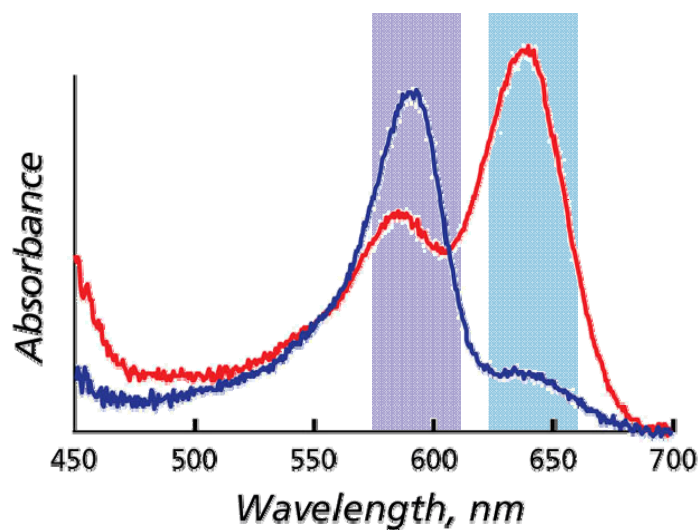
Non-uniform catalytic behavior of a H-ZSM-5 crystal

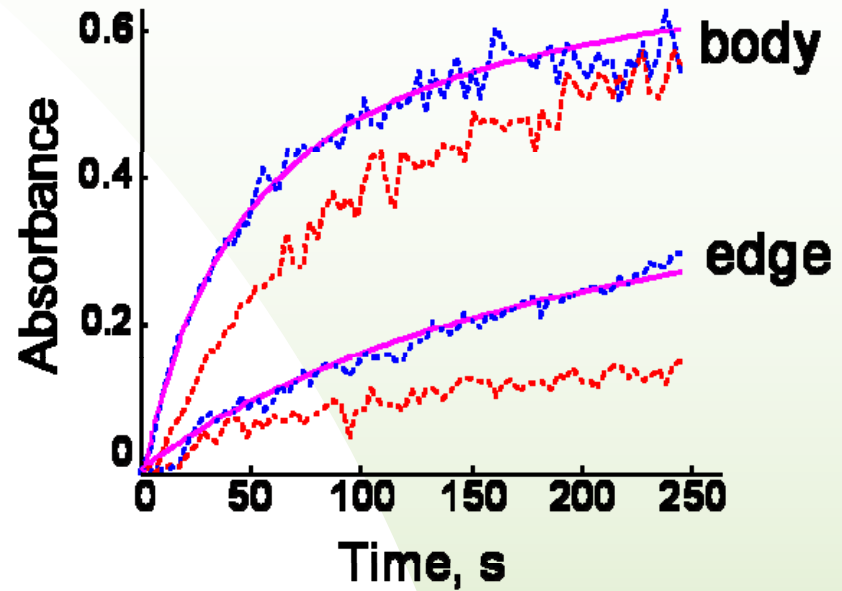
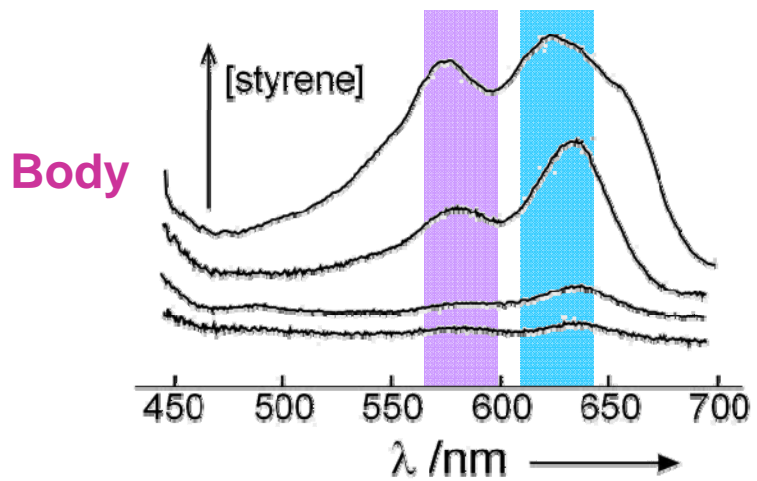
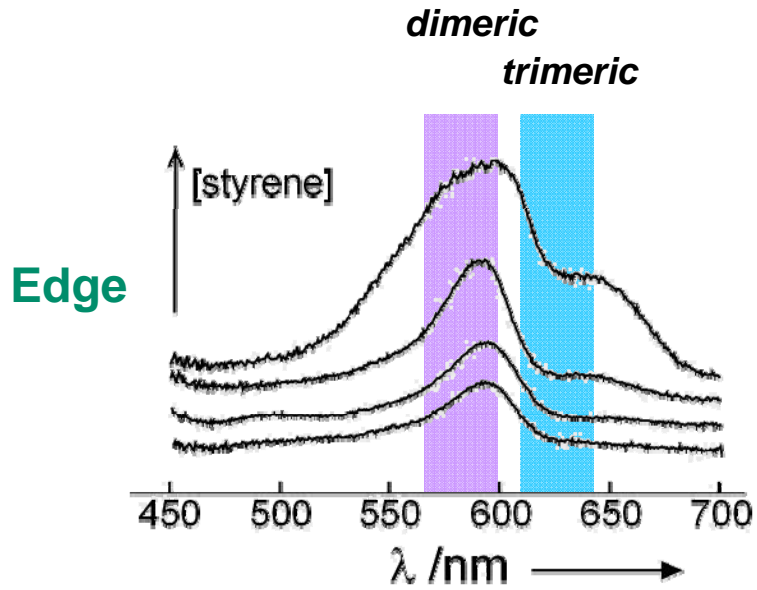


585 nm

More extended carbocations
(e.g. trimeric species)

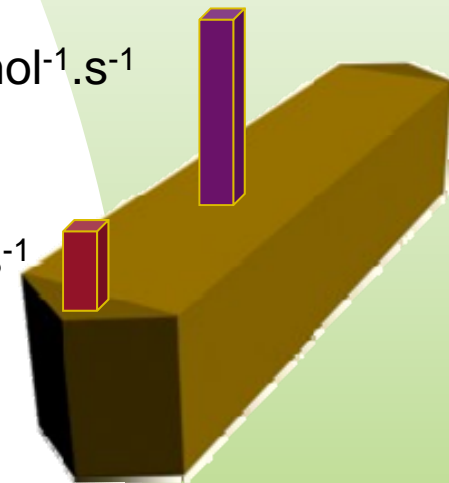
635 nm

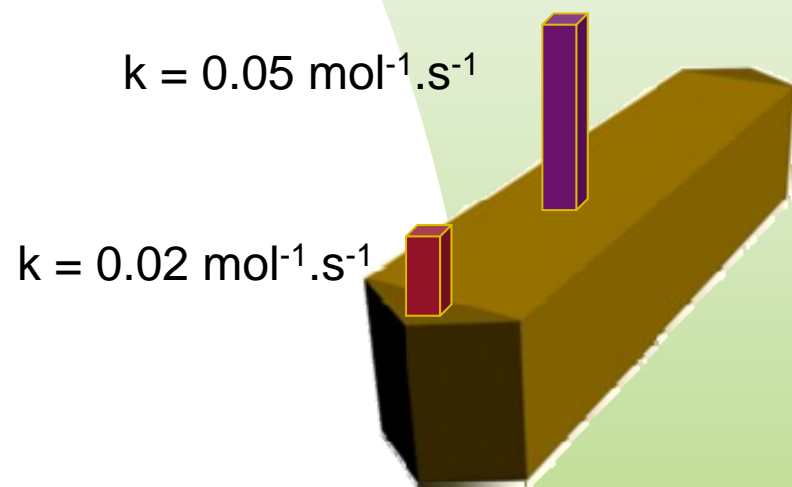
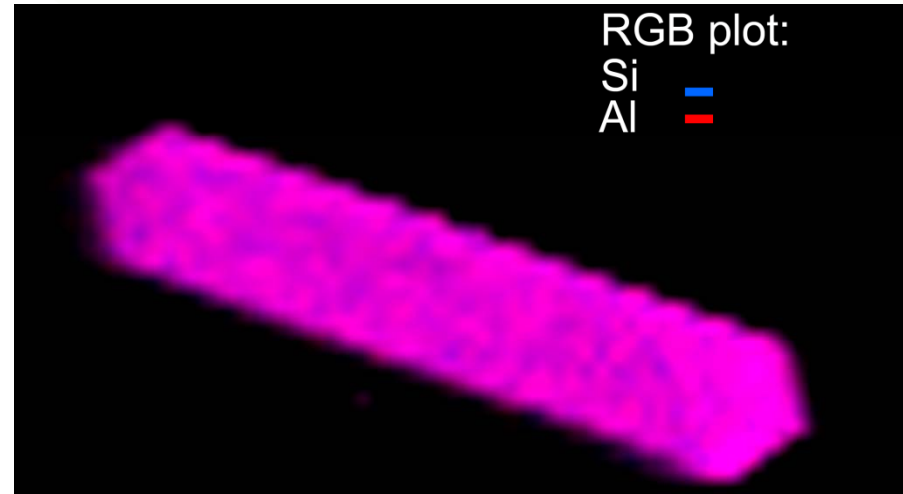
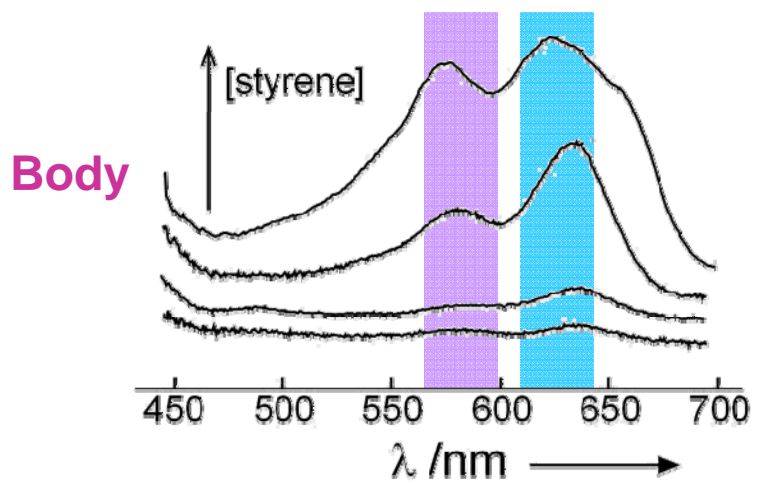
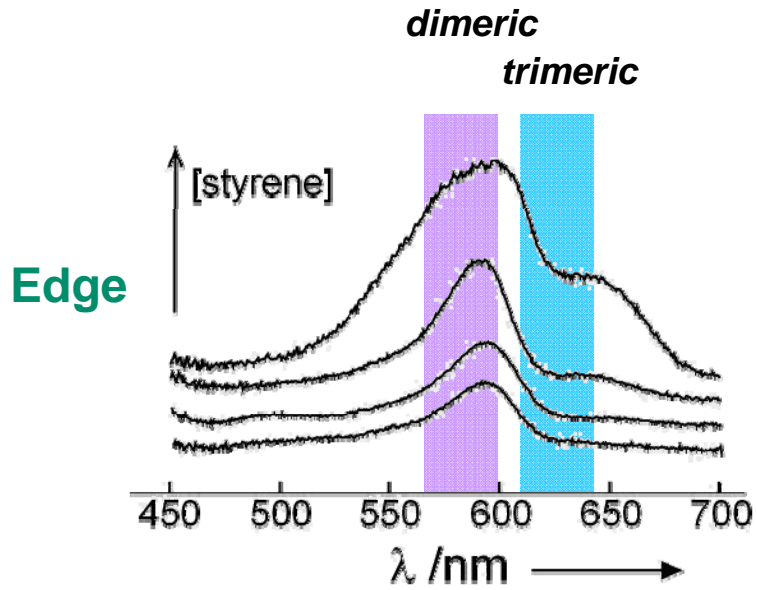




$k = 0.05 \text{ mol}^{-1} \cdot \text{s}^{-1}$

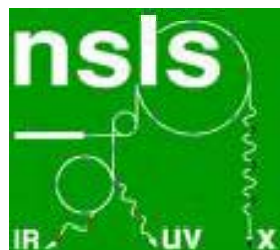
$k = 0.02 \text{ mol}^{-1} \cdot \text{s}^{-1}$



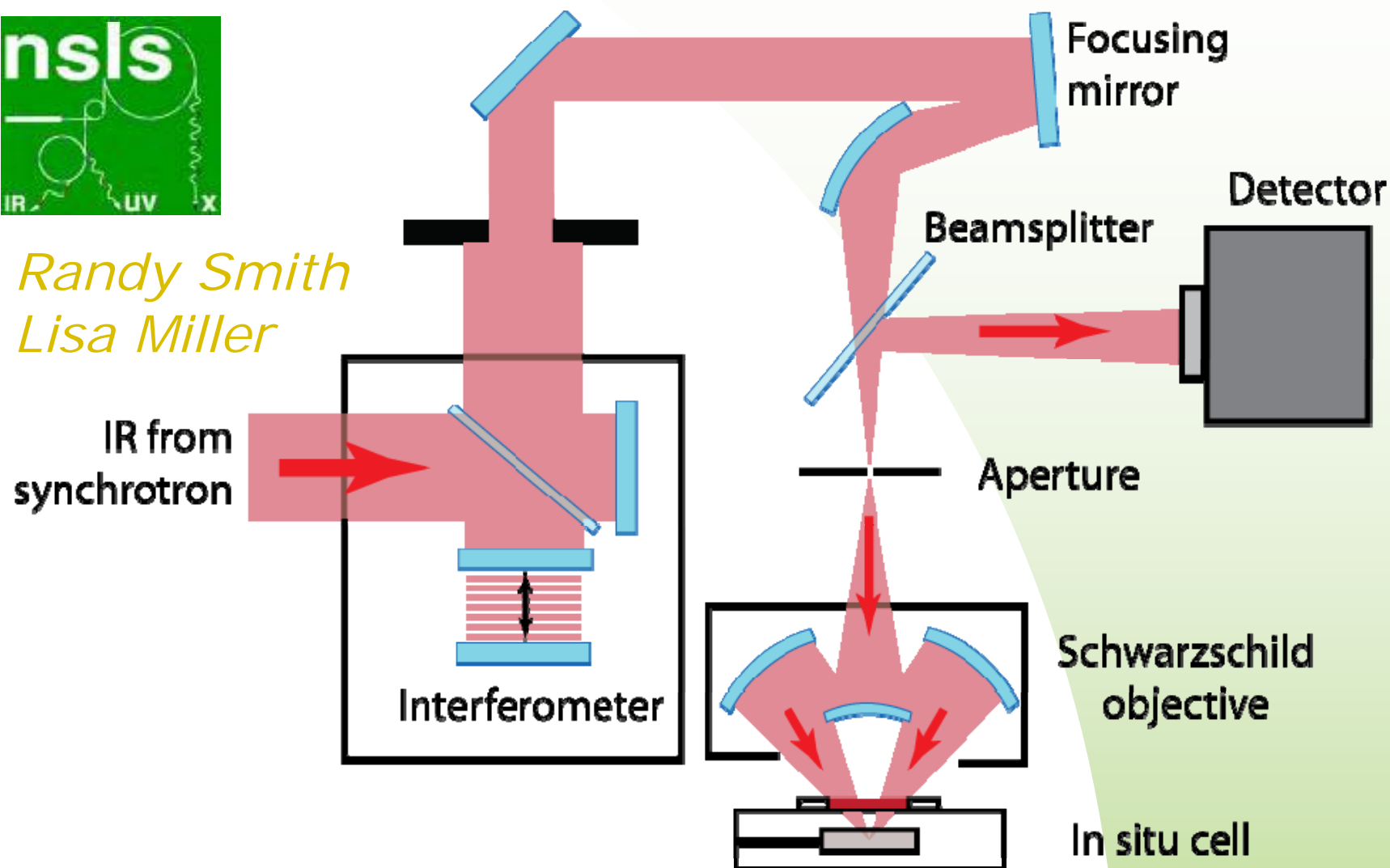




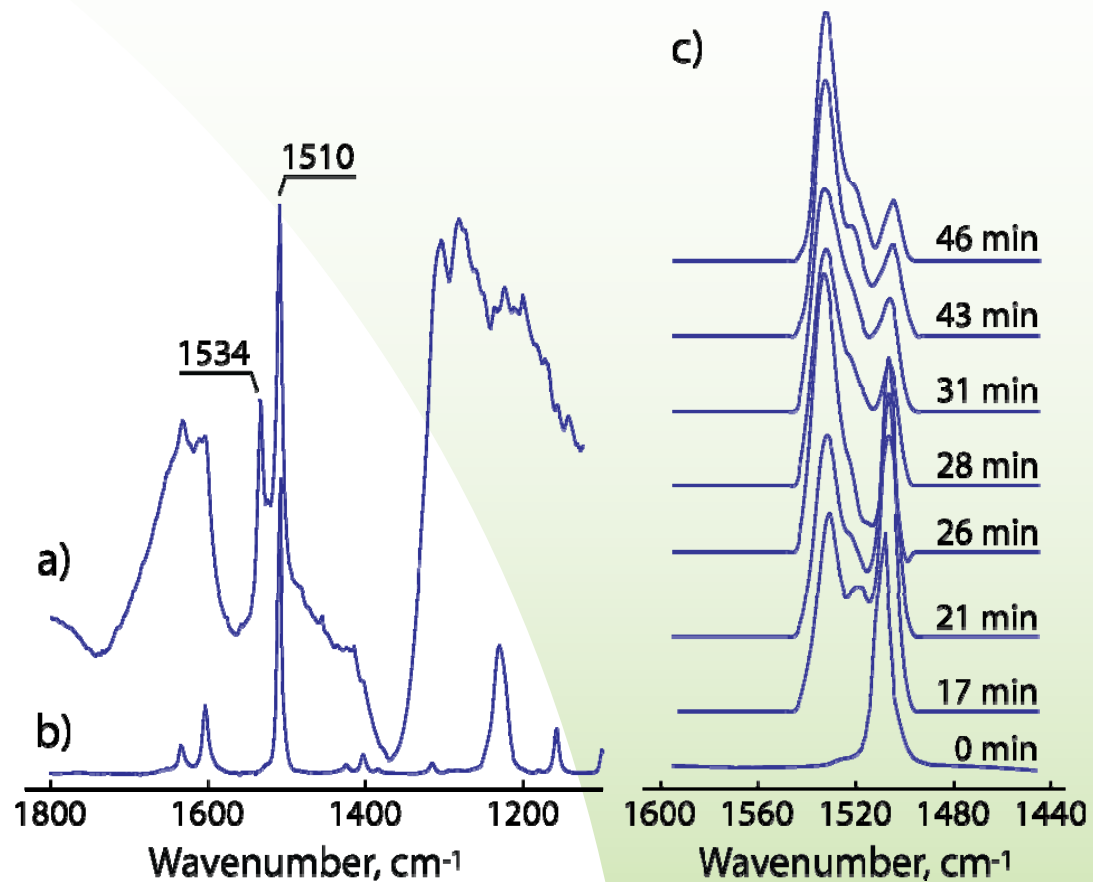
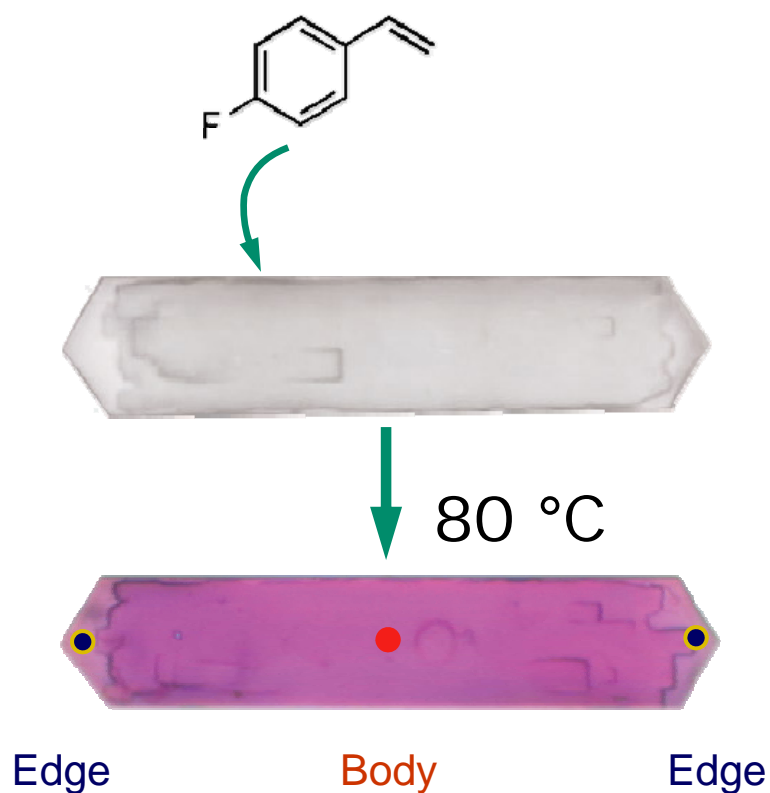
In situ synchrotron-based IR microscopy



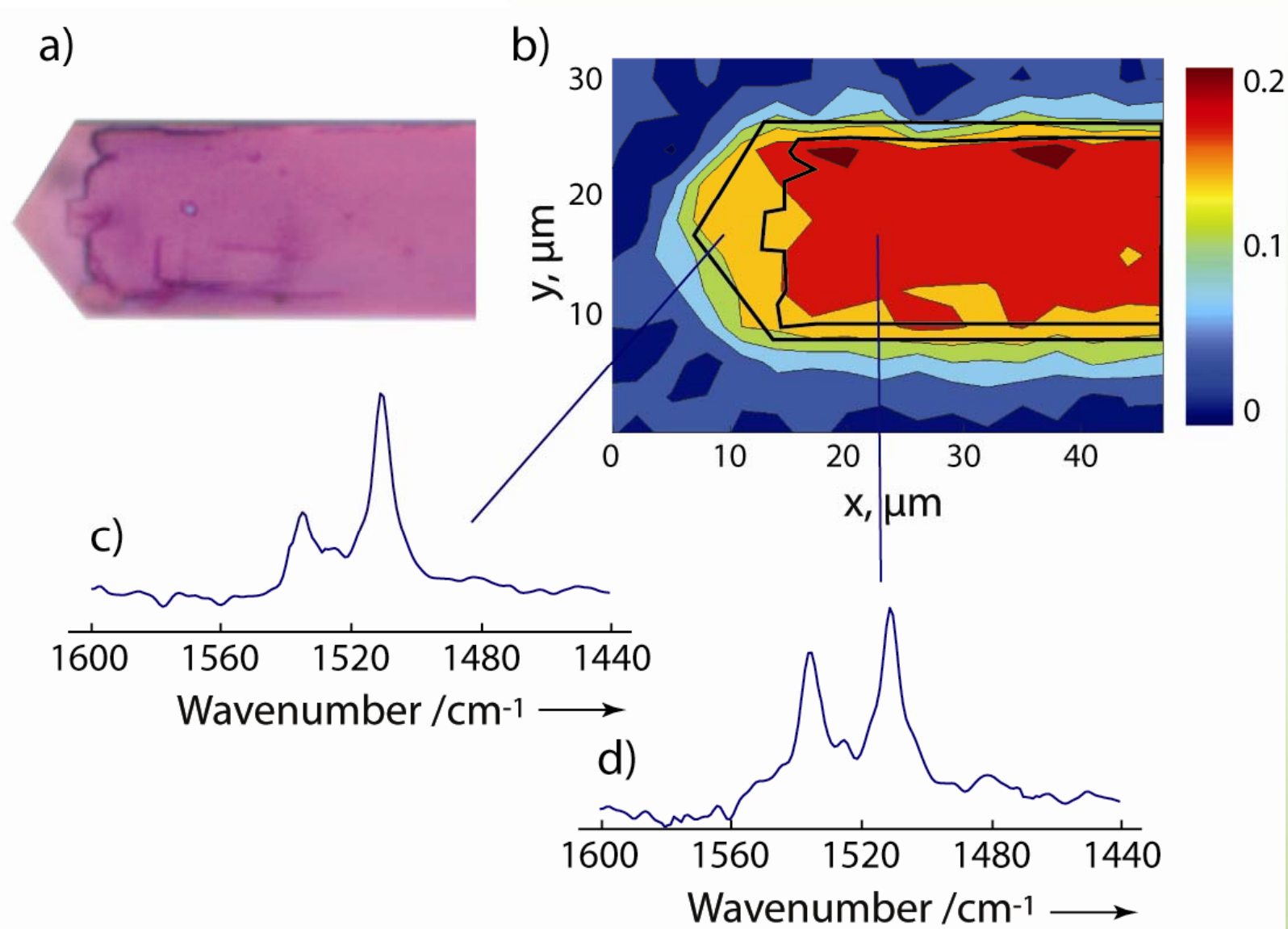
Randy Smith
Lisa Miller



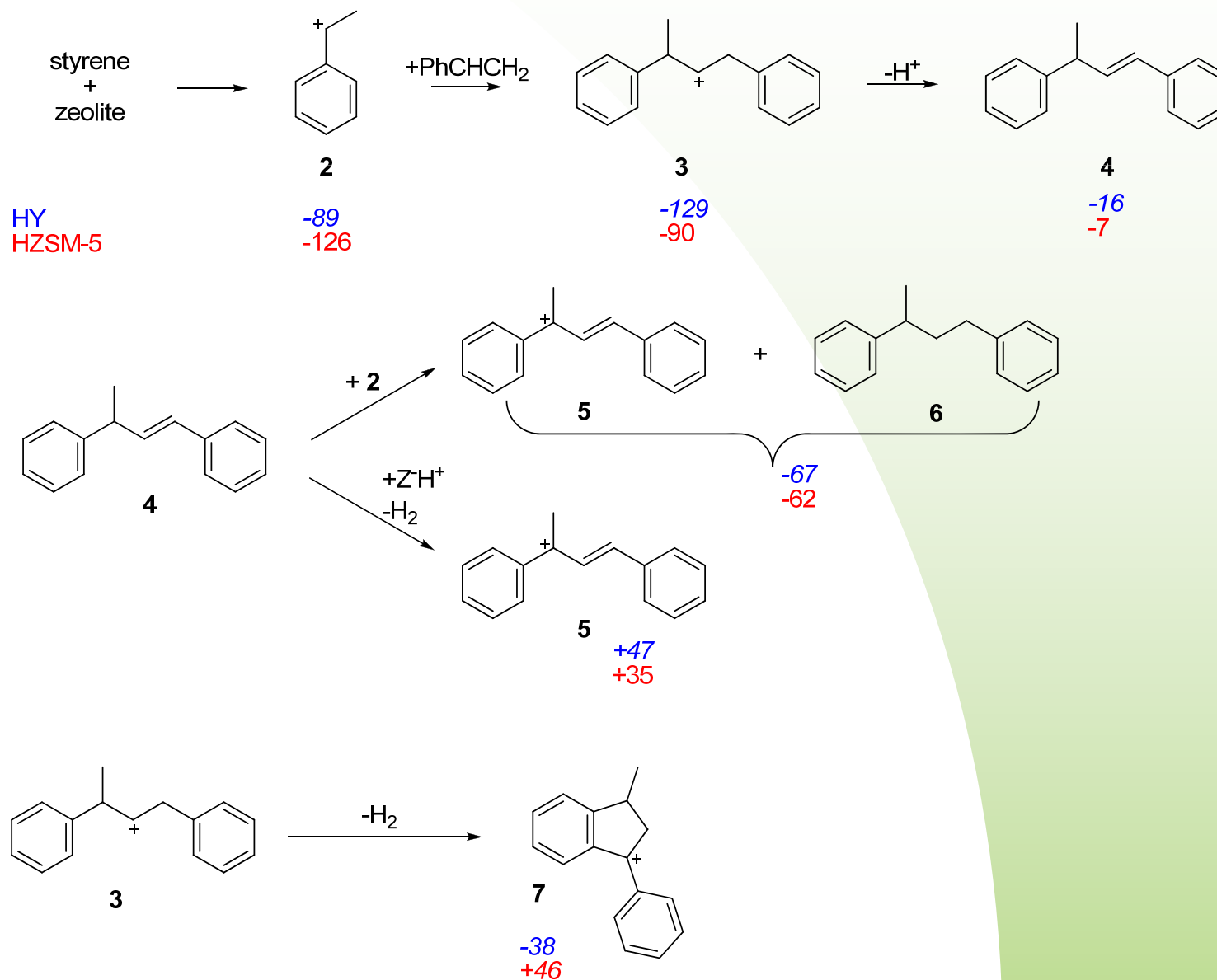
Identification of carbocationic species in H-ZSM-5



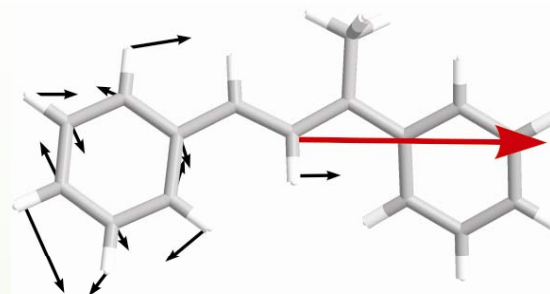
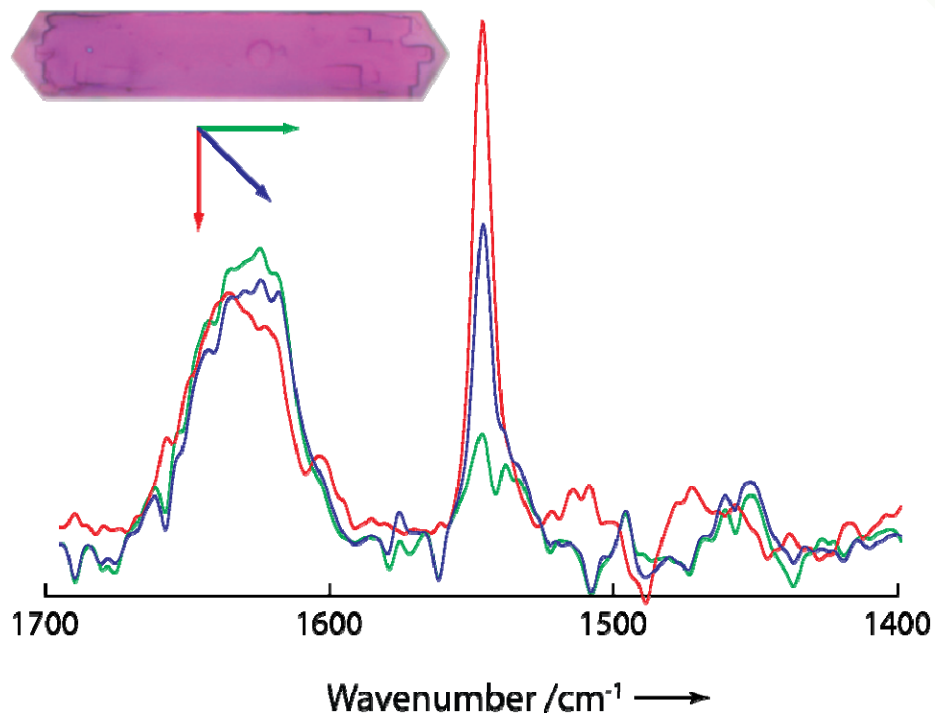
Identification of carbocationic species in H-ZSM-5



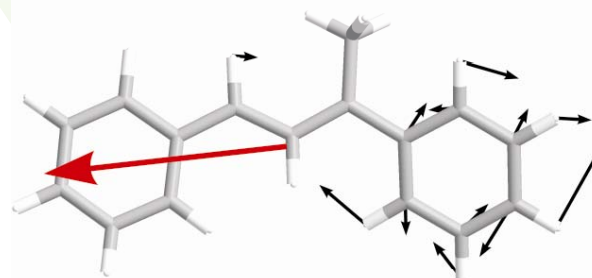
Styrene oligomerization over Bronsted acidic zeolites



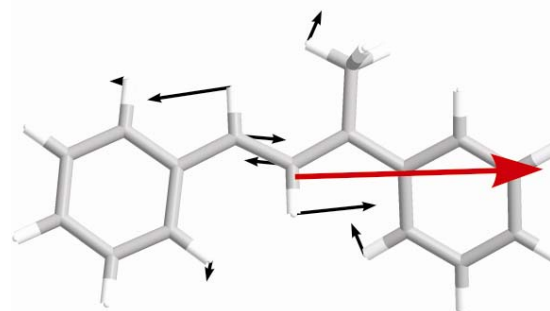
Species 5 and polarization dependent IR spectra



1552 cm⁻¹ (99 km mol⁻¹)

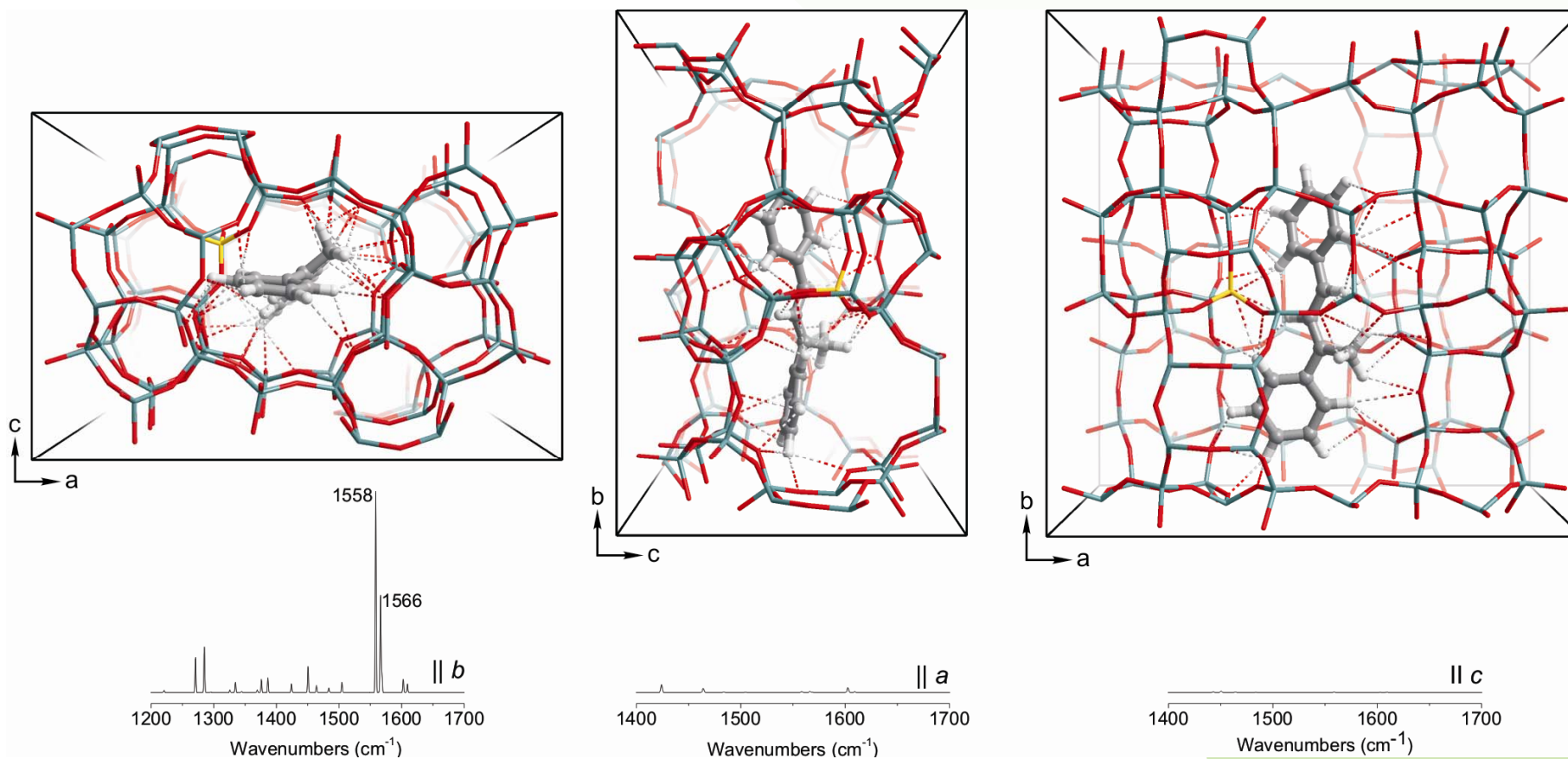


1554 cm⁻¹ (42 km mol⁻¹)



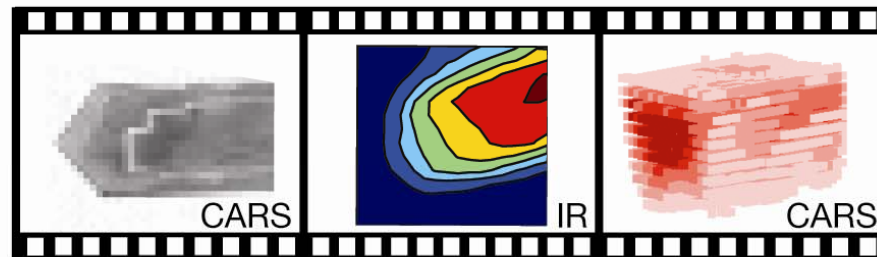
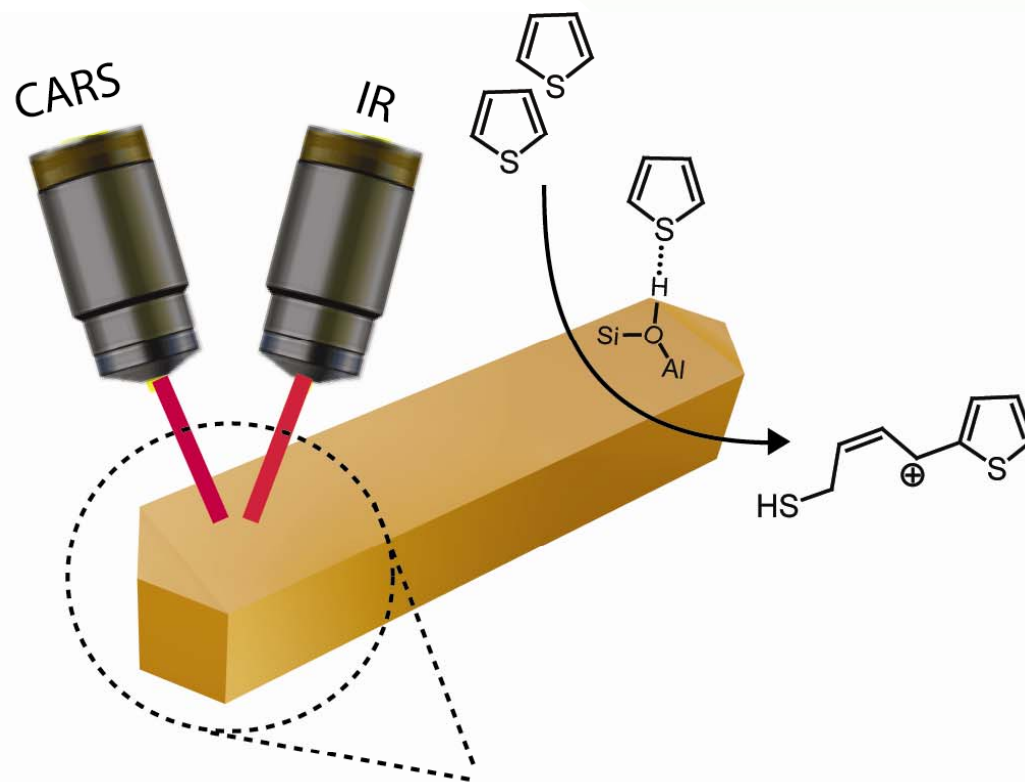
1567 cm⁻¹ (1501 km mol⁻¹)

Species 5 and polarization dependent IR spectra



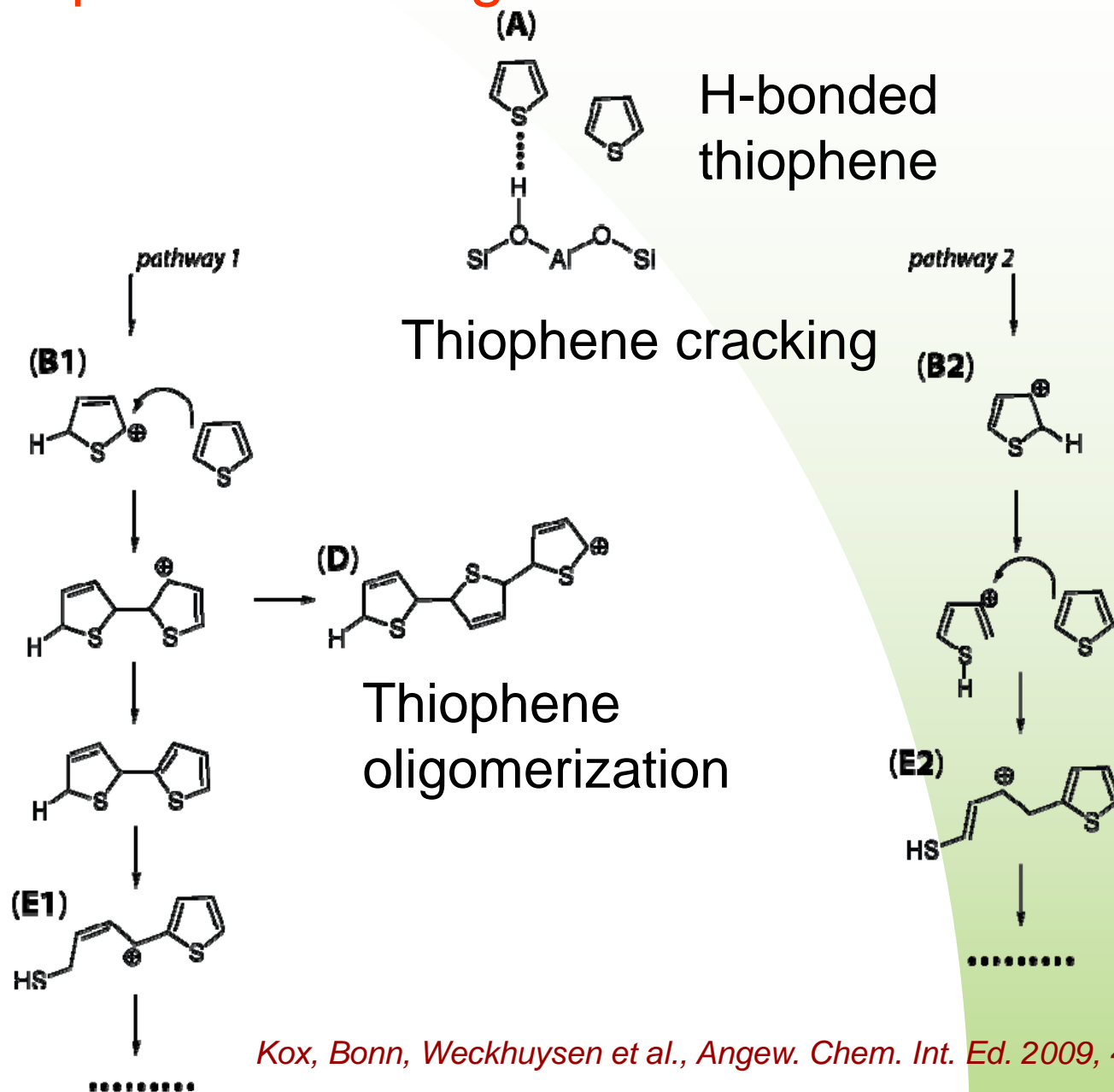


Showcase II: Thiophene cracking over H-ZSM-5

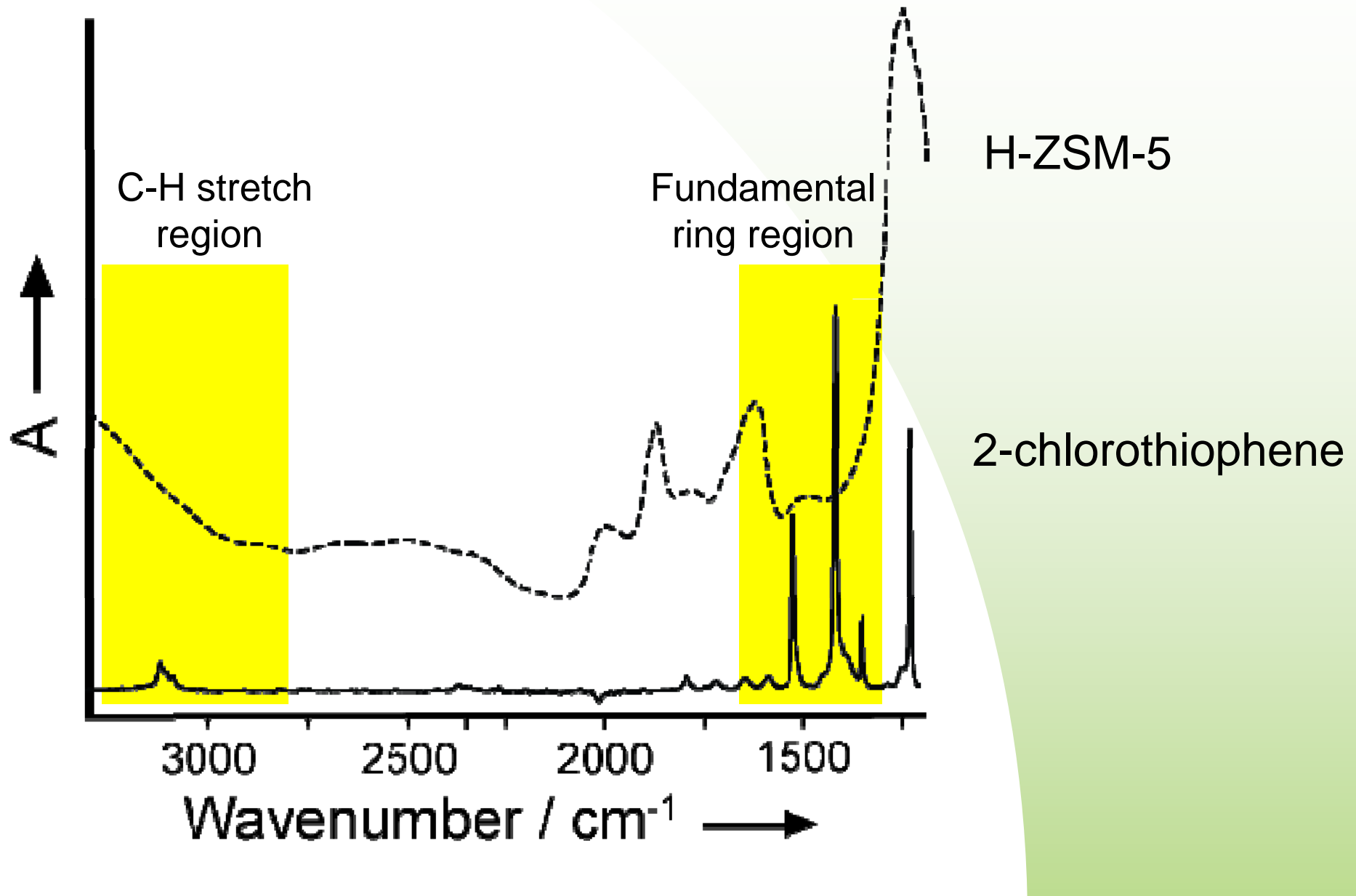




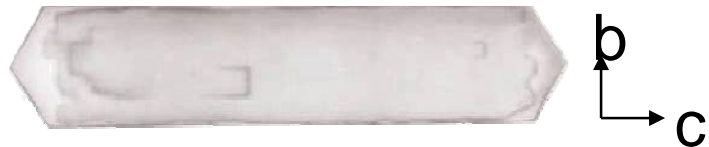
Thiophene cracking over H-ZSM-5 zeolites



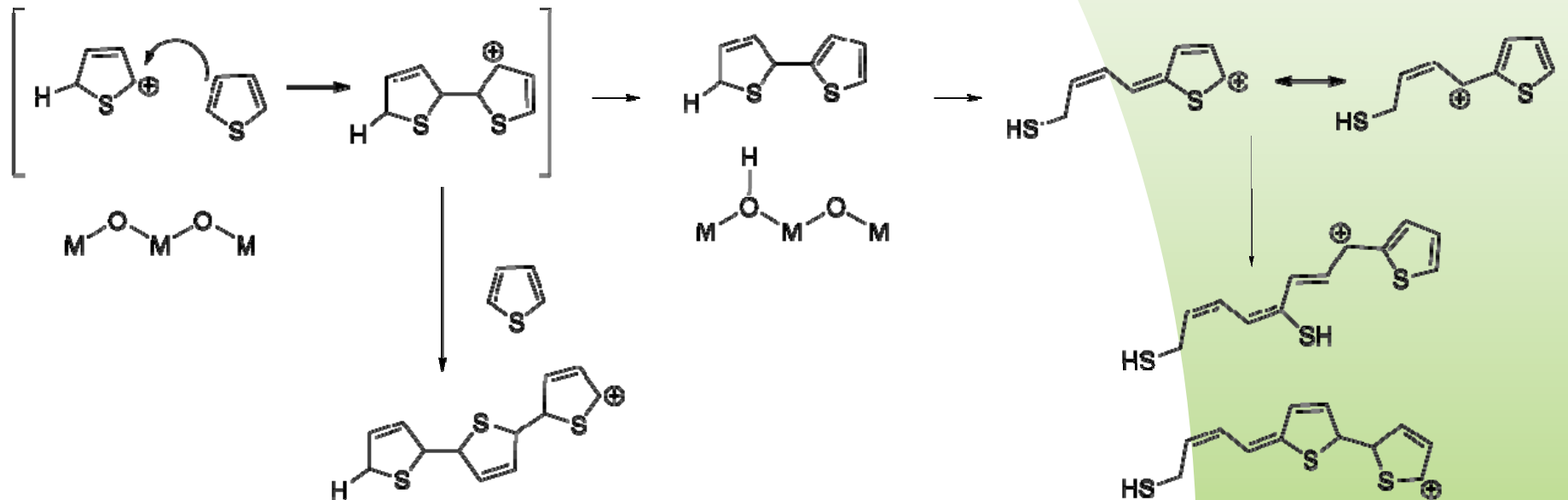
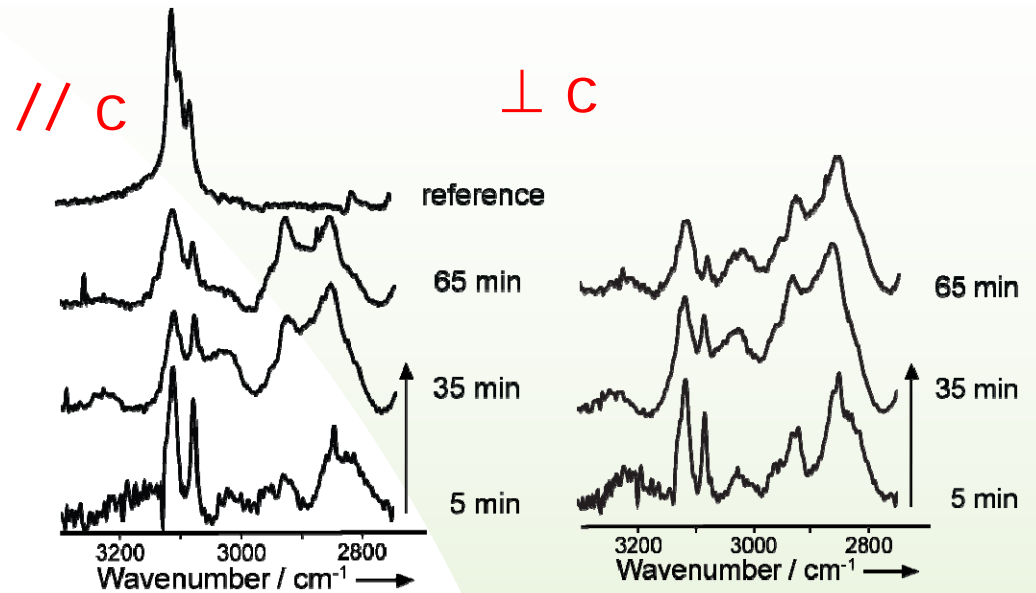
Thiophene cracking over large H-ZSM-5 crystals



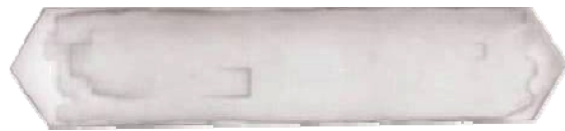
In-situ synchrotron IR microscopy at 220°C



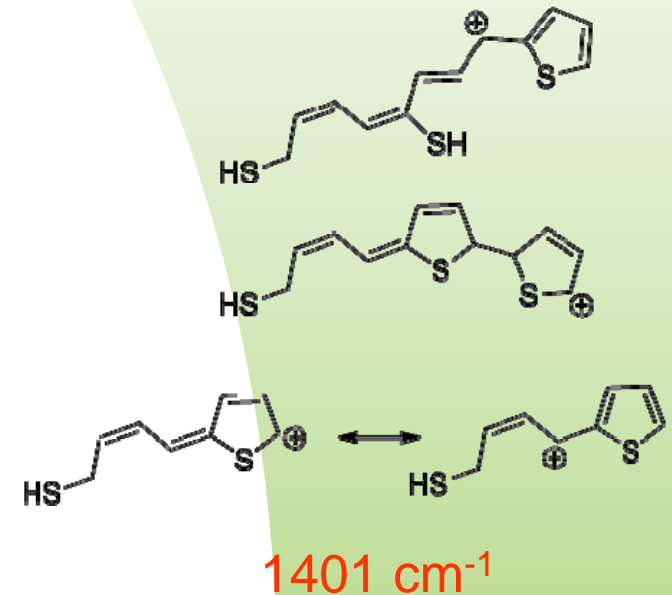
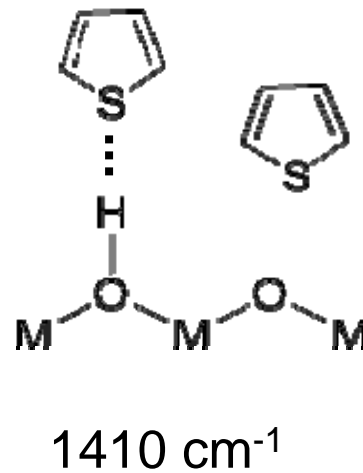
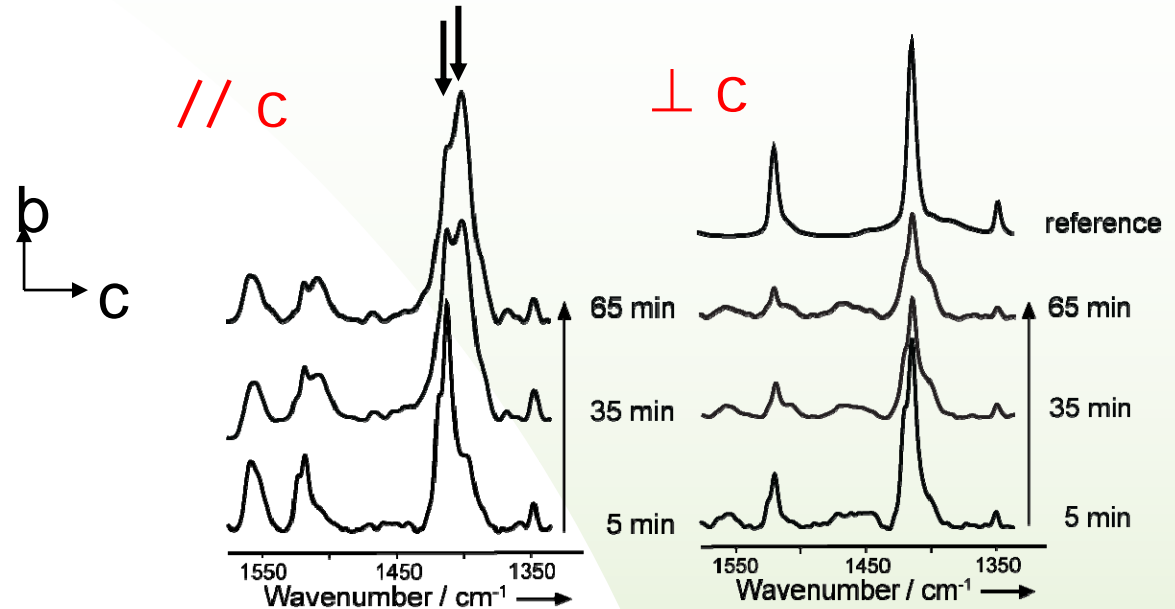
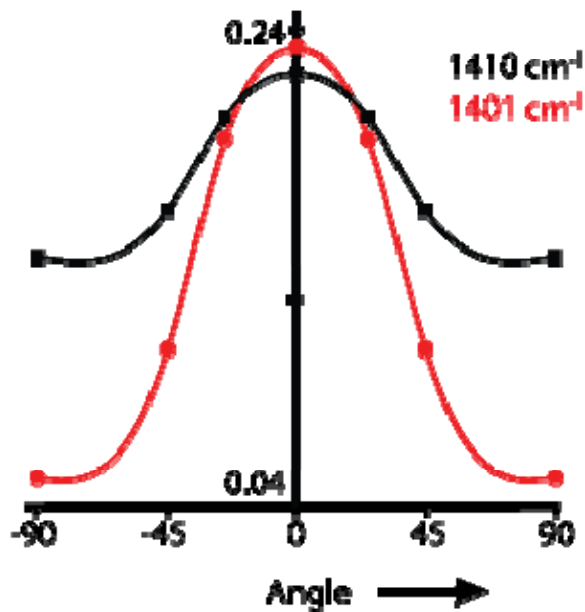
C-H stretch region



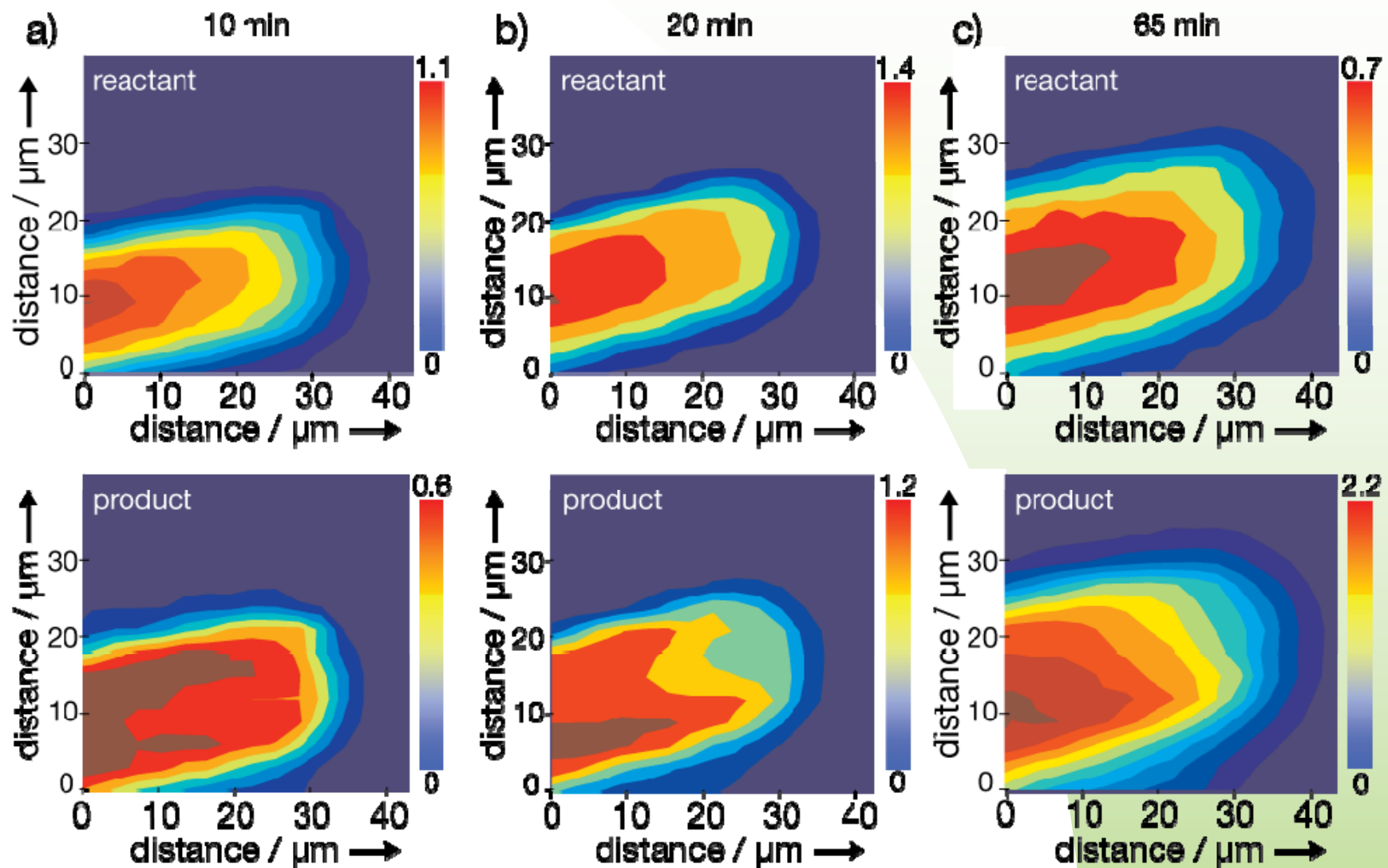
In-situ synchrotron IR microscopy at 220°C



Ring stretch region



2-D IR images of reactant (1410 cm^{-1}) and product (1401 cm^{-1})



Acknowledgements

-Bert Weckhuysen



-Marianne Kox and Eli Stavitski.



-Microscopy lab

