# Supercritical catalytic cracking of hydrocarbon feeds – Insight into selectivity and stability utilizing a combined kinetic and *operando* non-linear spectroscopy approach

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# BRI Project Objective

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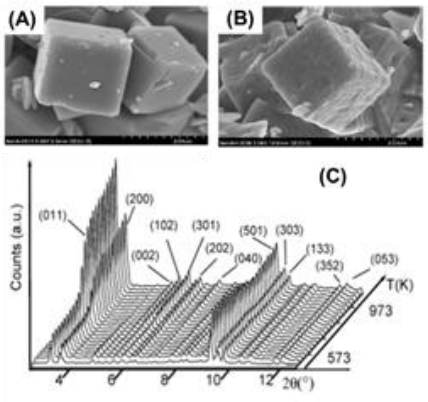
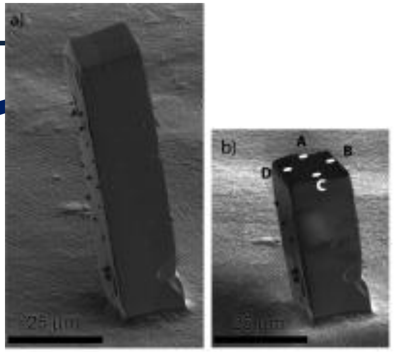
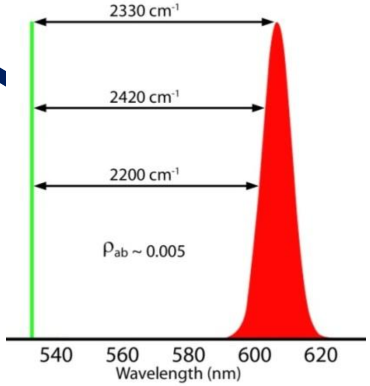
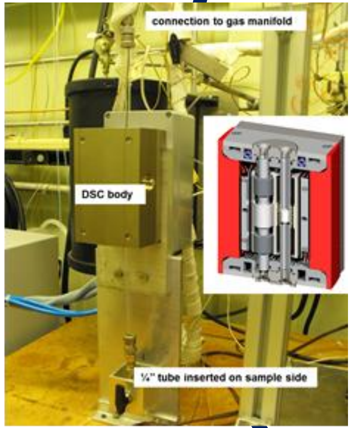
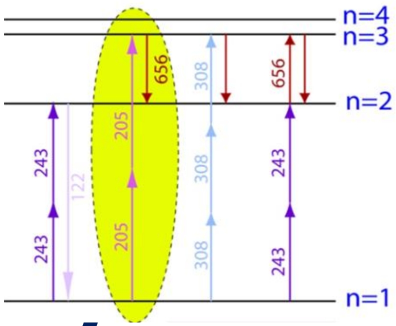



## Catalysis and *Operando* Non-linear Spectroscopy

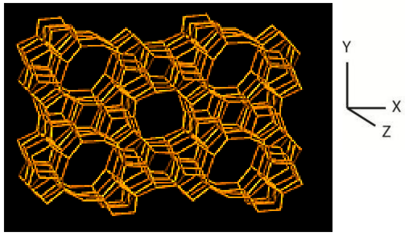


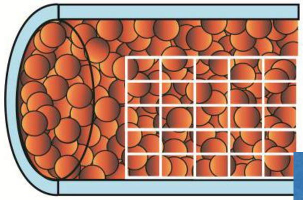

1. $A(g) + Z \underset{}{\overset{K_{ads}}{\rightleftarrows}} A(z)$

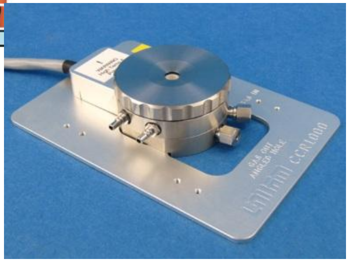
2. $A(z) + H^+Z^-$

$k_{int,c}$: $(AH^+ \cdots Z^-)^\ddagger \rightarrow P_C$ *(C-C-H)⁺-like*

$k_{int,D}$: $(AH^+ \cdots Z^-)^\ddagger \rightarrow P_D$ *(C-H-H)⁺-like*





# Catalytic Cracking is well-studied in the Petroleum Industry

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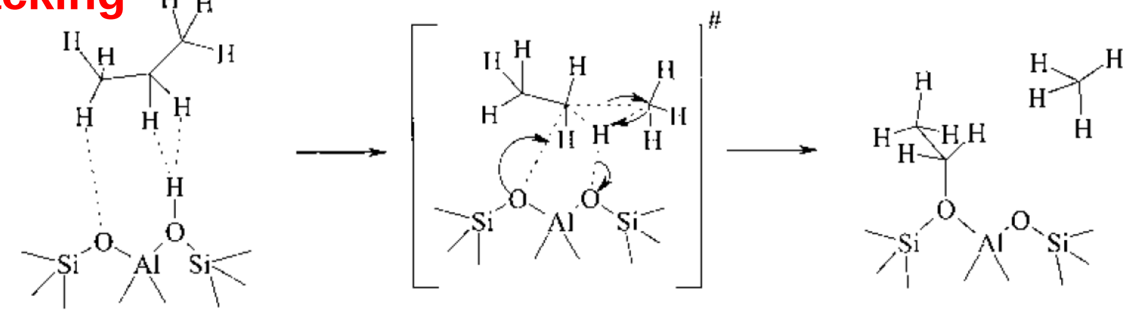
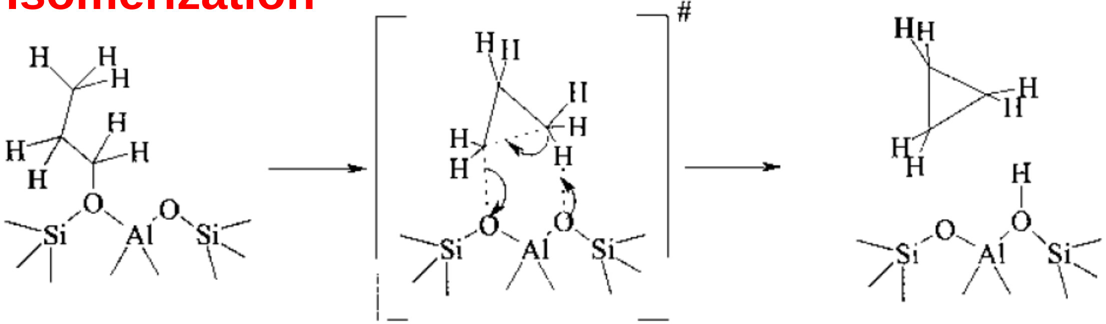
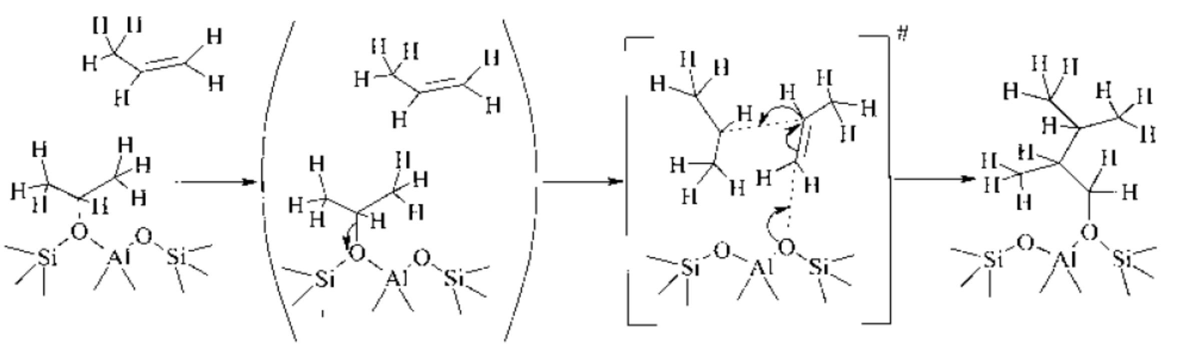
**Cracking**



**Isomerization**



**Oligomerization**



- **Product, intermediate and reaction steps can all be monitored**
  - Kinetic information
  - Reaction dynamics
  - Branching information
- **High data bandwidth allows for fast acquisition**
  - Transient phenomena
  - Time series
- **Multi-method approach**
  - CARS/SRS
  - TPLIF
- **Imaging capabilities**
  - Planar fluorescence
  - High-resolution
  - Label-free

# Diagnostic Methods for Supercritical Catalytic Cracking of Hydrocarbon Feeds

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1 8 5 5

**Challenge:** Understand the molecular scale phenomena that govern catalytic functionality in order to improve catalyst design.

**Approach:** Ultrafast, nonlinear spectroscopic methods such as coherent anti-Stokes Raman scattering (CARS) and two-photon fluorescence which have the **sensitivity**, **selectivity**, and **spatial resolution** required for studying the molecular scale phenomena.

## Ultrafast Advantages

High Peak Powers

- Nonlinear Phenomena

Ultrashort Pulses (ps-fs)

- Time Dynamics
- Spectral Bandwidth

High Repetition Rates (kHz-MHz)

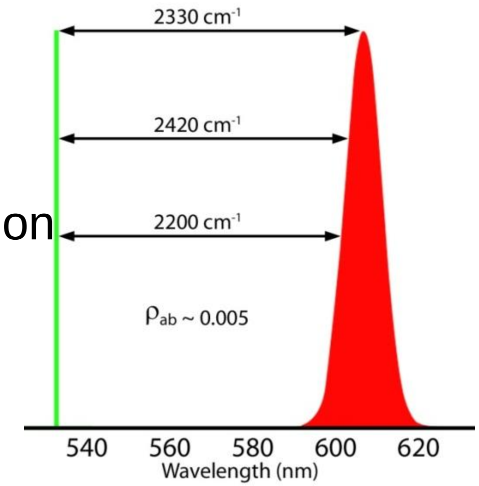
- Data-Acquisition Bandwidth
- Time Series, PSDs, Correlations

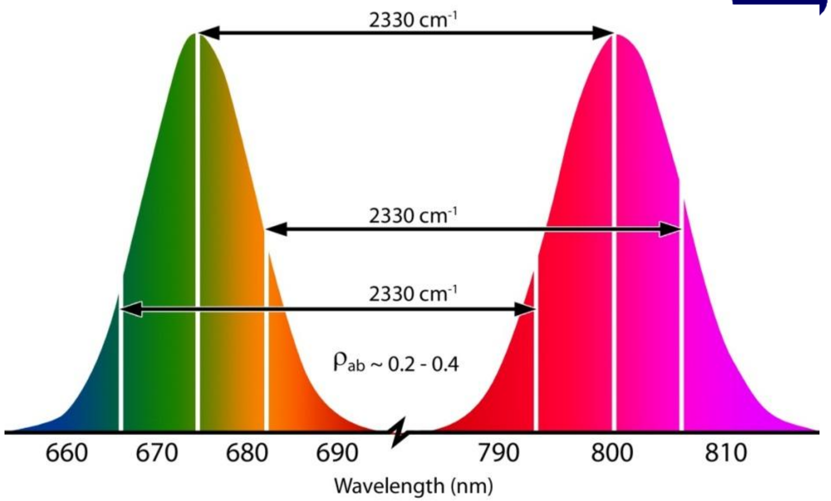
Potential to Simplify NL Spectroscopic Measurements

- Pulse-Shaping for Species Selective Detection
- Interference-free Atomic Species Measurements

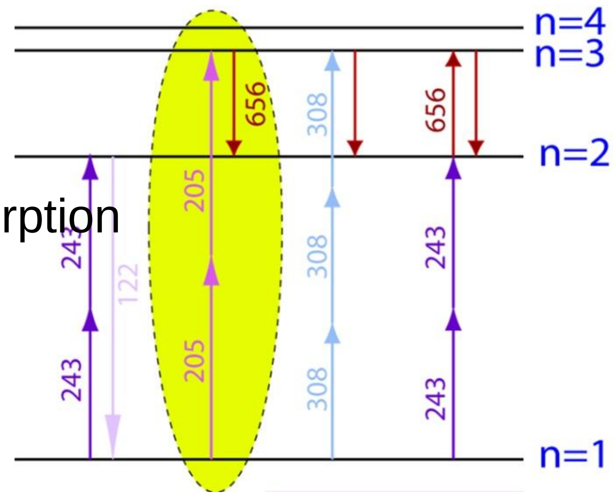
# Multi-Photon Excitation – Multiple Methods to be employed

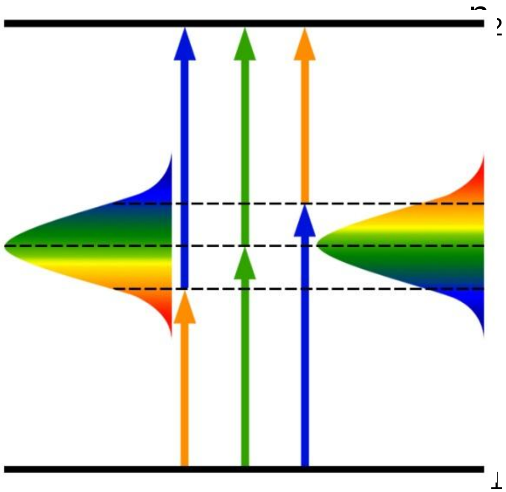
Raman Excitation




Multi-Photon Absorption
H-atom



# Coherent Anti-Stokes Raman Scattering Spectroscopy

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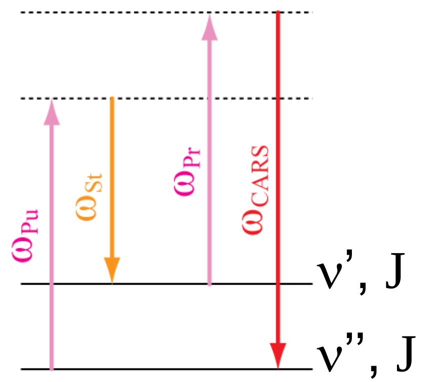
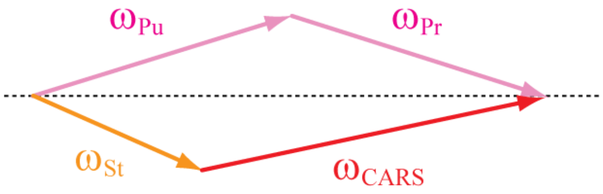
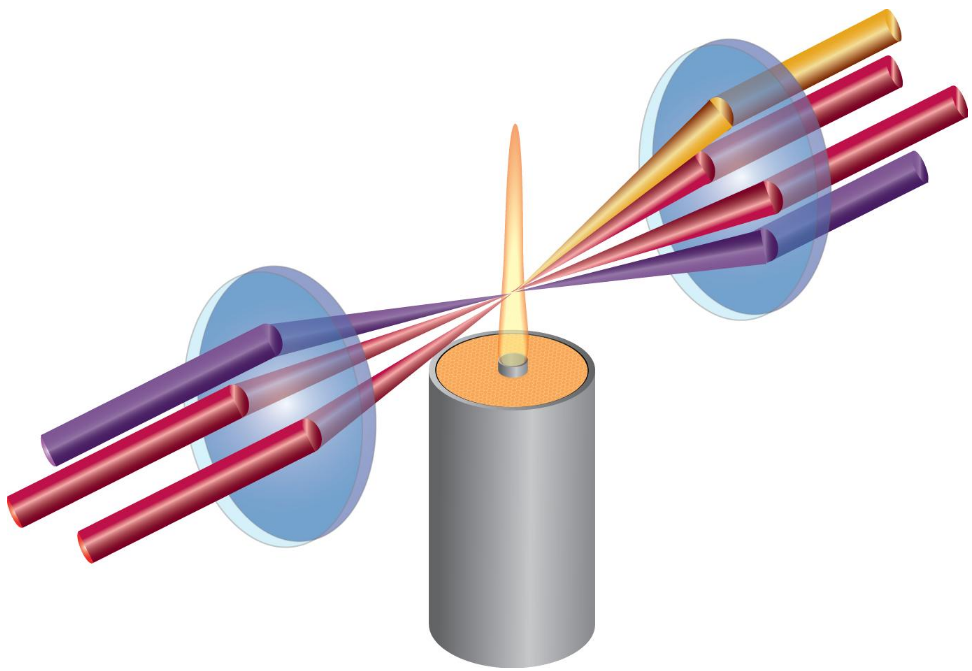
- Conventional "Single-Pump" CARS
- Noninvasive
- Coherent Laser-Like Signal
- Spatially and Temporally Resolved
- Excellent Gas-Temperature Data
- Non-resonant Background
- Collisional Effects
- Data-Acquisition Rates
- Major Species




CARS Energy-Level Diagram

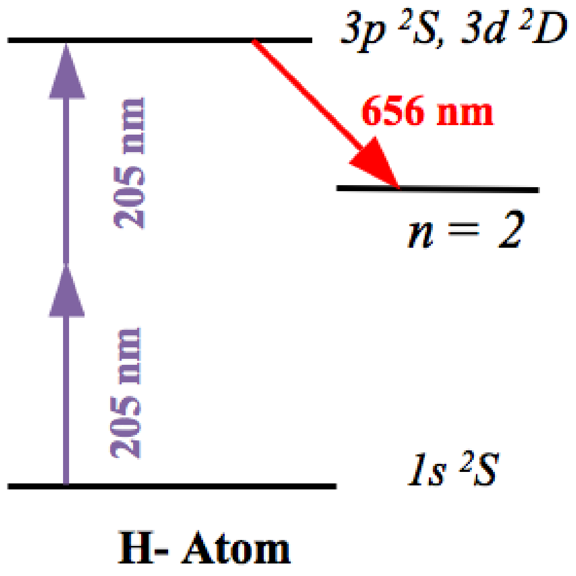



CARS Phase-Matching Diagram



# Multi-Photon Excitation in Flames

Efficient two-photon excitation

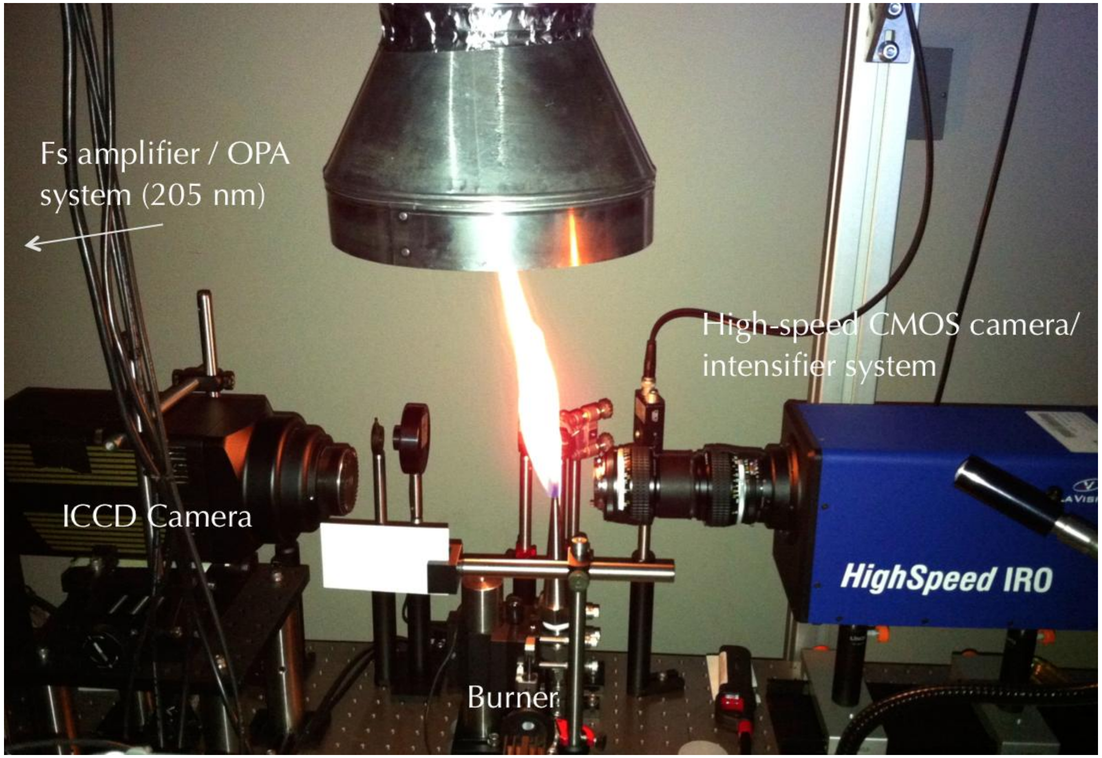



Laser System

- Ultrafast amplifier (80 fs FWHM, 2.5 mJ/pulse at 1 kHz)
- Femtosecond OPA (~ 8 μJ/pulse at **205 nm**)

Imaging System

- Intensified CCD (ICCD) camera
- High-speed visible intensifier, lens coupled to a CMOS camera



# Non-linear Spectroscopy in Catalytic Cracking-Dehydrogenation

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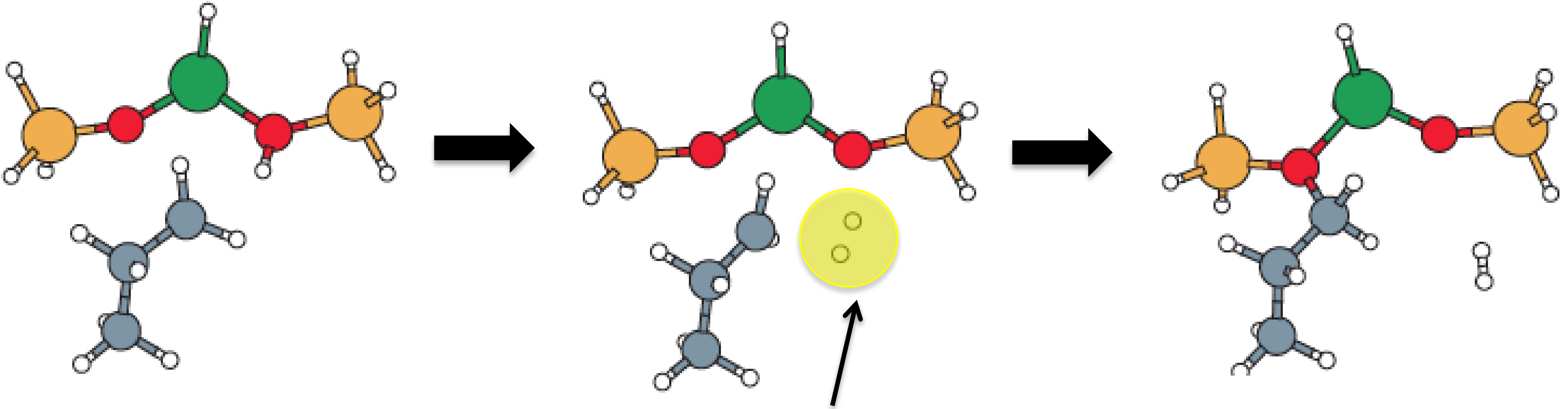
Zeolite Acid Site



Propane approaches acid site

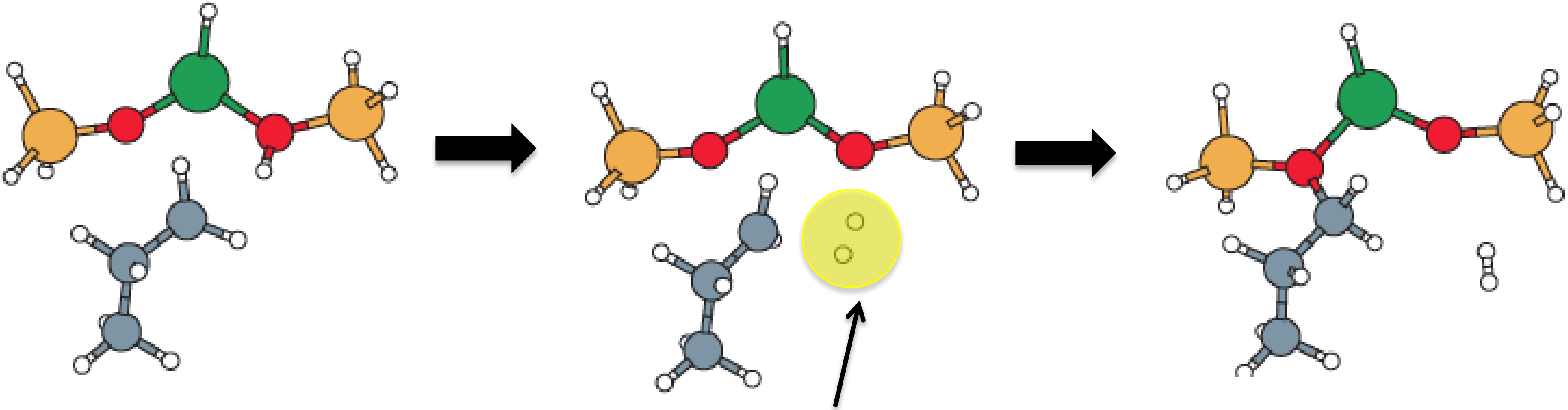
Simultaneous O-H and C-H bond breaking leading to carbocation formation

$H_2$ and *n*-alkoxy species formation which desorbs and leads to proplene formation

| Species | Formula | Raman transition ($cm^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| **dodecane** | $C_{12}H_{26}$ | 2964 | 2877 | 2855 | 1443 | 1306 | 896 |
| **methylcyclohexane** | $C_7H_{14}$ | 2940 | 2850 | 844 | 770 | -- | -- |
| **propylene** | $C_3H_6$ | 2925 | 1640 | 1415 | 1297 | 920 | -- |
| **ethylene** | $C_2H_4$ | 3020 | 1623 | -- | -- | -- | -- |

# Non-linear Spectroscopy in Catalytic Cracking-Dehydrogenation

Zeolite Acid Site



Propane transitions can be monitored for disappearance

H-atom TPLIF for formation and disappearance

Measure propene formation

| Species | Formula | Raman transition (cm$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| dodecane | $C_{12}H_{26}$ | 2964 | 2877 | 2855 | 1443 | 1306 | 896 |
| methylcyclohexane | $C_7H_{14}$ | 2940 | 2850 | 844 | 770 | -- | -- |
| propylene | $C_3H_6$ | 2925 | 1640 | 1415 | 1297 | 920 | -- |
| ethylene | $C_2H_4$ | 3020 | 1623 | -- | -- | -- | -- |

# Non-linear Spectroscopy enables us to access various C-H and C-C Transitions

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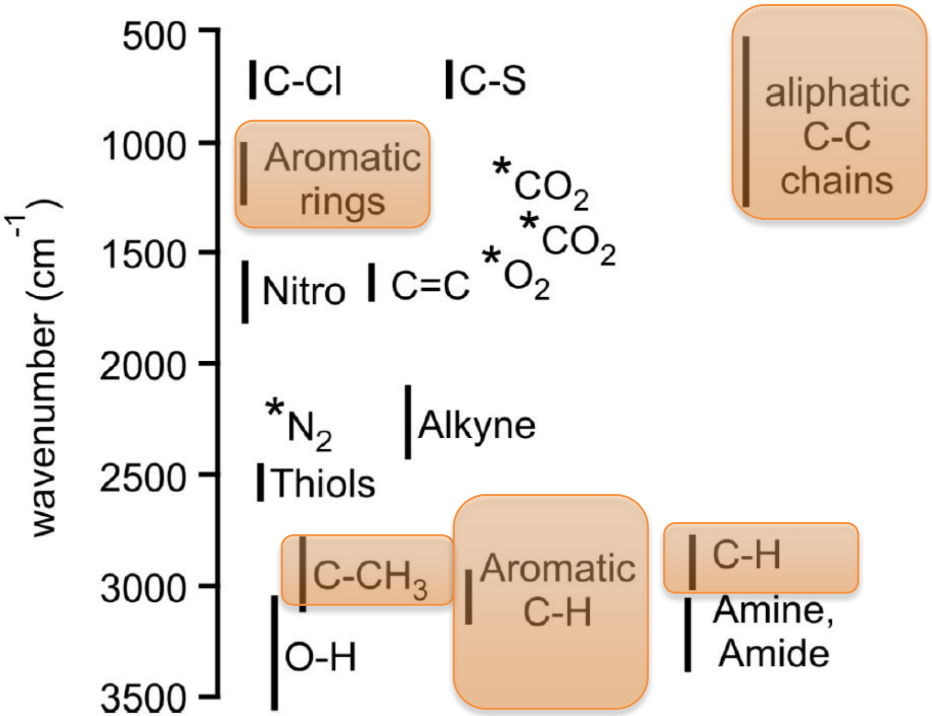
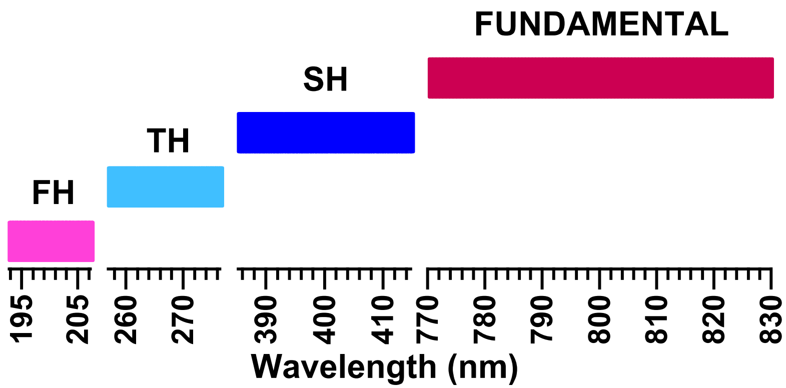
## Accessible CARS/SRS transitions



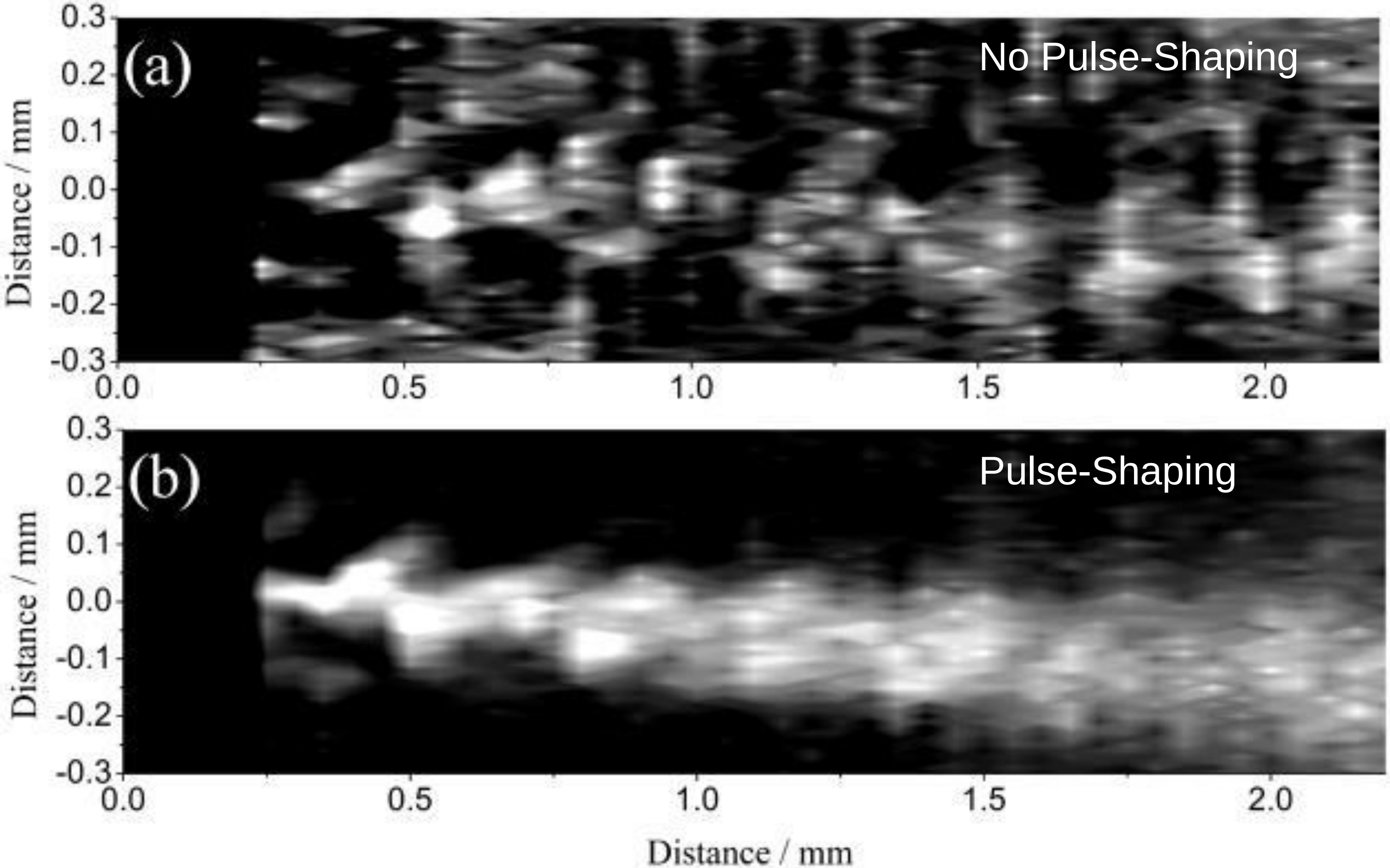

## TPLIF excitation wavelengths




- Cation formation during activation (Fundamental)
- Organic molecules and solvents (SH and TH)
- Atomic gas phase species (FH)

# Pulse-Shaping for Species Selective CARS Imaging

## Imaging of a $CO_2$ Jet

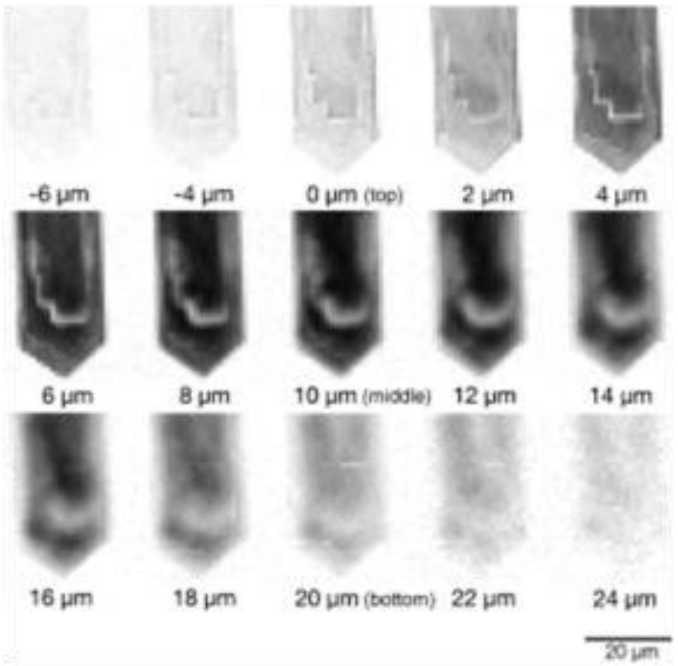



Wrzesinski *et al.*, J. Raman Spec. **42** (2011) 393

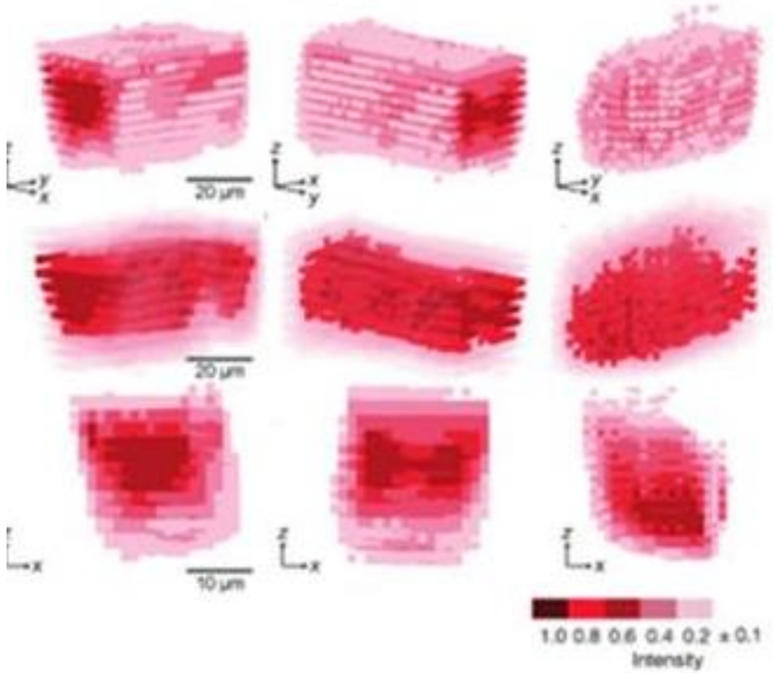
# CARS Imaging of Catalytic Materials – Two Approaches

- 3D-CARS imaging of single-bodied catalyst demonstrated
  - High spatial resolution
  - No molecular tagging needed

**2-D**



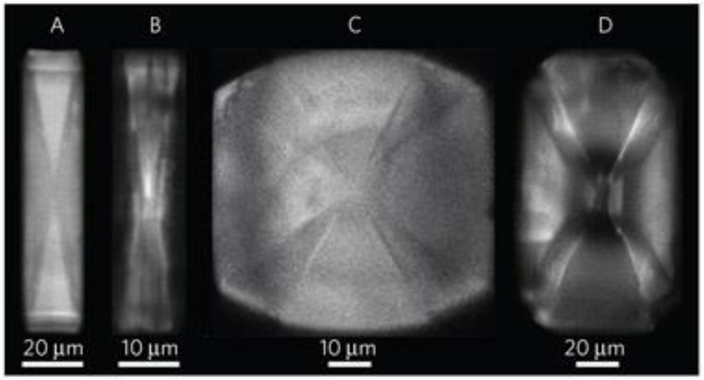

**3-D reconstruction**



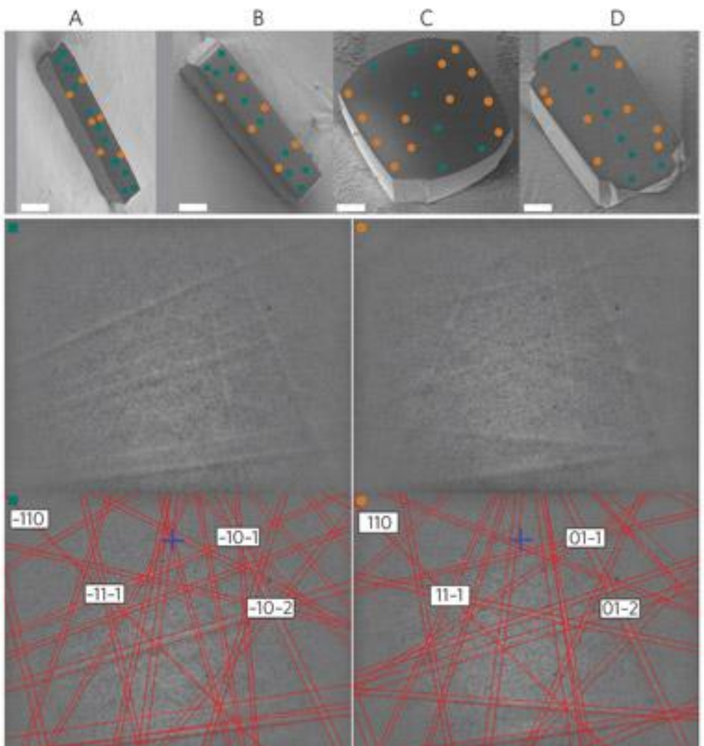

Kox *et al.*, Agnew. Chem. Int. Ed **48** (2009) 8990

# Complete SEM-EBD Crystallographic Determination of Single Catalyst Bodies Combined with Chemical Imaging

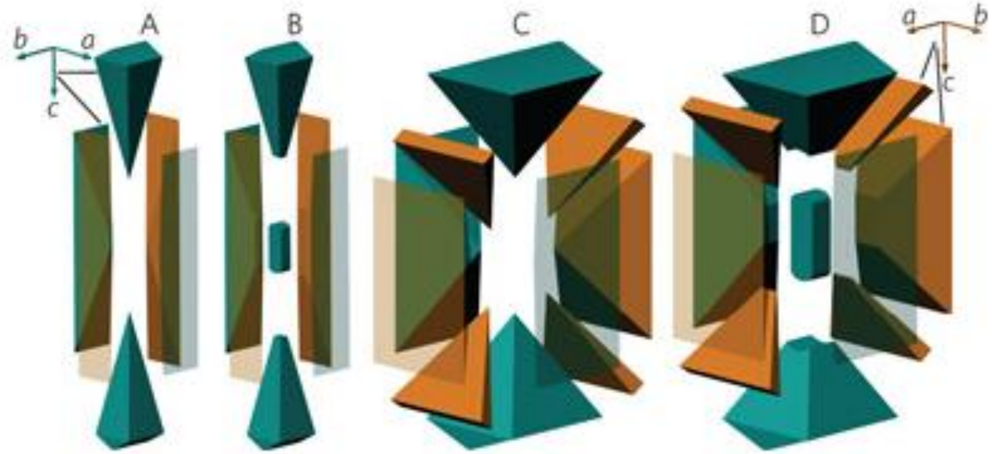
SEM



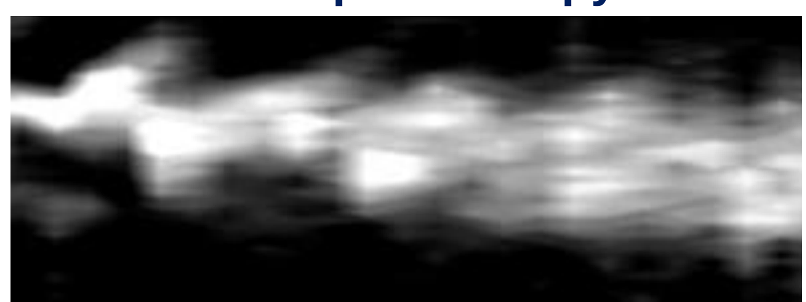

EBSD




**COMPLETE crystallographic determination**




**COMPLETE chemical imaging by non-linear spectroscopy**



# Misaligned Interfaces between Sub-units in Zeolite Single Bodies give Rise to Diffusion Limitations

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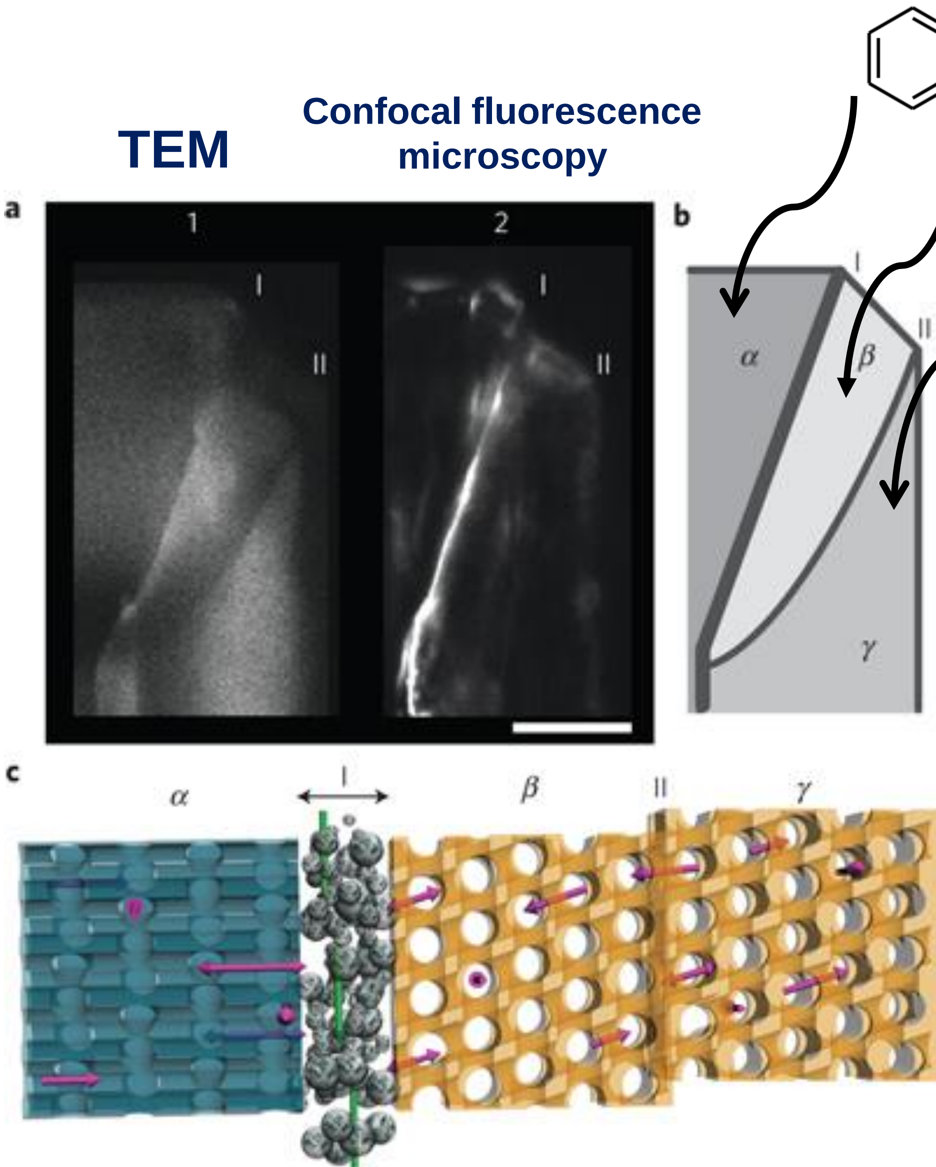


**Are these diffusional barriers responsible for PAH/coke formation?**

**Can one identify that the space created by misalignment of subunits is the nucleation site of coke formation?**

**We plan to utilize non-linear chemical imaging spectroscopies to fingerprint the species in these misaligned zones?**

# Focused Ion Beam (FIB) Milling allows Materials Profiling in the Third Dimension

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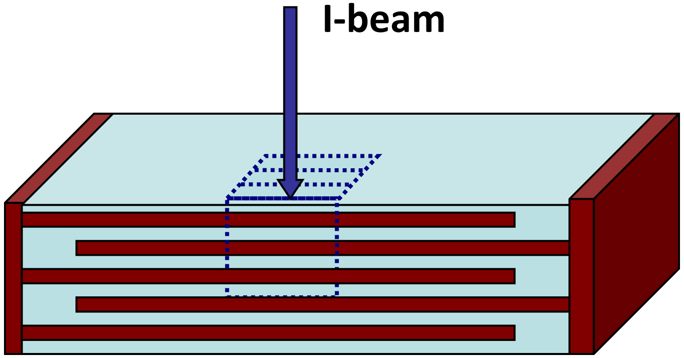
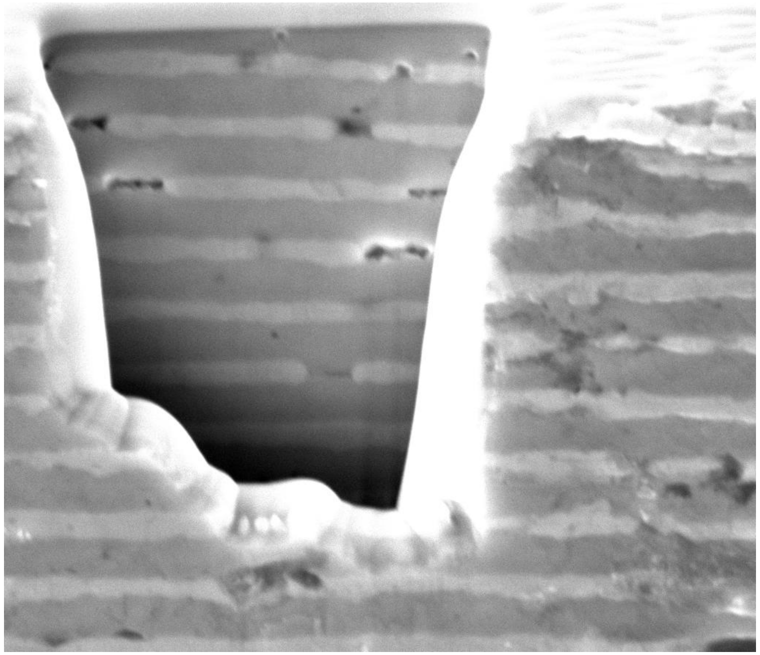
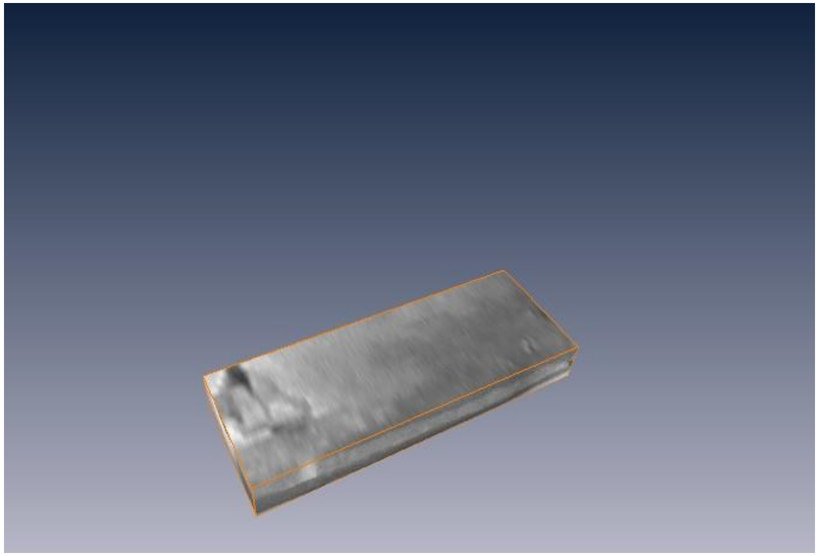


~ 1 µm

**Serial sections reveal heterogeneities in third dimension**



# CARS Imaging of Single Catalyst Bodies Modified by Focused-Ion Beam Milling

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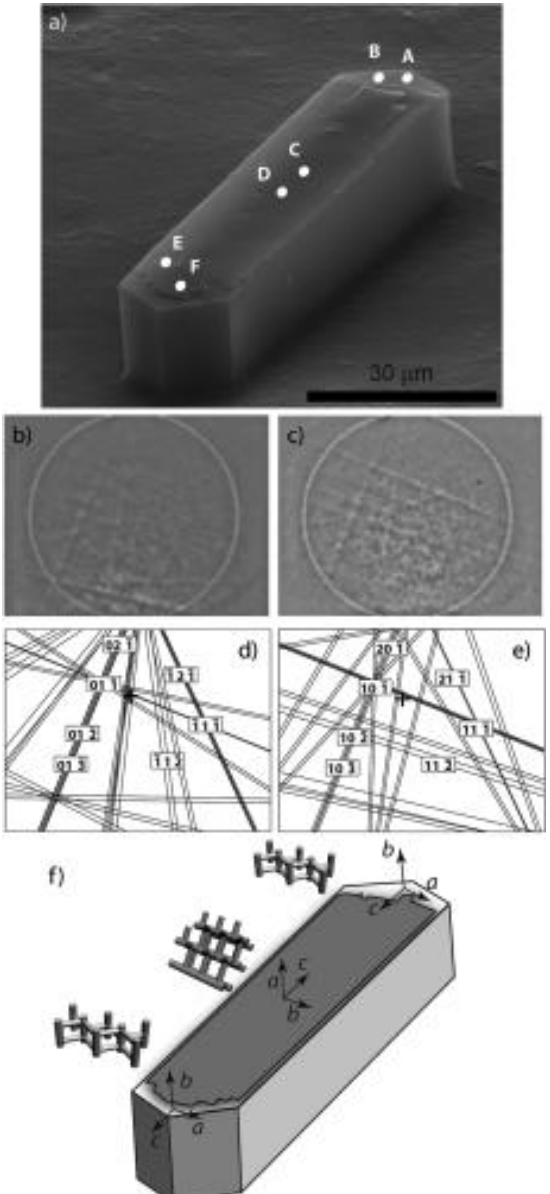
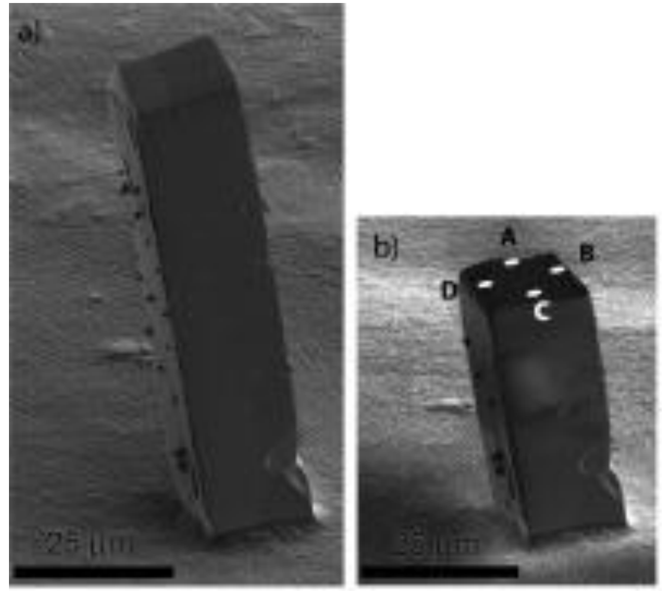
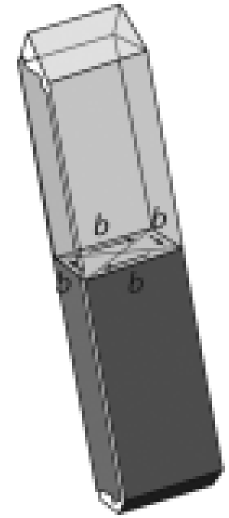



## Utilize FIB to selectively remove sub-sections




## COMPLETE chemical imaging by non-linear spectroscopy

# *Operando* Non-linear Spectroscopy Measurements of Catalyst Bodies and Reactor Beds

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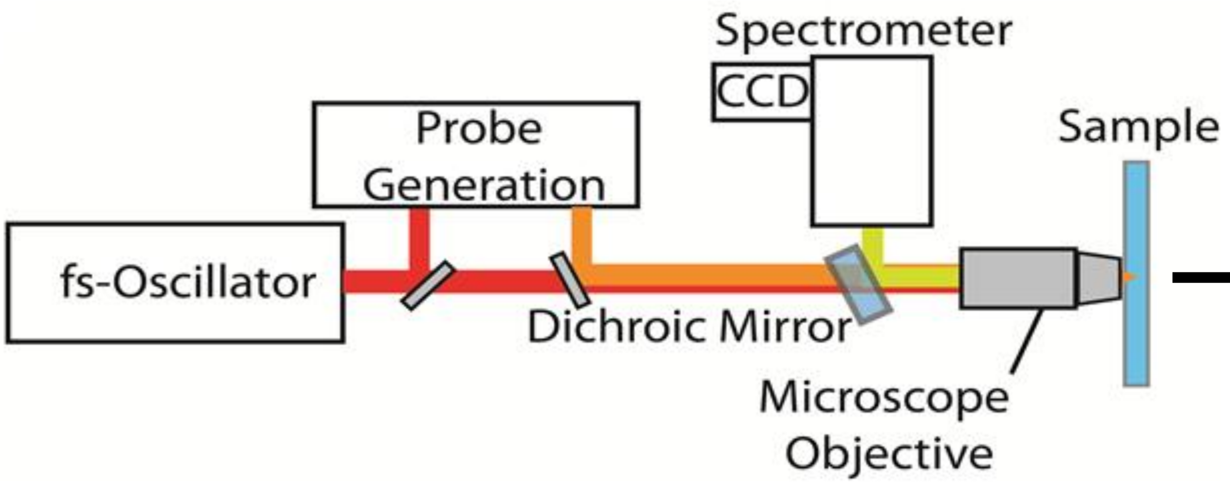
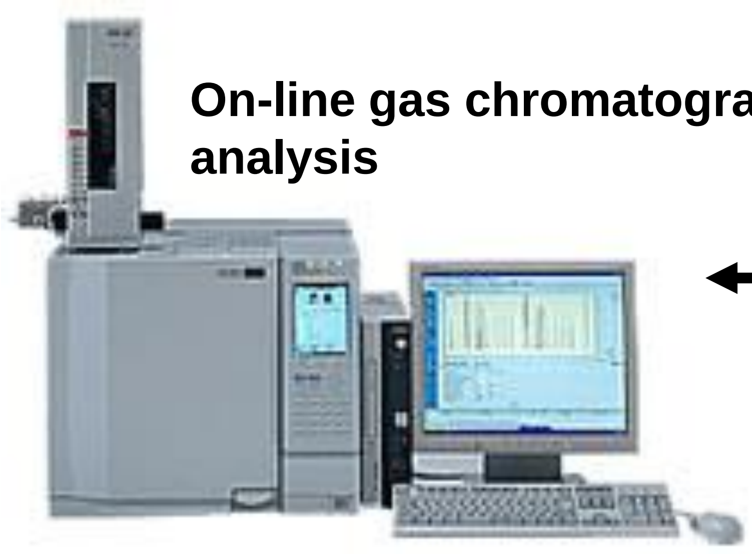
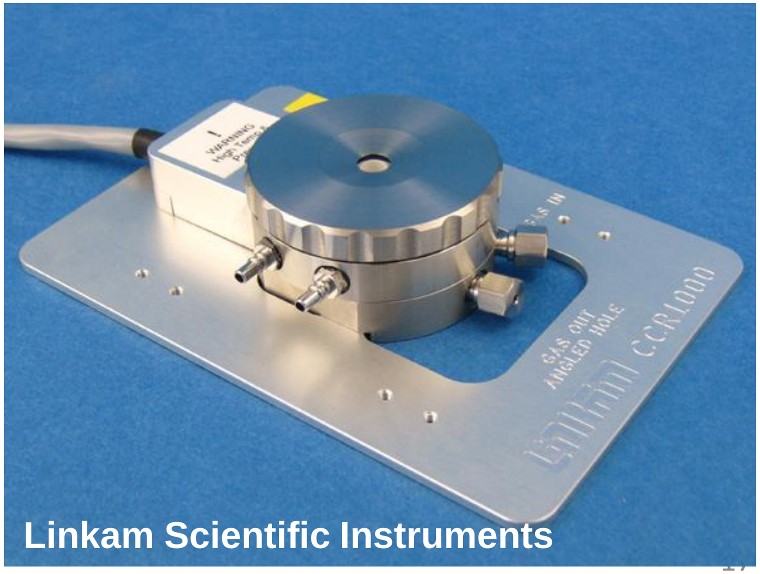
## *General set-up at Spectral Energies for gas-phase imaging*




**Replace burner with *in-situ* flow cell**

**On-line gas chromatography analysis**






Linkam Scientific Instruments

# 3D CARS Imaging of Real Reactor Beds

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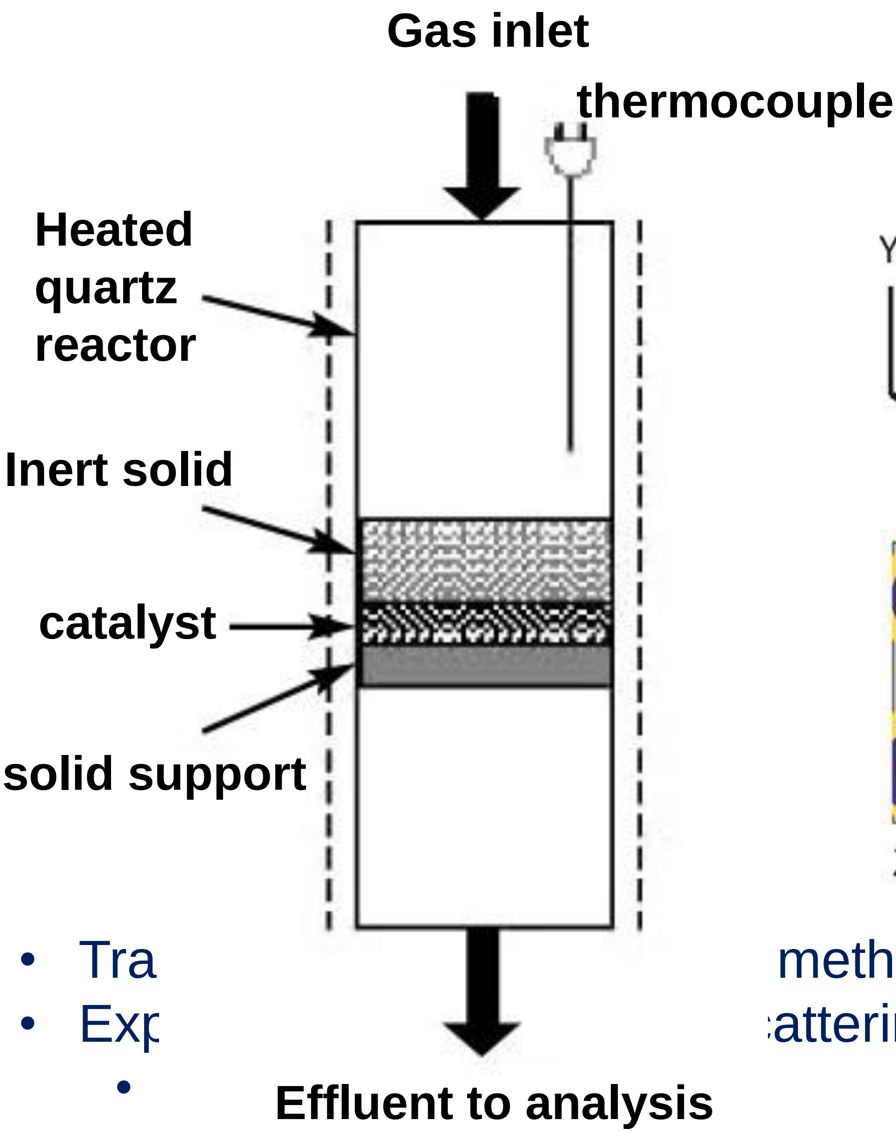


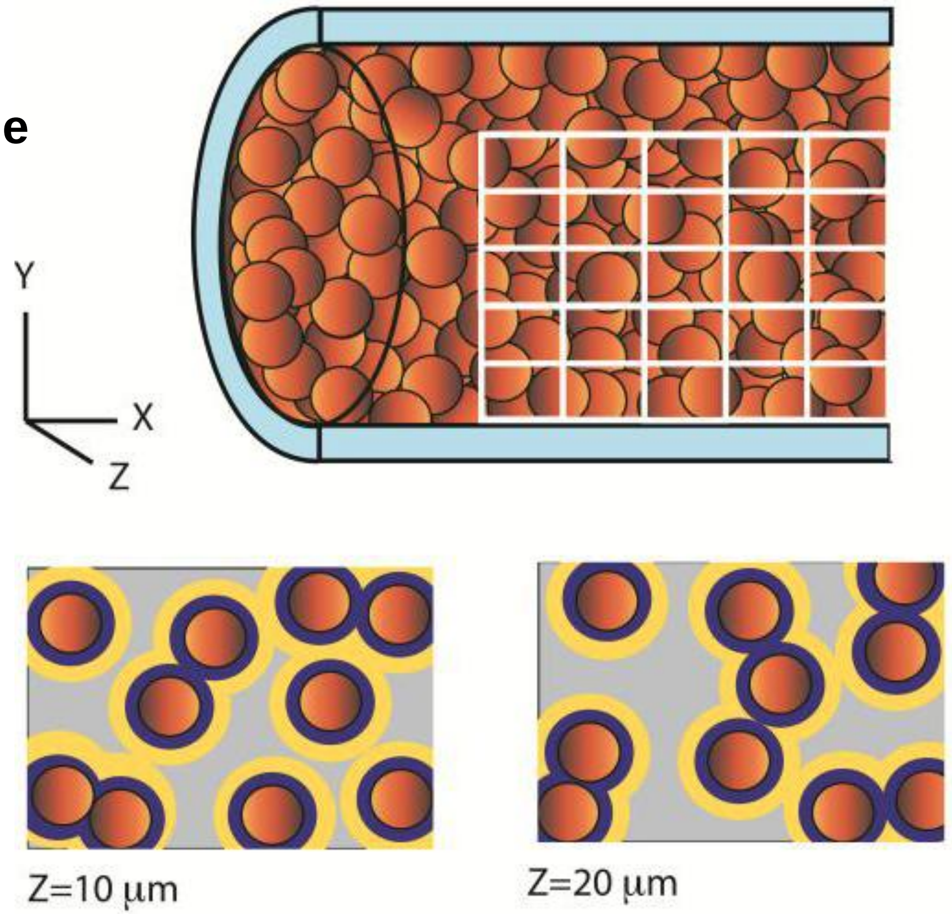


- Tra methods for use in reactor beds
- Exp attering (SRS) imaging for catalytic materials
  - 
  - Non-resonant elimination

# Atomic Two-photon Fluorescence Imaging using Femtosecond Excitation

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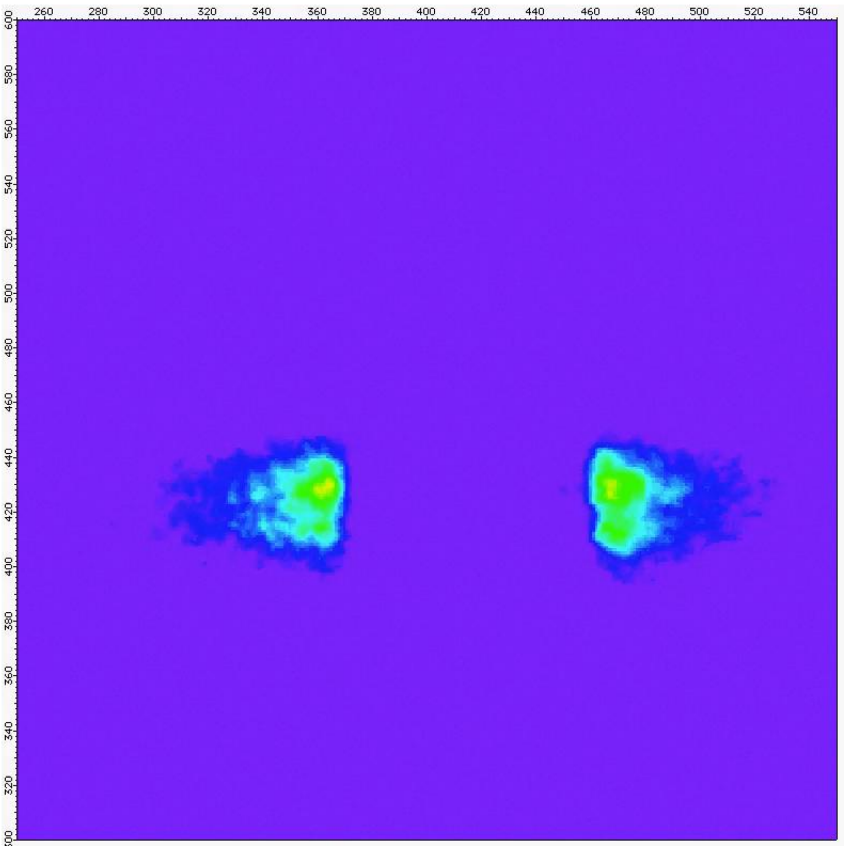
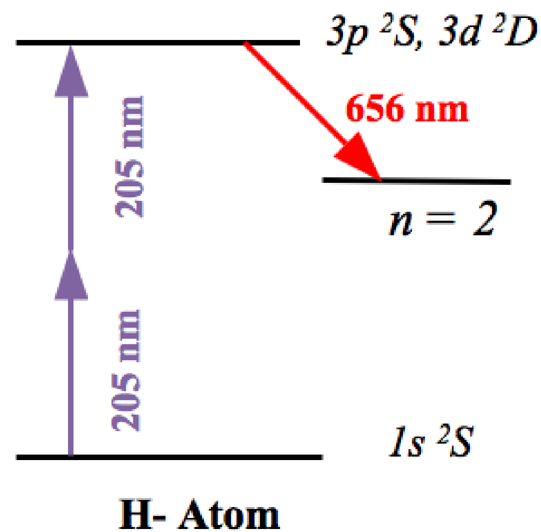
## Planar Imaging of Atomic Hydrogen (2D)




- Access to VUV transitions via 2-photon pathways
- Imaging 1-10 kHz rates
- Full 2D imaging (PLIF)

# Atomic Two-photon Fluorescence Imaging using Femtosecond Excitation

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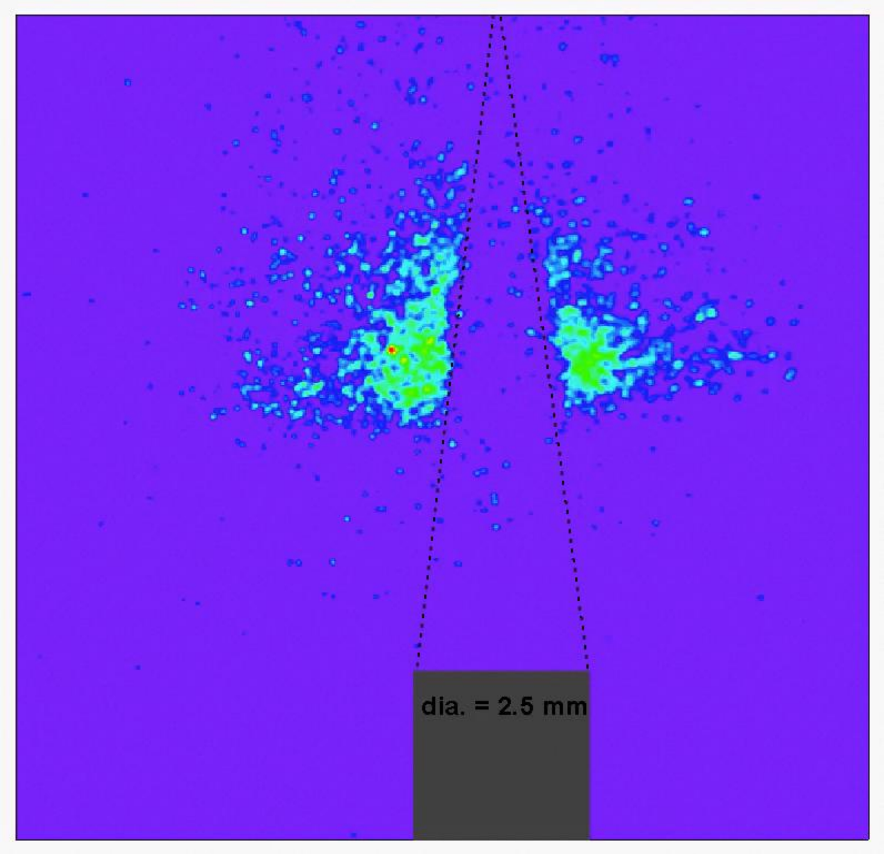
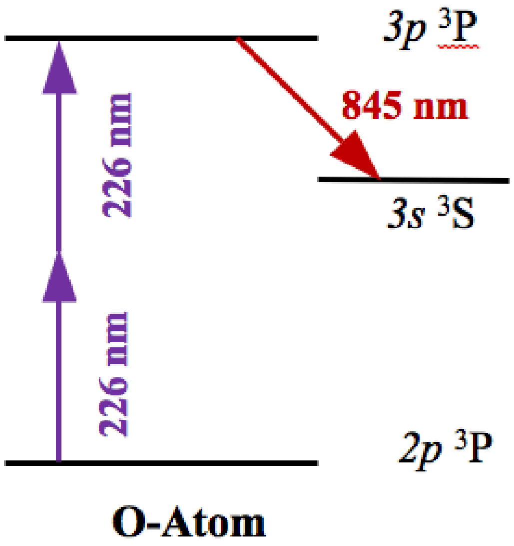
### Planar Imaging of Atomic Oxygen (2D)



# Femtosecond TPLIF Line Imaging allows for Interference-free Imaging of Atomic Species

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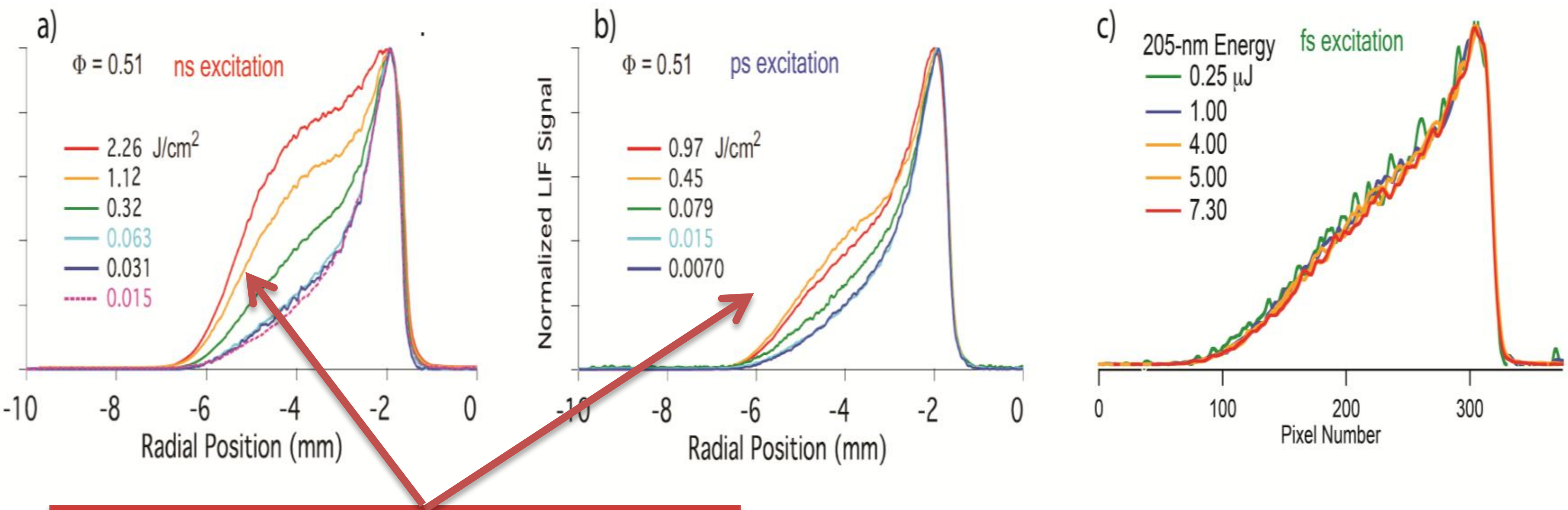


Photolytic production of H-atom

- Femtosecond excitation eliminates photolytic production
- Imaging rates of 1-10 kHz
- Critical for hydrocarbon fuels which contain large amounts of hydrogen

Kulatilaka *et al.*, Appl. Opt. **47** 4672-4683 (2008)
Kulatilaka *et al.*, Opt. Letters. **37** 3051-3053 (2012)

# Task Breakdown for Catalysis Portion of BRI

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| | Year 1 | Year 2 | Year 3 |
|---|---|---|---|
| Conduct baseline kinetic studies utilizing MFI- and other zeolite topologies for dodecane cracking at sub- and supercritical conditions | X | X | X |
| $^{13}C/^{12}C$ and $^{1}H/^{2}H$ isotope exchange experiments to elucidate mechanism for cracking and dehydrogenation pathways for single and multi-component feedstreams at sub- and supercritical conditions | | X | X |
| Synthesize zeolite single body catalysts, and examine their reactivity utilizing GC/MS | X | X | |
| Perform on-line calorimetric measurements to determine heat duty and correlate with activity/selectivity and stability of zeolite material | X | X | |
| Perform carbon mass balance via on-line TGA as a function of zeolite composition and single body dimensions. Identify 'soluble' carbon species formed inside of zeolite bodies by combined HPLC-UV-Vis-LC measurements (Wornat); Compare with 3D imaging studies | X | X | X |
| Examine stability of zeolites (w/ and w/o metal incorporation) by Bragg XRD and synchrotron-based total scattering with PDF analysis | X | X | |
| Synthesis, characterization, and reactivity studies of single lamellar zeolite films | | | X |

# Task Breakdown for Chemical Imaging of BRI

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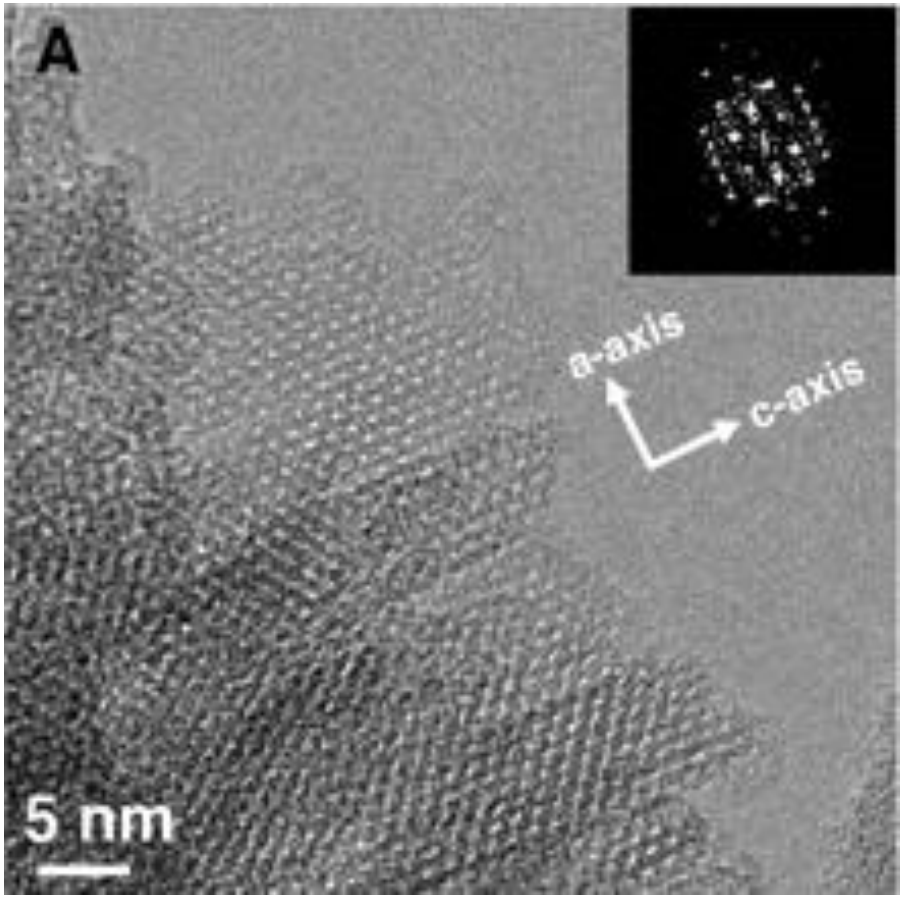
| | Year 1 | Year 2 | Year 3 |
|---|---|---|---|
| Complete set -up of imaging system for single catalyst bodies. | X | | |
| Perform fundamental imaging study on single catalyst bodies to determine instrument response function (i.e. sensitivity, resolution, acquisition rate). Develop data processing procedure and software for single catalyst bodies. | X | | |
| Perform atomic multi-photon imaging on single catalyst bodies, reaction bed and reaction gases. | X | X | |
| Complete set-up CARS microspectroscopy. Perform imaging studies for 3D measurement of reaction dynamics in single catalyst bodies and imaging studies for 3D measurement of PAHs in single catalyst bodies | X | X | X |
| Perform CARS microspectroscopy and imaging on reaction beds for measurements of carbon deposition. Verify carbon deposition measurements with HPLC-UV-Vis-LC measurements. | | X | X |
| Purchase components and complete set-up for 3D SRS imaging. Perform 3D SRS imaging on single catalyst bodies. | | X | X |
| Complete operando measurements of the reactor-bed and the interacting gas-phase. Continue studies on reactor beds using developed CARS and multi-photon methods. | | X | X |

# Catalyst *Design* for Endothermic Cooling via Hydrocarbon Cracking




Zhang *et al. Science* **336** (2012) 1684

Repetitive branching during one-step hydrothermal crystal growth to synthesize a new hierarchical zeolite made of orthogonally connected microporous nanosheets

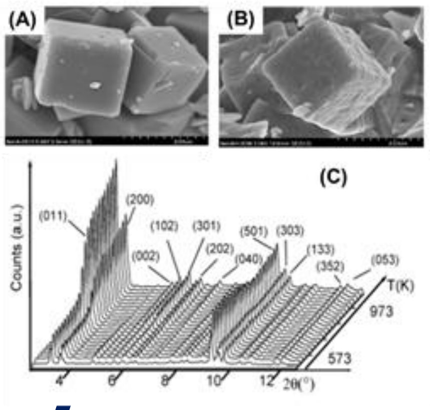
nanosheets are 2 nm thick and contain a network of 0.5 nm **micropores**.

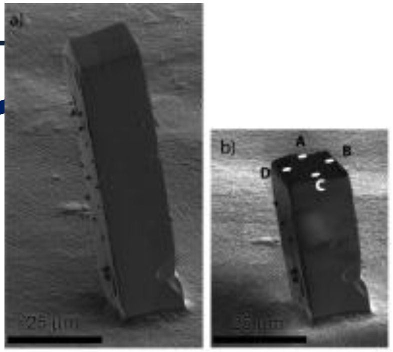
permanent network of 2- to 7-nanometer **mesopores**

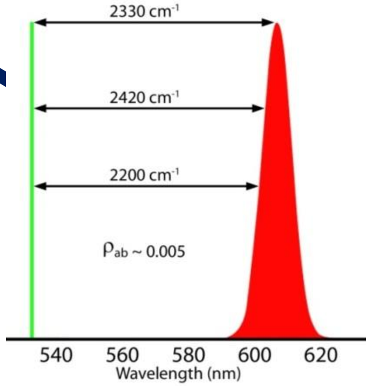
high external surface area

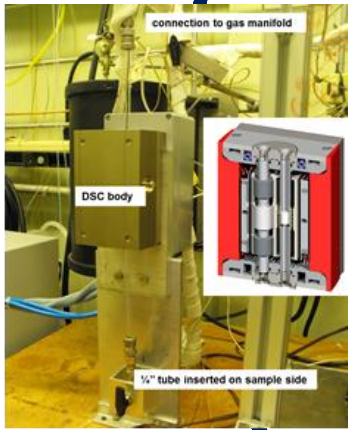
**reduced micropore diffusion length**

# BRI Project Objective

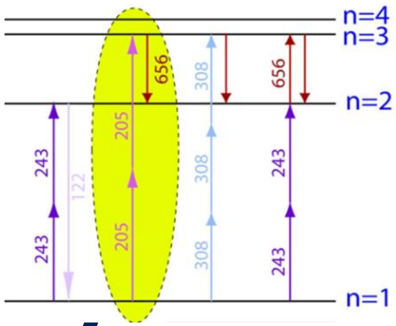



## Catalysis and *Operando* Non-linear Spectroscopy




1. $A(g) + Z \underset{}{\overset{K_{ads}}{\rightleftarrows}} A(z)$

2. $A(z) + H^+Z^-$

$k_{int,c}$: $(AH^+ \cdots Z^-)^\ddagger \rightarrow P_C$ *(C-C-H)⁺-like*

$k_{int,D}$: $(AH^+ \cdots Z^-)^\ddagger \rightarrow P_D$ *(C-H-H)⁺-like*