Laboratoire
Catalyse & Spectrochimie

Vibrational Spectroscopy for porous functional materials

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Normandie Université

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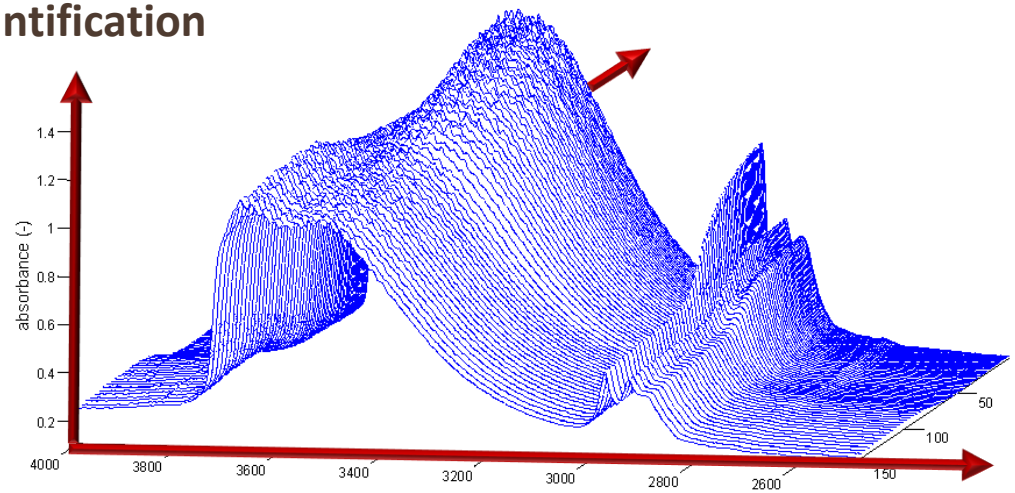
Outline

- Which informations can be obtained ?
- Recent instrumental developments
- Examples
- Perspectives

Vibrational spectroscopies: which informations ?

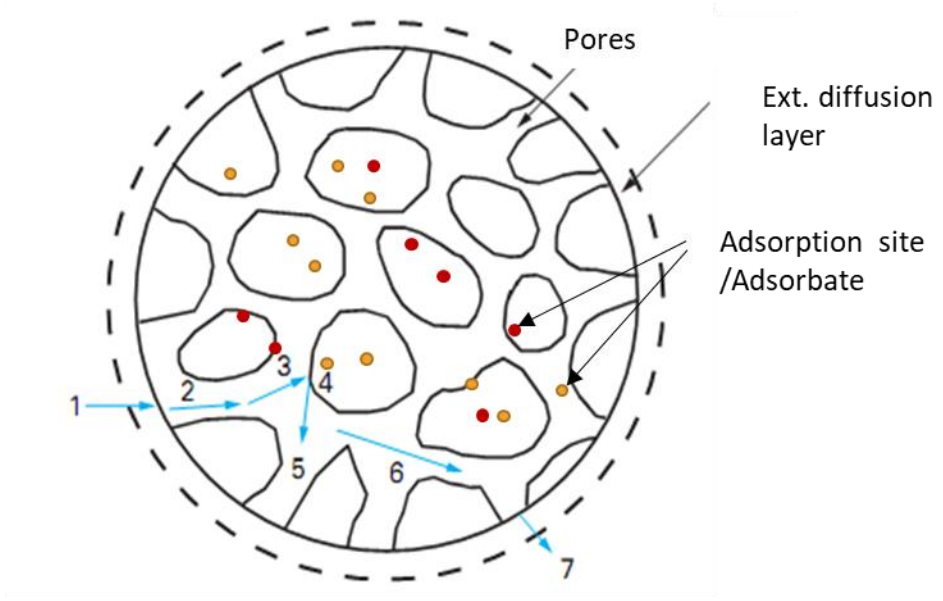
Band intensities
Quantification

Experimental variable: t, T, P, Ci
Thermo / kinetic parameters



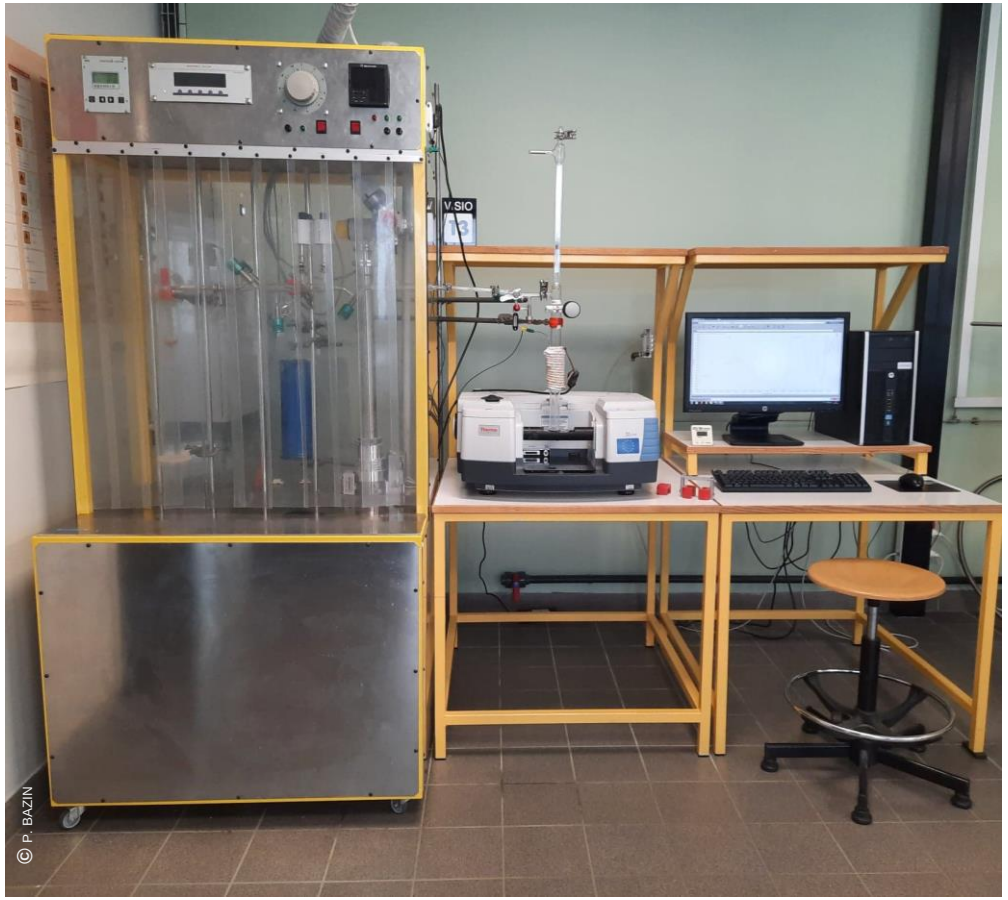
Band frequencies:
Identification

In porous adsorbants or catalysts:



- Nature/number of adsorption sites/adsorbates
- Internal diffusion rate
- Adsorption parameters / « strength » of adsorption sites
- Surface reaction rate constants and parameters

In situ vs *Operando*



- Vacuum or static atmosphere
- Clean/activated surfaces
- => materials characterization

- Flow of reactants
- Simultaneous recording of activity
- => reaction mechanisms

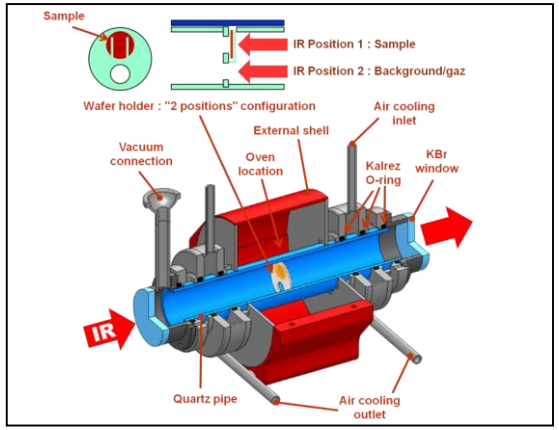
in situ cells

RT

Low T

Classic designs

RT



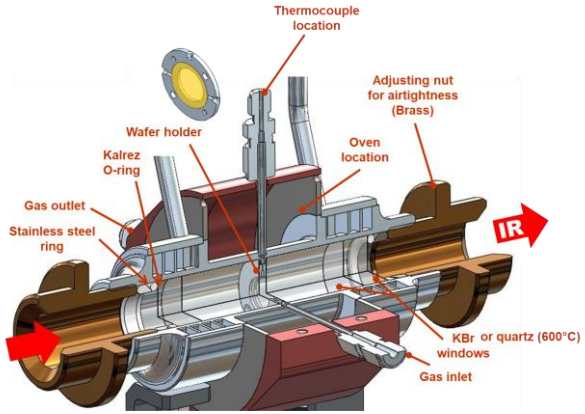
High T

Multi-sample

Fully automated

Operando cells

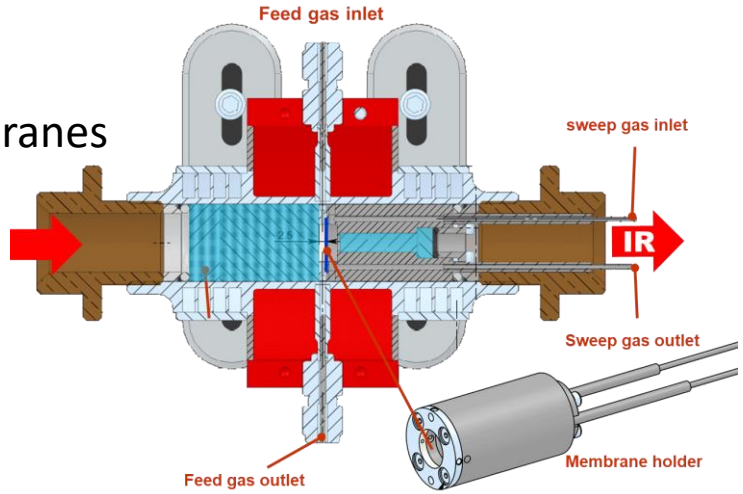
Sandwich cell
"workhorse" Operando cell

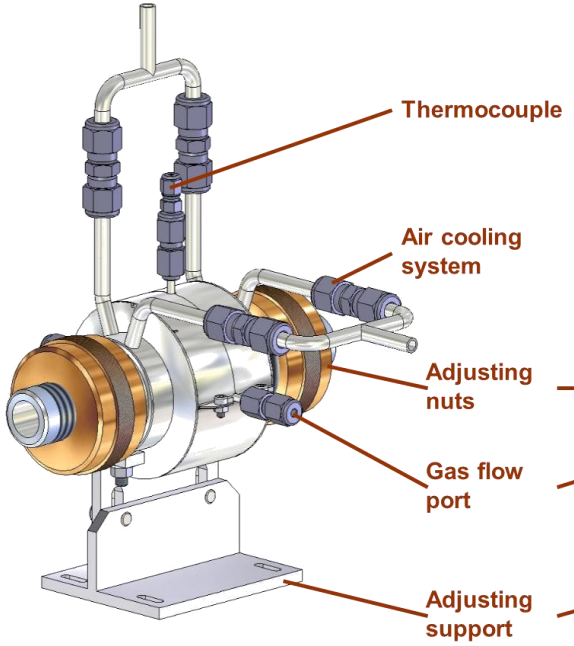


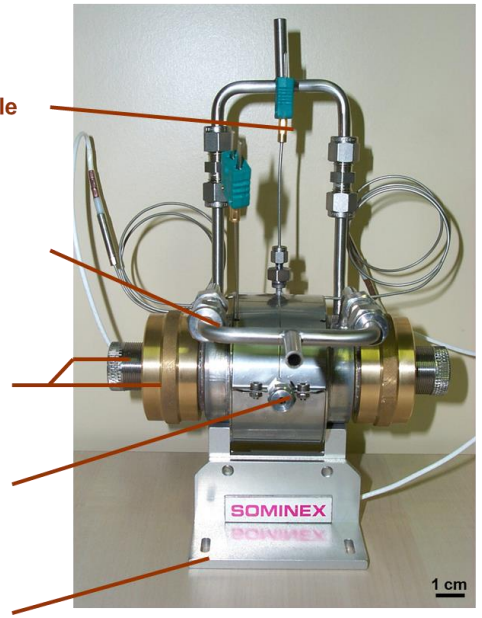
OPERATING CONDITIONS

T & P ranges : 25 - 450°C & 1 - 30 atm
Dead volume = ~ 0.42 cm³

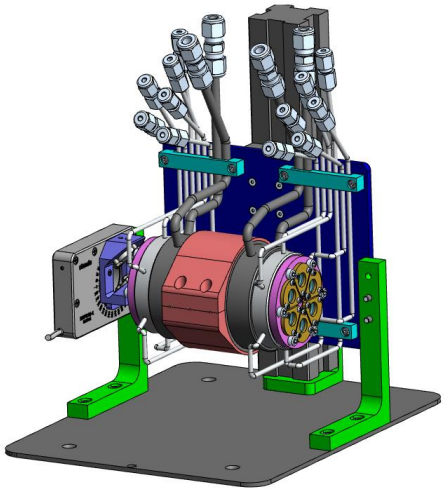
Sandwich cell
Adaptation to membranes

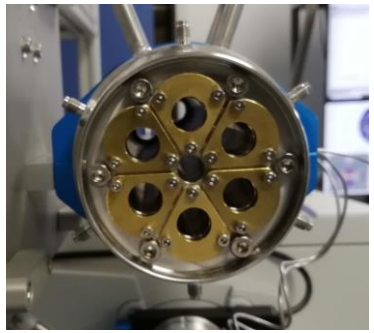






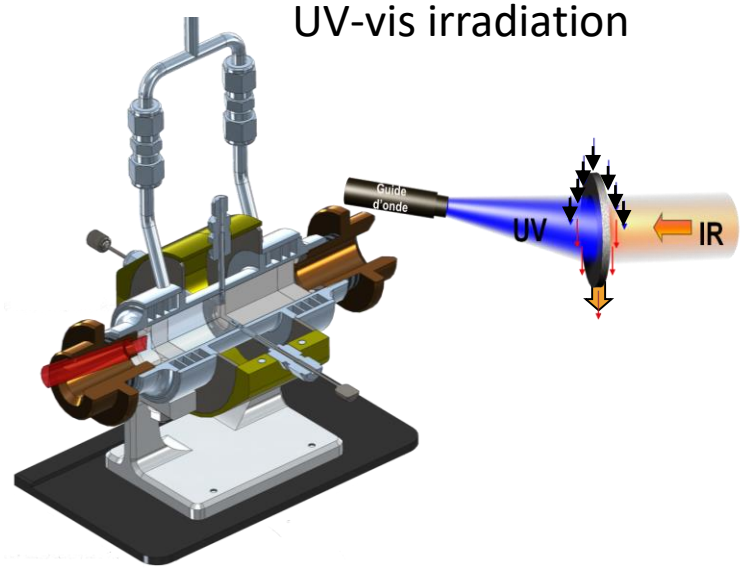
Revolv'IR
"high-troughput" Operando

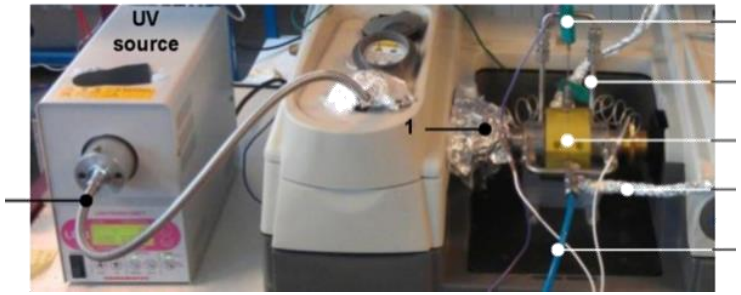




Operando cells for “special environments”

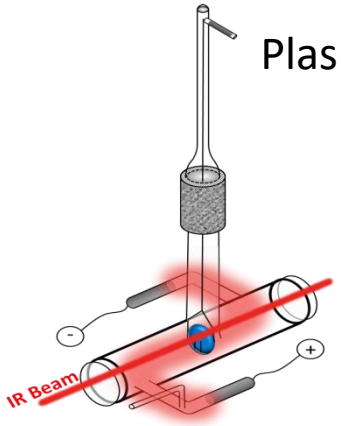
UV-vis irradiation

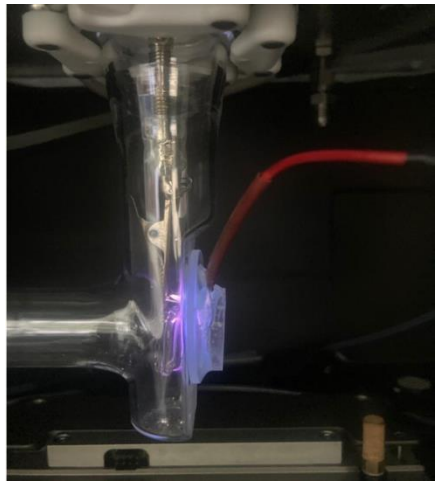




El Roz et al , *Phys.Chem.Chem.Phys.,* 2015, 17, 11277

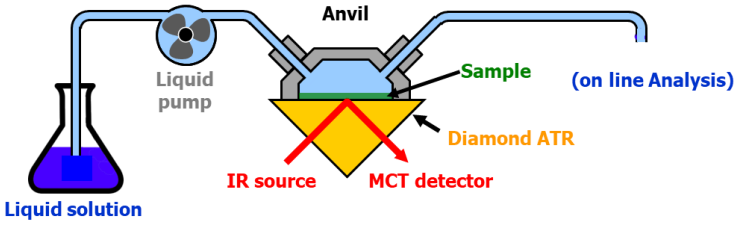
Plasma

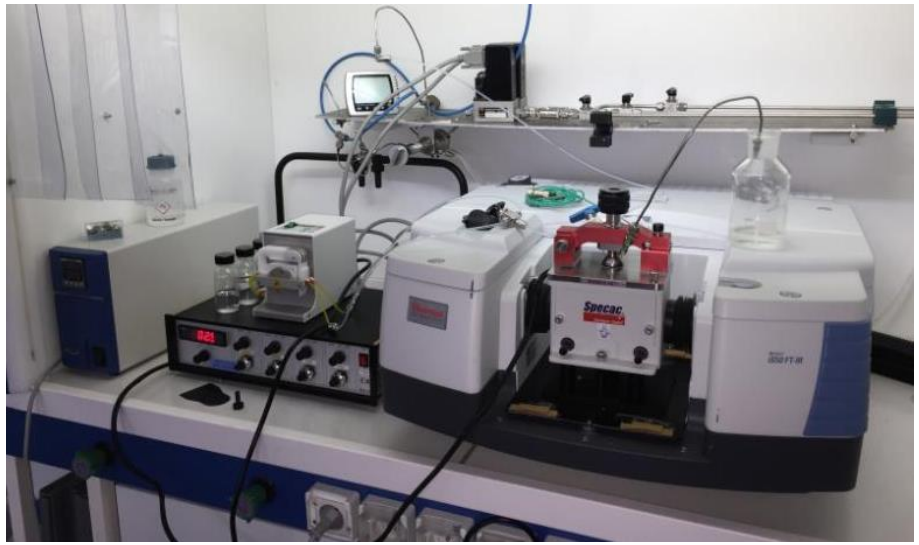




Van Thurnout et al. . 2022, Catal. Sci. & Tech., under revision

Liquid phase

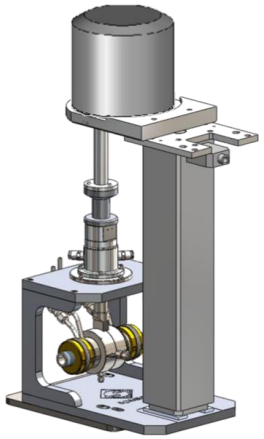




I. Khalil et al., J. Hazard. Mater., 2020, 384, 121397

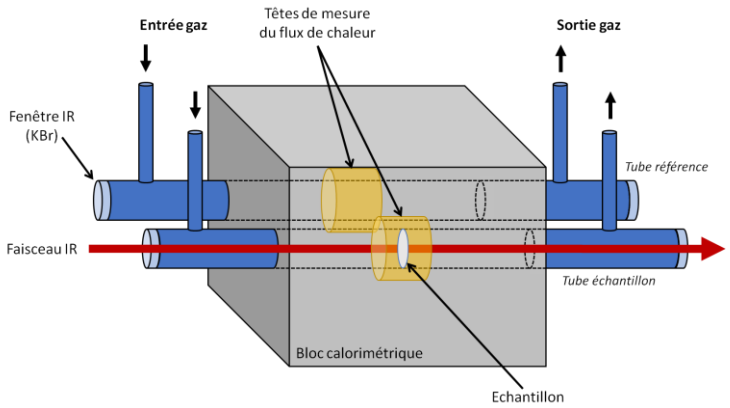
Couplings

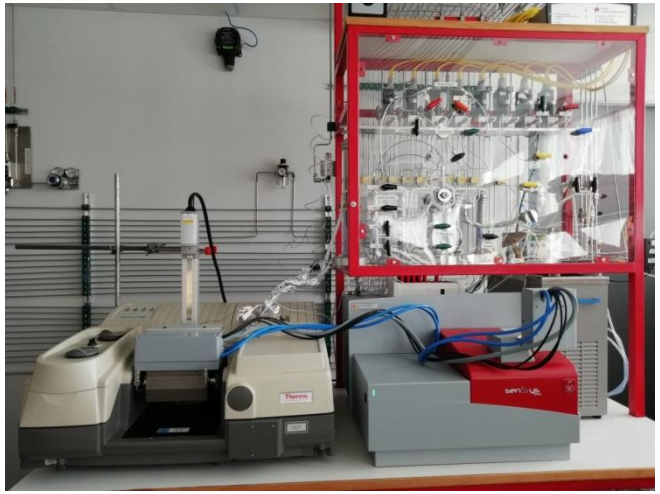
TGA-IR



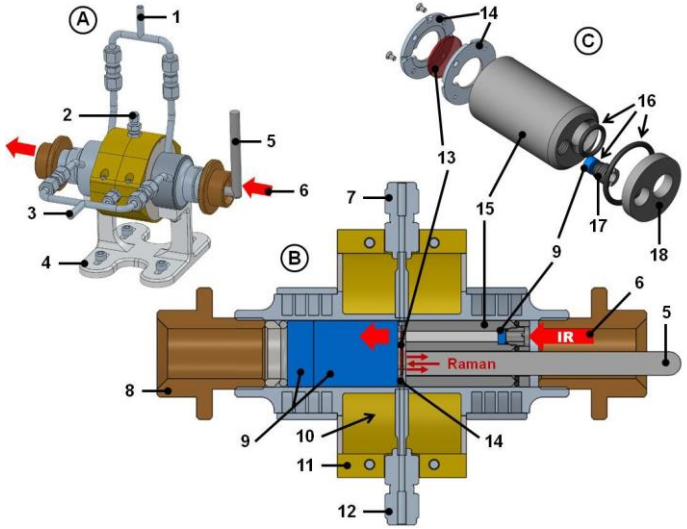
P. Bazin et al., Dalton Trans., 39 (2010) 8432

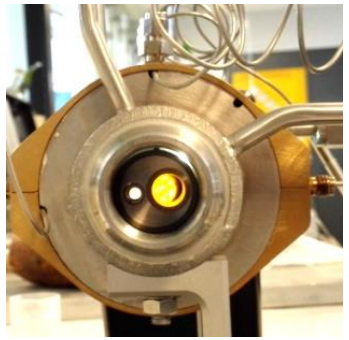
DSC-IR





IR-Raman

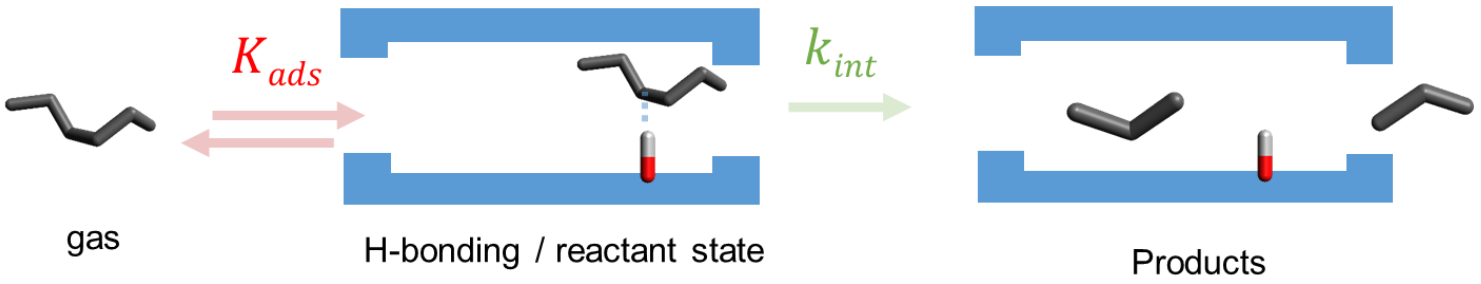


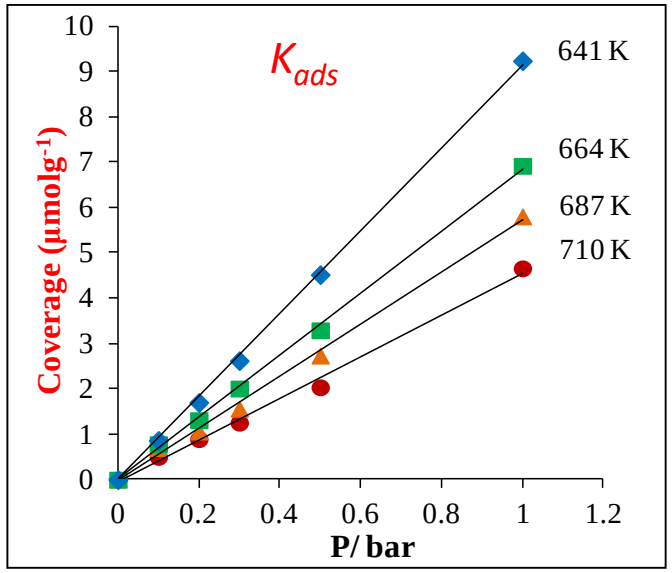


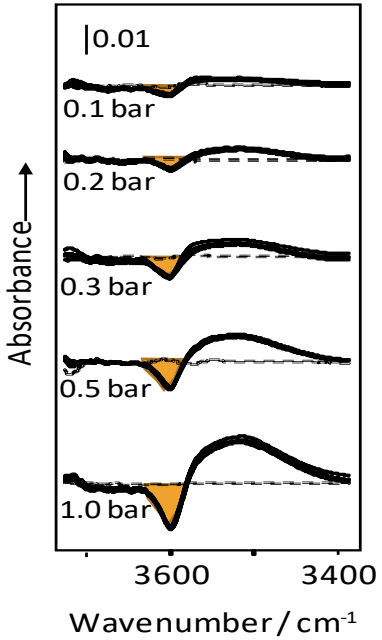
J. Ternero et al.,
Anal. Chem., 2020, 92, 5100–5106
Catal. Today, 387 (2022) 197-206

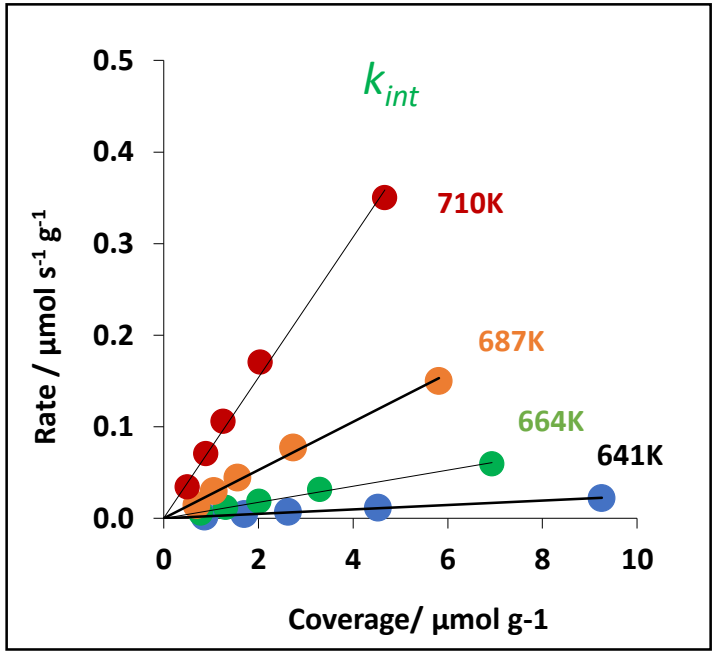
Structure-activity in alkane protolytic cracking in zeolites

Simple reaction but highly controversial explanations of SAR



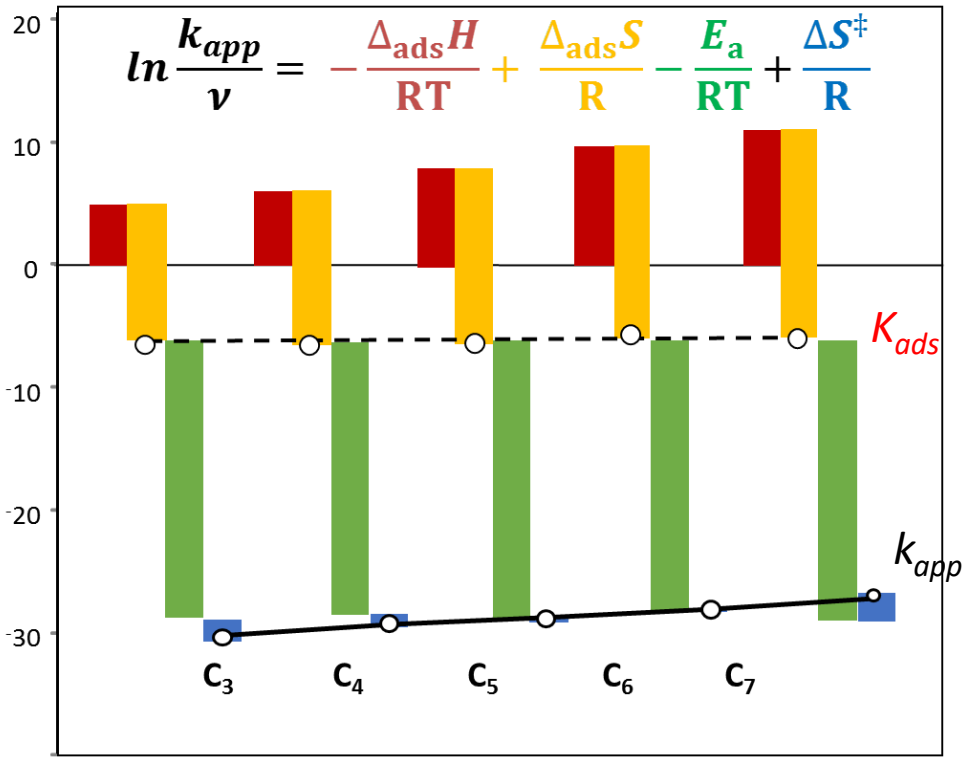




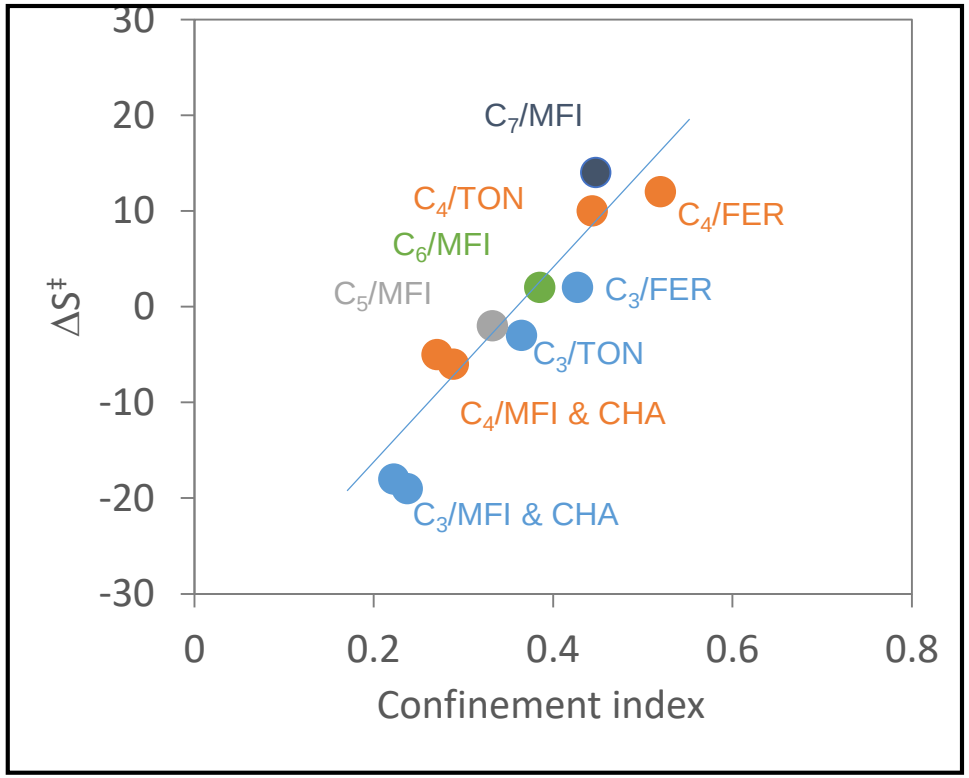


Li et al. *ACS Catal.* **2016**, 6, 4536. ; Kadam et al., Chem. Eur. J. 2018, 24, 5489

Structure-activity in alkane protolytic cracking in zeolites



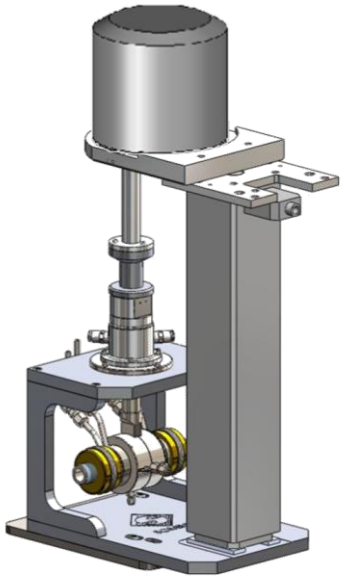
Activation entropy is the driving factor…

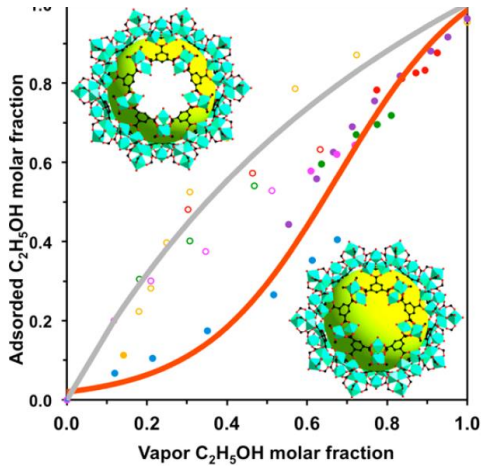


… and can be related to a structural descriptor

Li et al. *ACS Catal.* **2016**, 6, 4536. ; Kadam et al., Chem. Eur. J. 2018, 24, 5489

Adsorption of binary mixtures in porous materials





THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
pubs.acs.org/JPCC

Pore Occupancy Changes Water/Ethanol Separation in a Metal–Organic Framework—Quantitative Map of Coadsorption by IR

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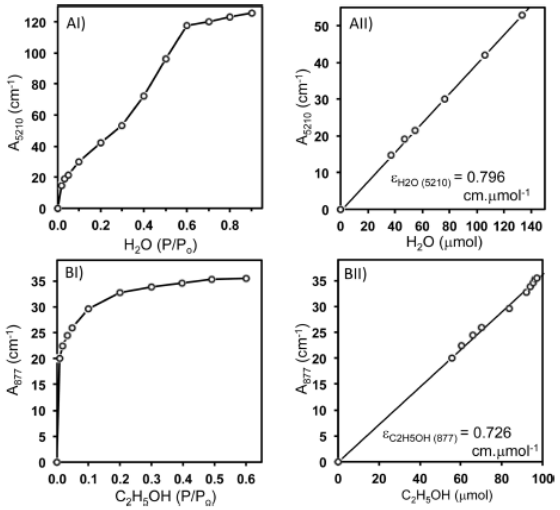
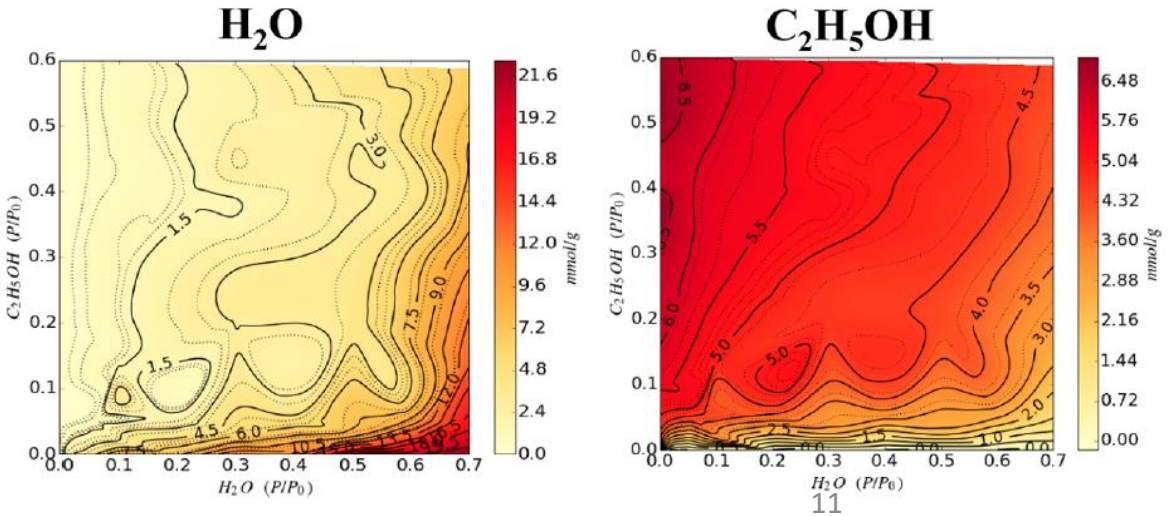
[‡]Laboratory for Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubjana, Slovenia
[§]University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

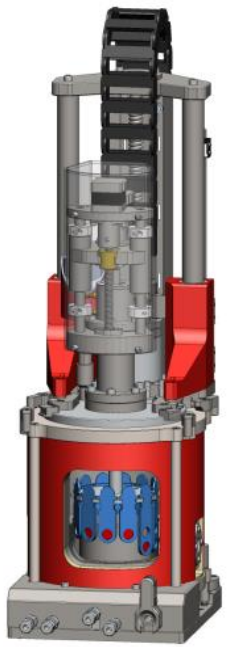
Preferential adsorption of ethanol even at low P_{H2O}

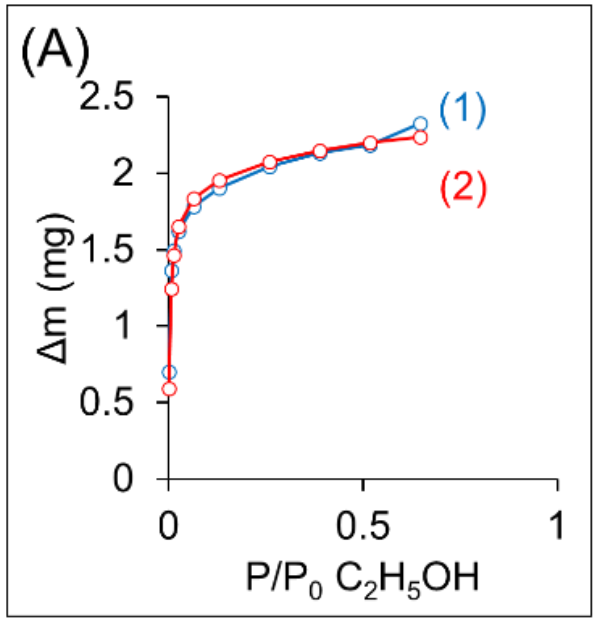




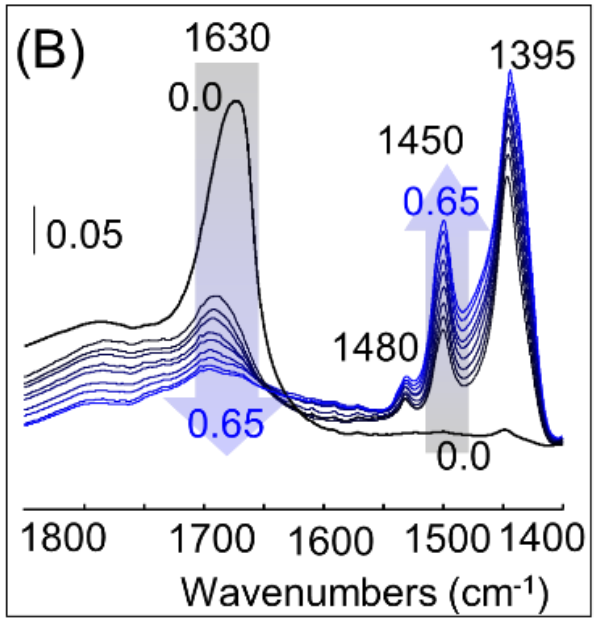
M. El-Roz et al., J. Phys. Chem. C, 119 (2015) 22570-22576

Adsorption of binary mixtures in porous materials

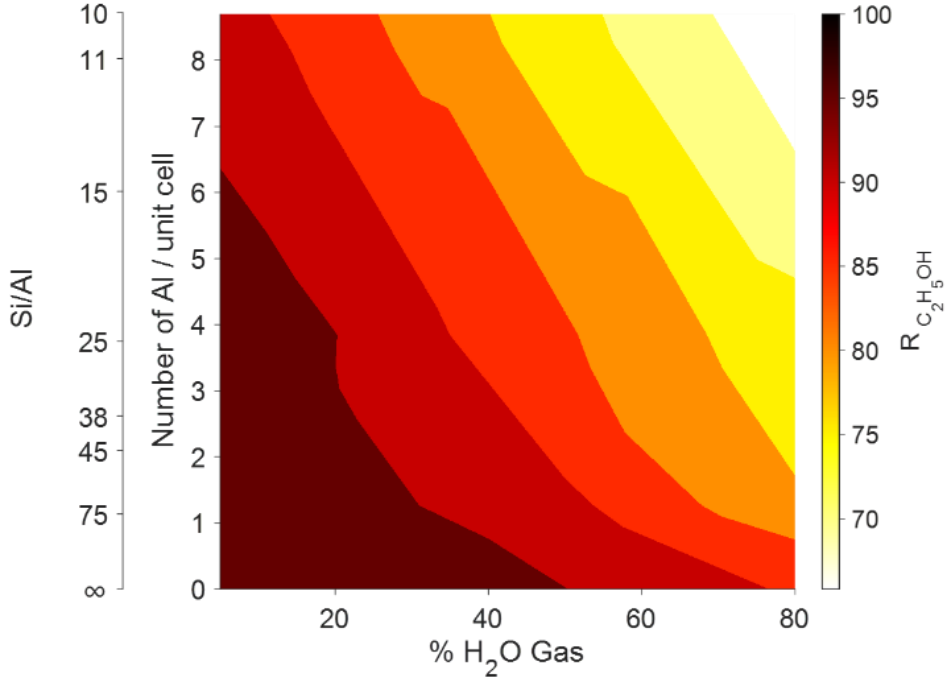




C2H50H uptake at 0% H20
(1) AGIR – (2) Carroucell



Adsorption of EtOH at fixed humidity (32%)



Relative amount of EtOH in presence of water

Coping with heterogeneity

Example: CO2 adsorption on ZrO_2 vs P
- All bands increase simultaneously
- Curve fitting not applicable

If coverage of individual species obey a known dependence on P, $\boldsymbol{\theta}(K,P)$:

$$a(\nu,P) = \int_{-\infty}^{+\infty} \boldsymbol{\theta}(K,P)\ f(\nu,K)\, d\ln K$$

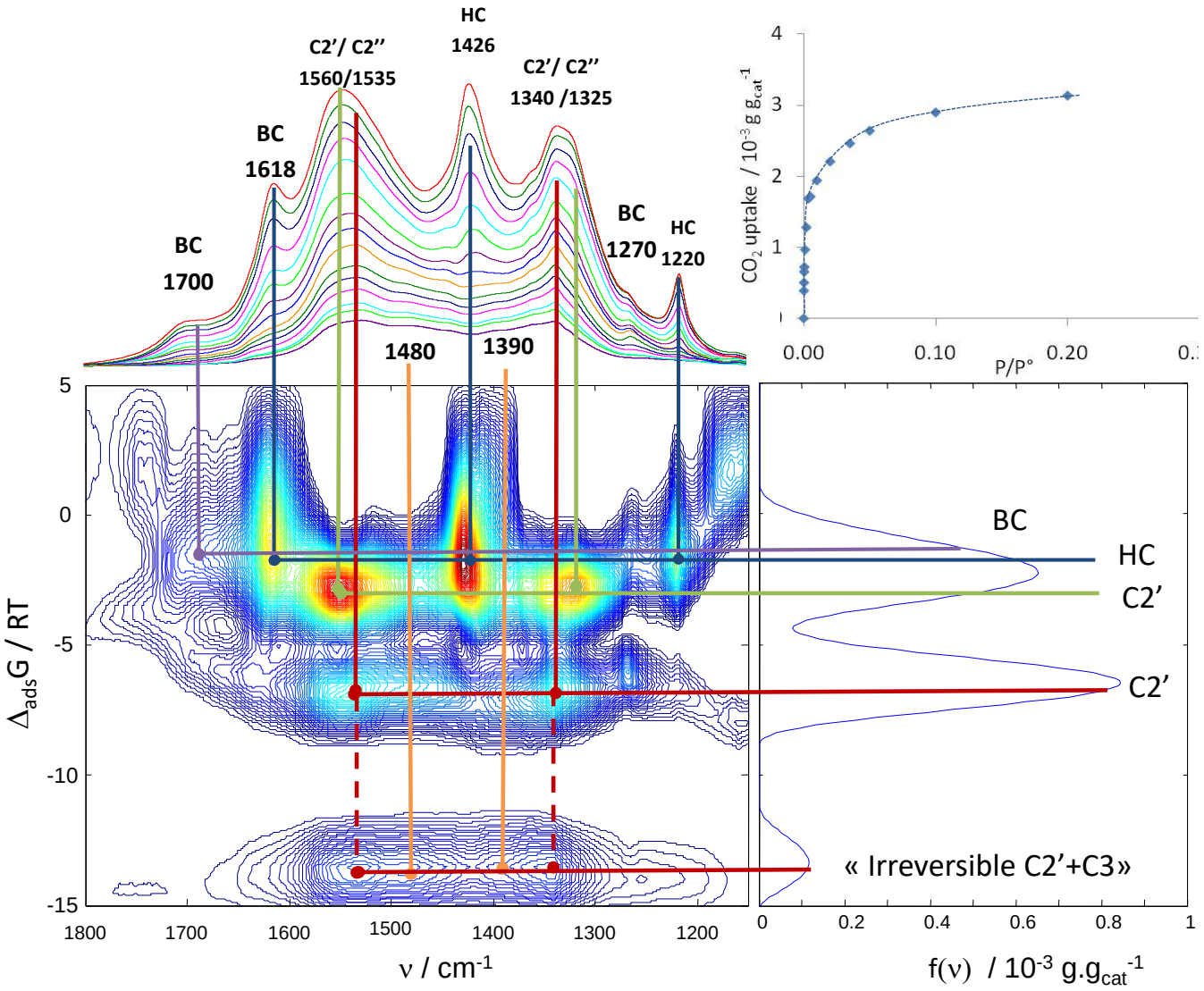
IR spectra

2D Distribution function

Resolves individual spectra on the energy scale.

$\Rightarrow$ Nature & Stability of distinct species.

=> Quantification with AGIR

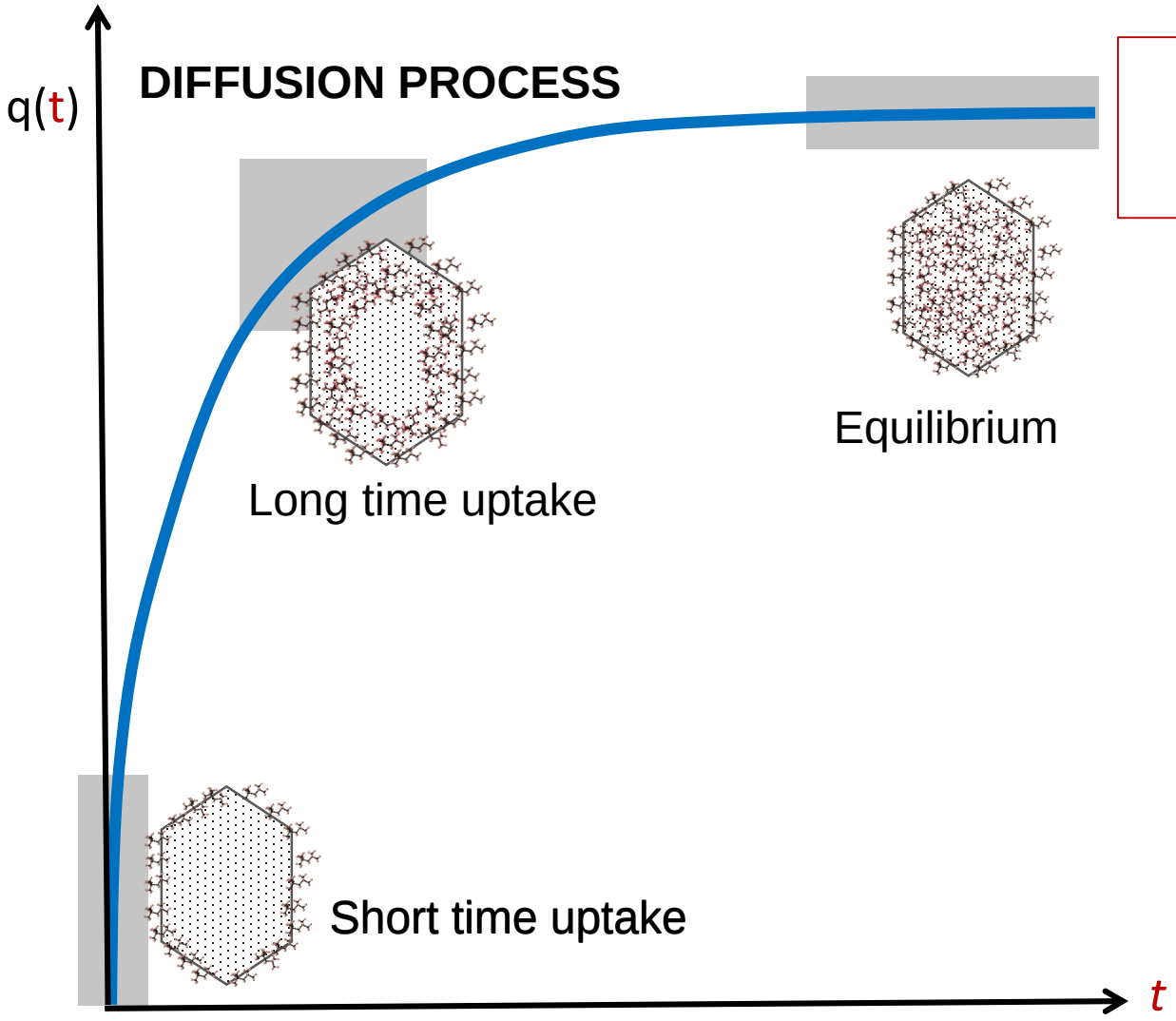


Stelmachowski et al. Phys.Chem. Chem. Phys., 2015, **15**, 9335

Extension to other processes

	p	q	$\theta_i = K(p,q)$
Adsorption	p	K_{ads}	$\theta_i = \dfrac{K_{ads}\,p}{1 + K_{ads}\,p}$
First order rxn, reactant	t	k	$\theta_i = \exp(-kt)$
First order rxn, product	t	k	$\theta_i = 1 - \exp(-kt)$
Internal diffusion	t	D/L^2	$\theta_i = 1 - \dfrac{6}{\pi^2}\sum_{n=1}^{\infty}\dfrac{1}{n^2}\exp\left(-\dfrac{n^2\pi^2}{9}\dfrac{D}{L^2}t\right)$
TPD, first order	T	E	$\theta_i = \exp\left[-\frac{\nu_0}{\beta}\left(T\exp\left(-\frac{E}{RT}\right) - T_0\exp\left(-\frac{E}{RT_0}\right) - \frac{E}{R}\left(\mathrm{expint}\left(\frac{E}{RT}\right) - \mathrm{expint}\left(\frac{E}{RT_0}\right)\right)\right)\right]$

Internal diffusion in zeolite-based materials



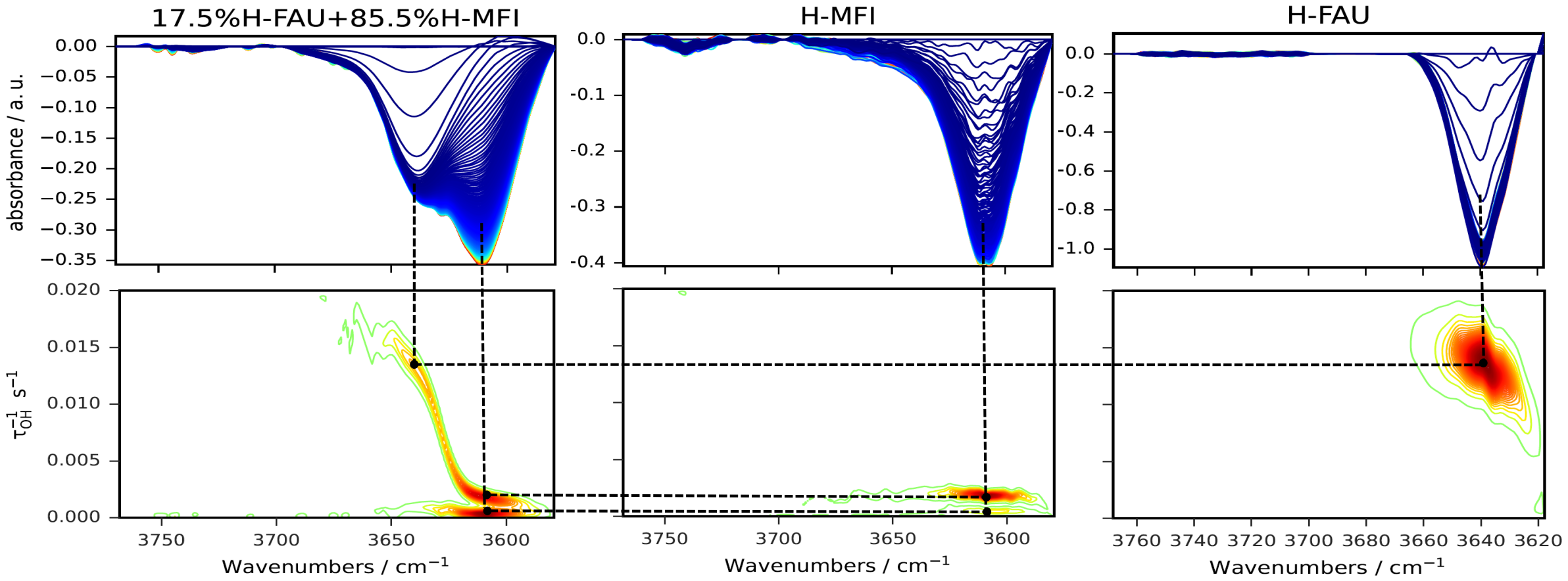
$$q(t,\tau^{-1}) = \frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2\tau^{-1}}{9}t\right)$$

characteristic diffusion rate $\tau^{-1} = \frac{D_e}{L^2}$

Current limitations of classical approach:

- ❑ A single average value of diffusion rate
- ❑ Does not indicate where the molecular probe adsorbs

Internal diffusion in zeolite-based materials



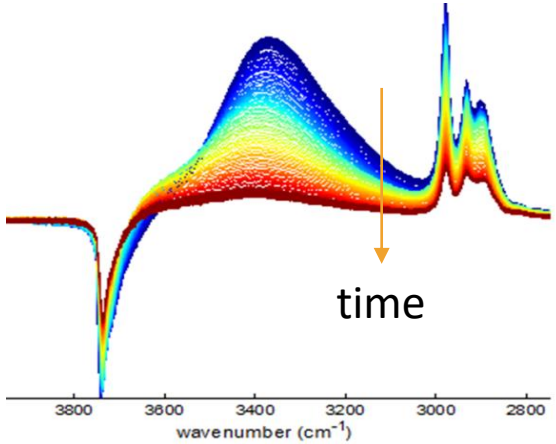
Ait Blal et al. 2022,. submitted

Peng et al. *ACS Catal.* **2020,** 10, 12, 6822–6830

MCR-ALS to unravel complex transformation processes

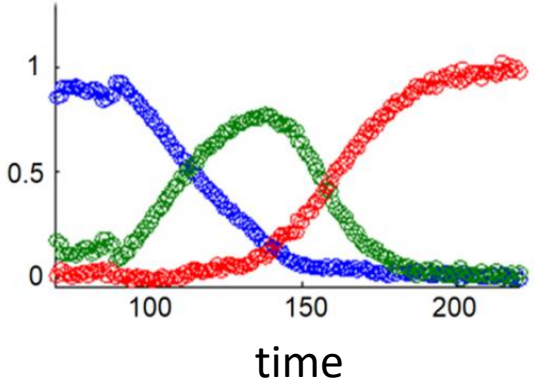
Factorization of the matrix of experimental spectra into concentration profiles and pure species spectra

$$D = C\,S^T + E$$



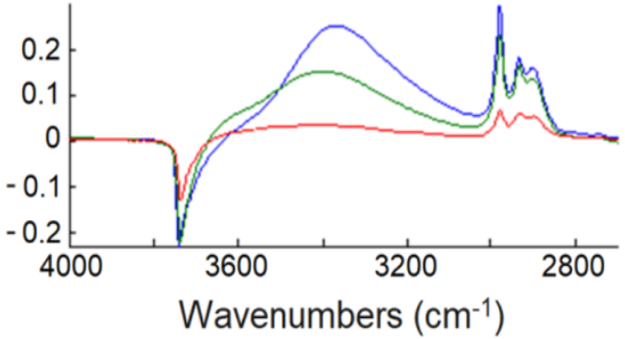
D

=



C

x



S^T

The solution is not unique.

Getting chemically meaningful species requires adding constraints

Classical constraints and algorithm

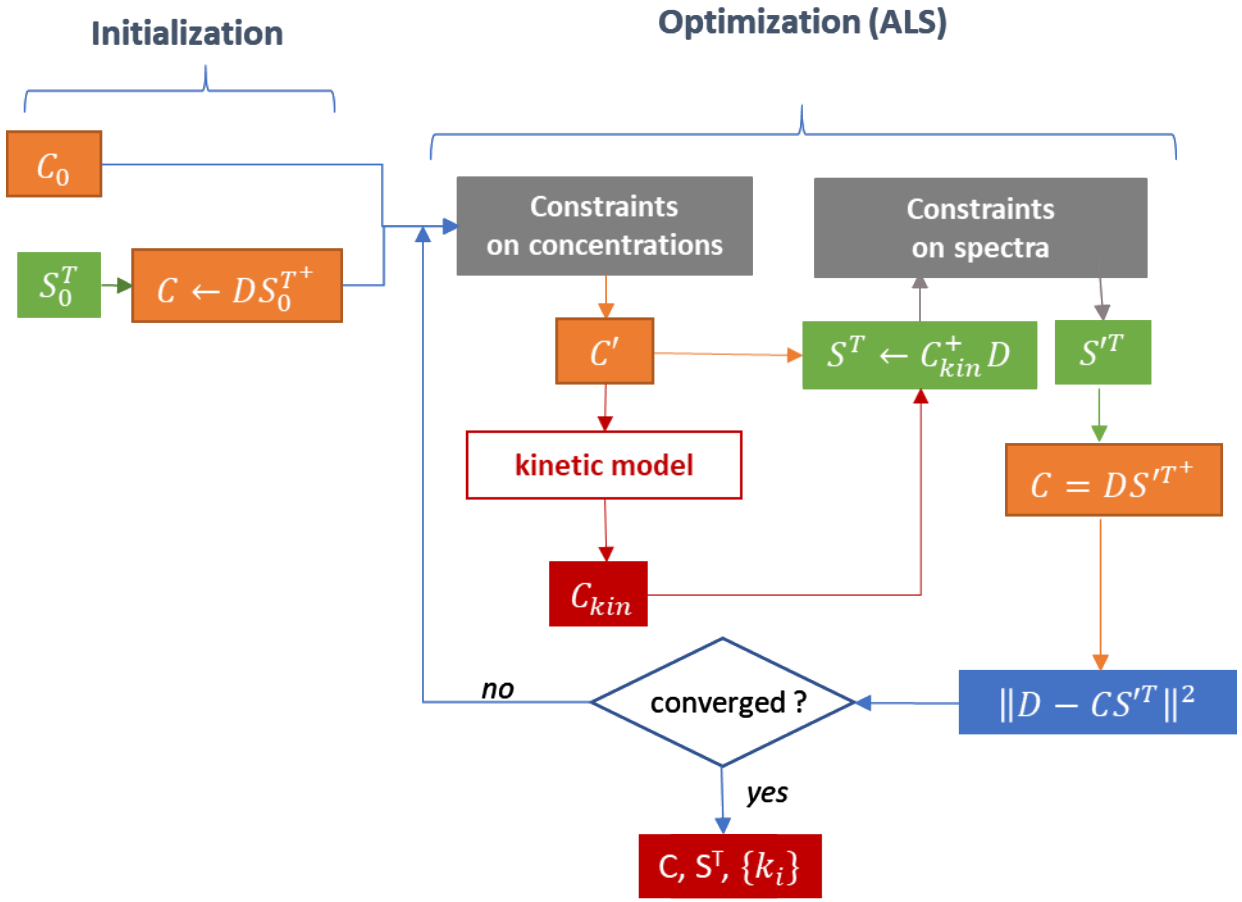
Constraints on C and/or S^T

- Non-negativity of C (and/or S^T)
- Unimodality
- Monotonic
- Closure (material balance)
- Normalization
- …

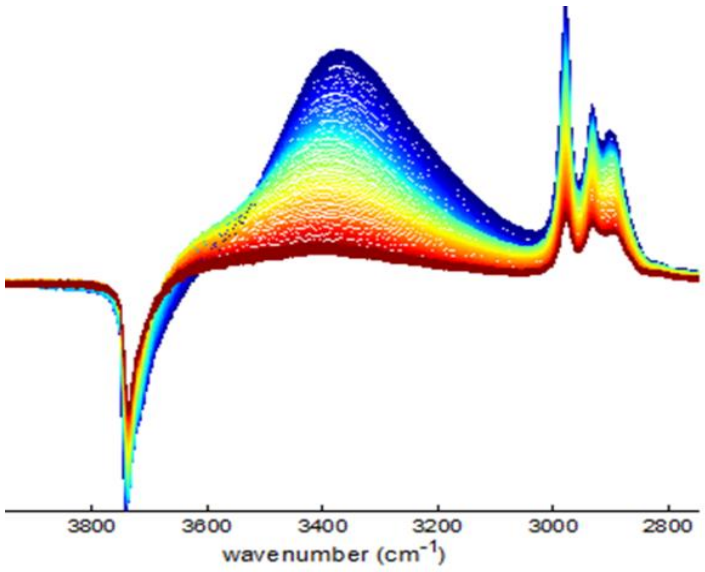
« Hard » constraints on C and/or S^T

- part C or S^T a priori known
  - Spectrum of known species
  - Concentration profile (full or partial)

Inclusion of a Kinetic model



Example: Silane grafting on SiO2



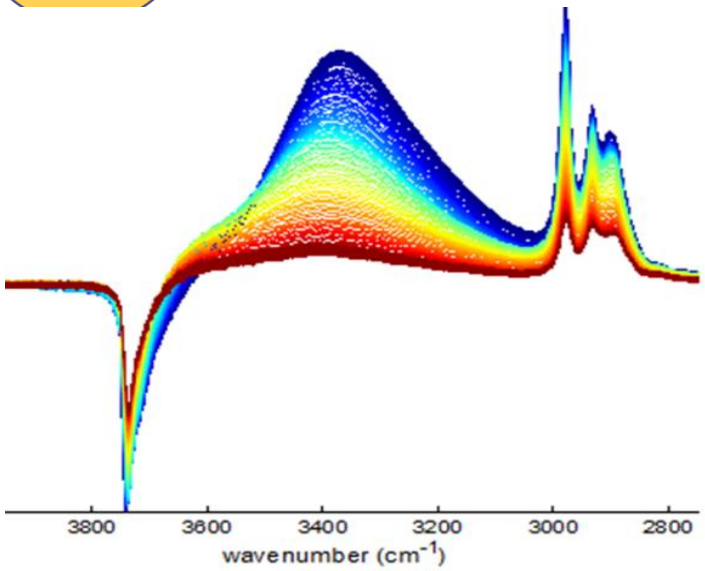
Hydrolysis	$A + H_2O_{ads} \rightarrow B$	$\sim Si(Et)O\cdots HOSi\equiv + H_2O\cdots HOSi\equiv \rightarrow \sim Si(H)O\cdots HOSi\equiv + HOSi\equiv + EtOH_{(g)}$
Direct Graft.	$A \rightarrow C_g$	$\sim Si(Et)O\cdots HOSi\equiv \rightarrow \sim SiOSi\equiv + EtOH_{(g)}$
Condens.	$A + B \rightarrow C_p$	$\sim Si(Et)O\cdots HOSi\equiv + \sim Si(H)O\cdots HOSi\equiv \rightarrow \sim SiOSi\sim + 2\ HOSi\equiv + EtOH_{(g)}$
H2O desorpt.	$H_2O_{ads} \rightarrow H2Og$	$H_2O\cdots HOSi\equiv \rightarrow HOSi\equiv + H_2O_{(g)}$

Single-site formal kinetics model

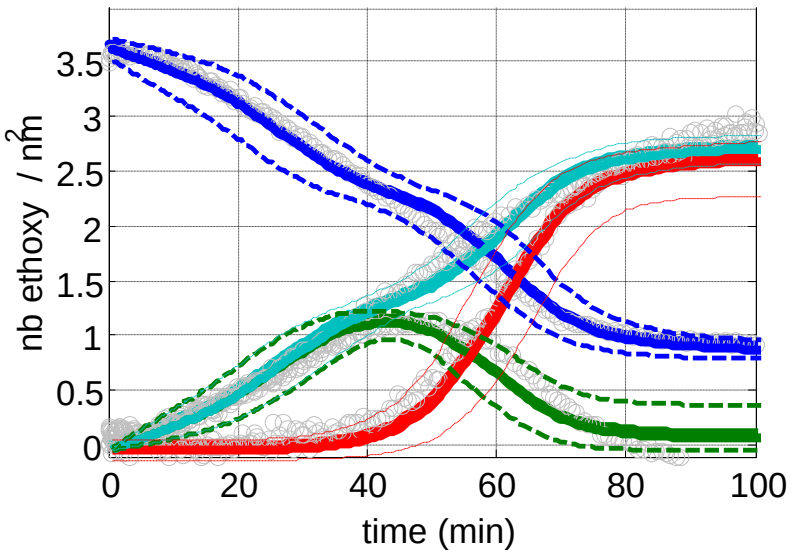
Validation on **four independent** experiments in **various conditions**

Vilmin et al. Analytica Chimica Acta, **2015**
Vilmin et al. J. Phys.Chem.C, **2014**
A. Hamadeh, **PhD 2020**

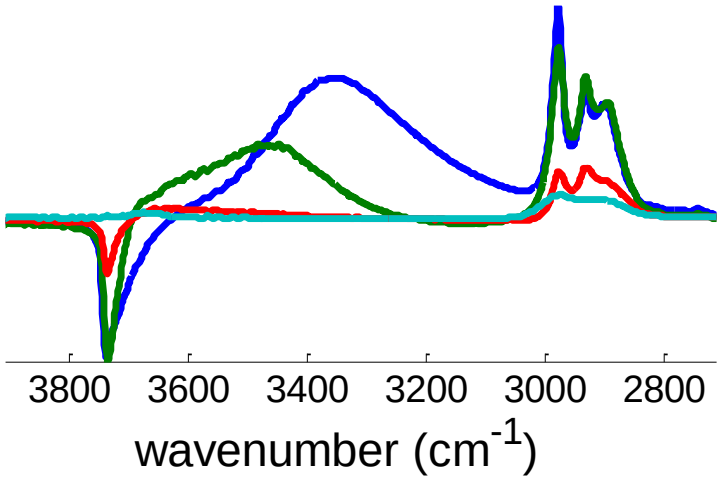
Example: Silane grafting on SiO2



Concentration profiles

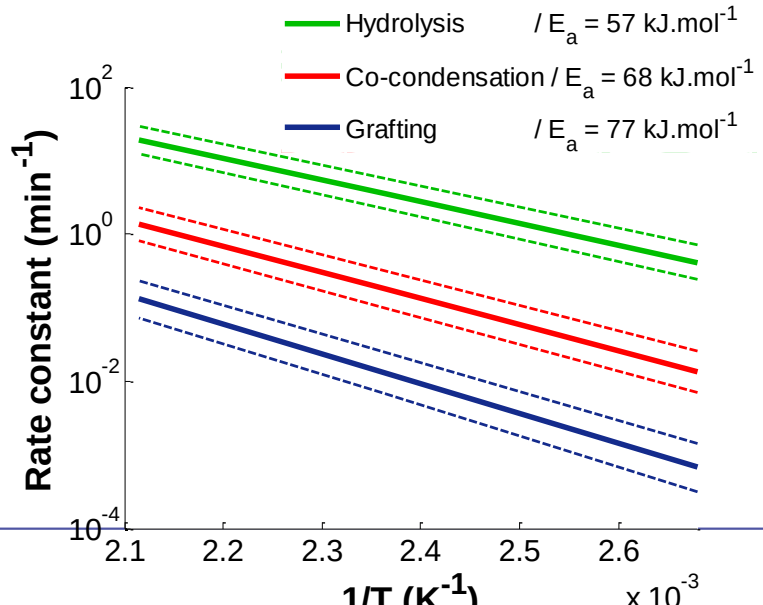


Spectra of pure species



A (surf) = **Physisorbed**
B (surf) = **Hydrolysed**
C (surf) = **grafted** + **co-condensed**

Rate constants and activation energies



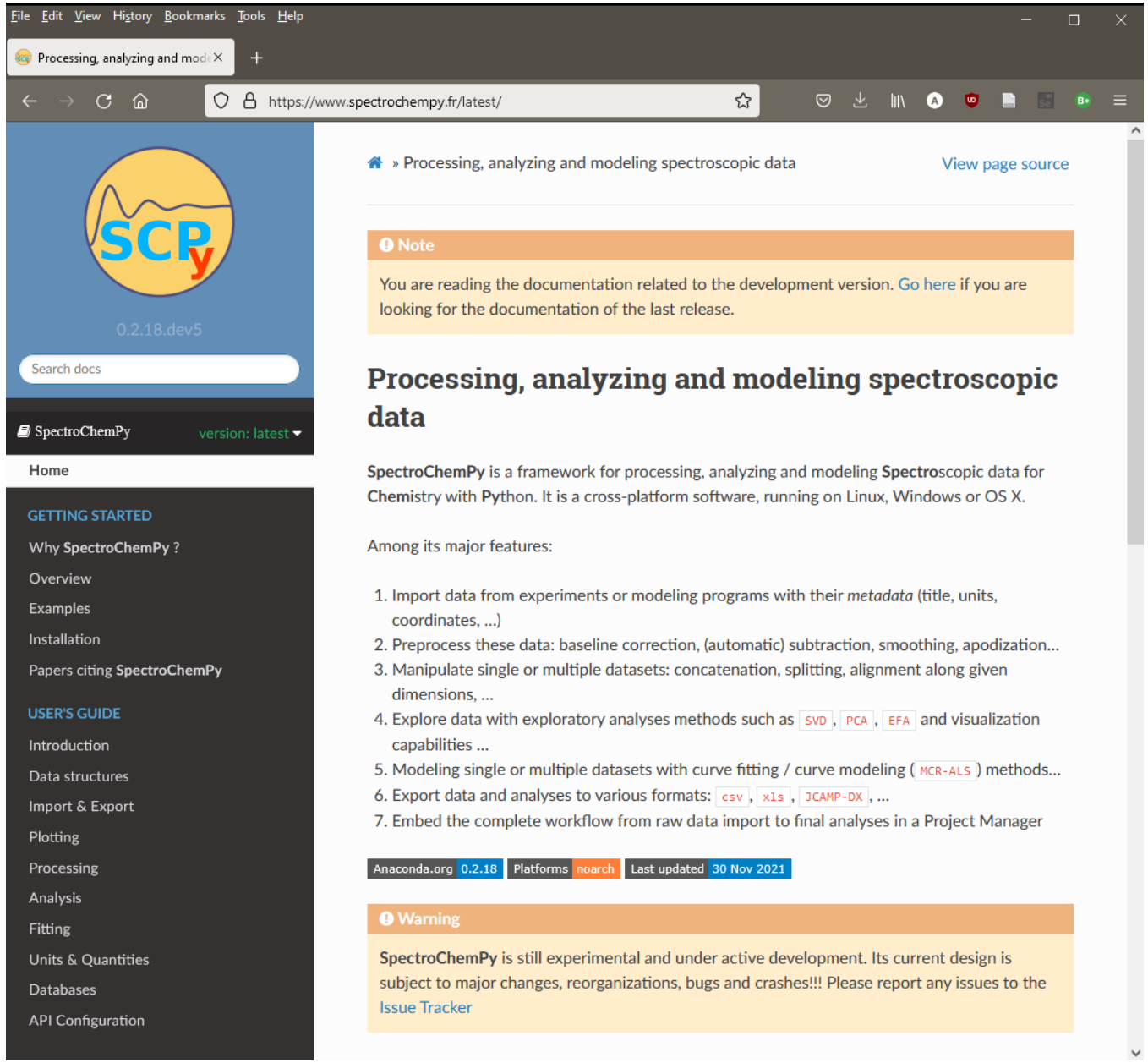
Vilmin et al. Analytica Chimica Acta, **2015**
Vilmin et al. J. Phys.Chem.C, **2014**
A. Hamadeh, **PhD 2020**

Spectrochempy

Python API for processing and analysis of spectral data

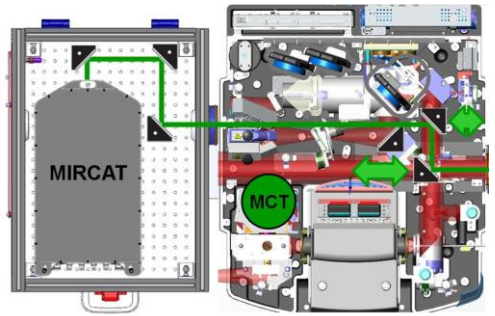
- Open Science
  - Free and Open Source Software (https://github.com/spectrochempy/)
  - Cross platform (win/mac/linux)
  - Releases archived on zenodo (https://doi.org/10.5281/zenodo.3823841)

- User friendly
  - Online documentation, examples, tutorials…
  - No need of extended python knowledge
  - Usable with Notebooks (Jupyter)
  - No need of local python installation (Google Colab)

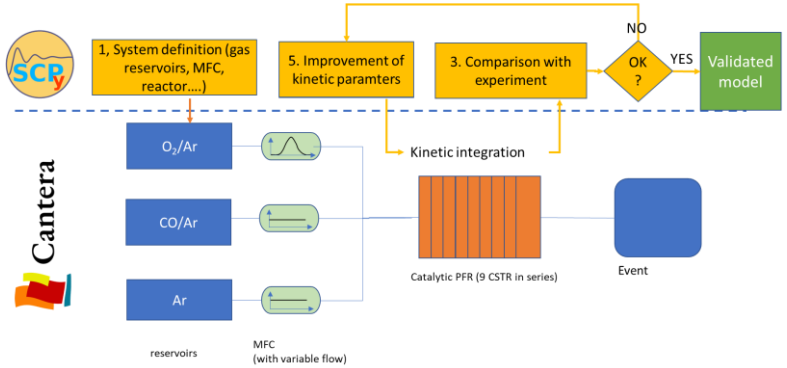


Current developments and Perspectives

- **Instrumentation: IR LASERS**
  - Tunable lasers : time resolution
  - MIR Supercontinuum Lasers: brightness



- **Data processing**: full modeling of operando setups



- **HTE: multi**-sample / **multi-**spectroscopy experiments