



Laboratoire
Catalyse & Spectrochimie

Vibrational Spectroscopy for porous functional materials

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Rueil Malmaison, May 22nd 2022



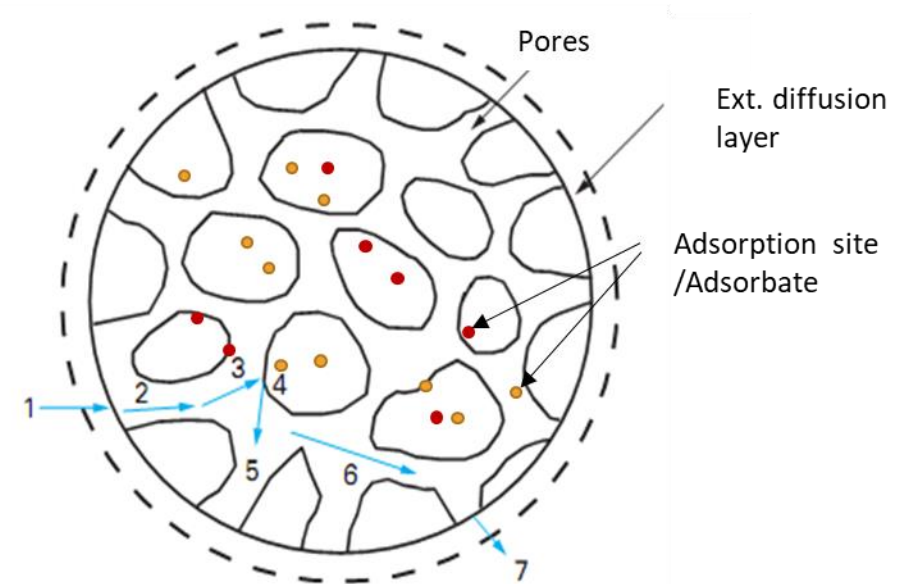


Outline

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

Vibrational spectroscopies: which informations ?

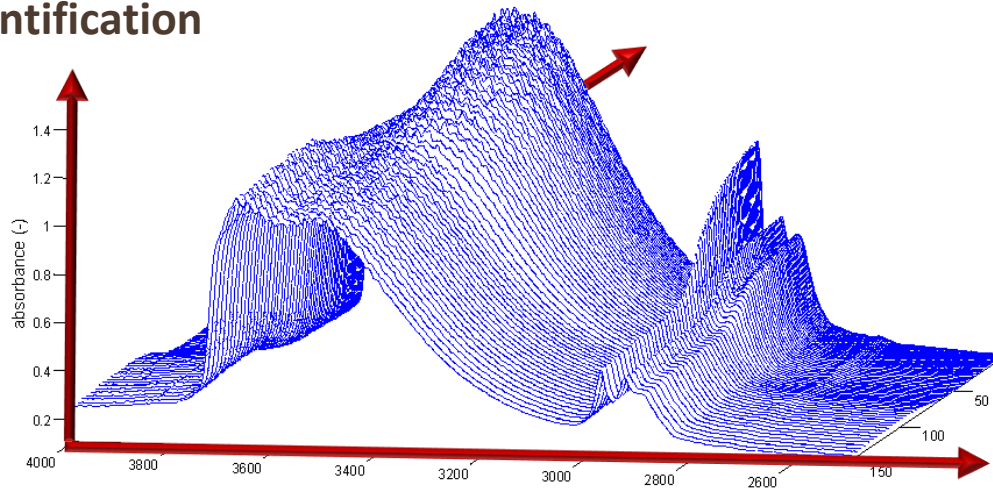
In porous adsorbants or catalysts:



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

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

Band intensities
Quantification



Band frequencies:
Identification



In situ vs Operando



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



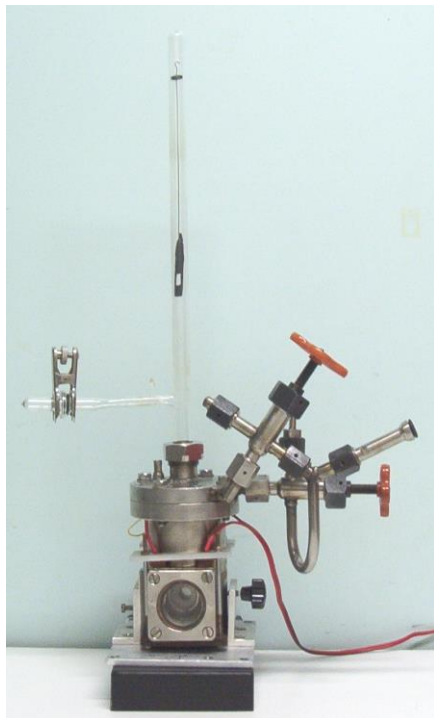
- **Flow of reactants**
- **Simultaneous recording of activity**
- **=> reaction mechanisms**



in situ cells

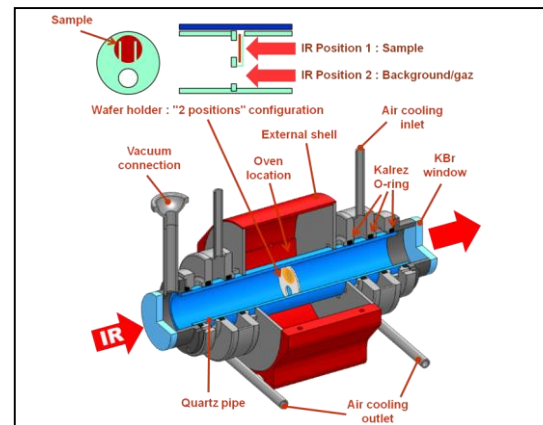


RT



Low T

Classic designs



RT



High T



Multi-sample

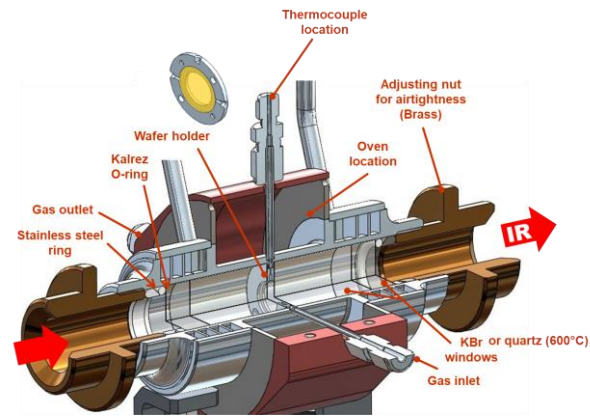
Fully automated



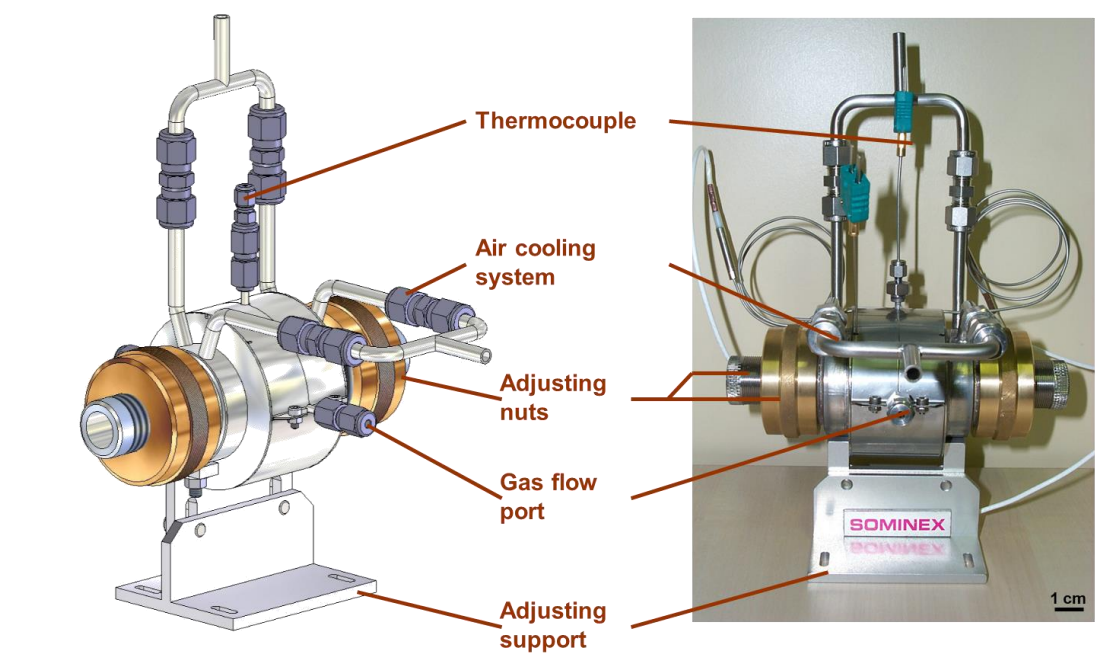
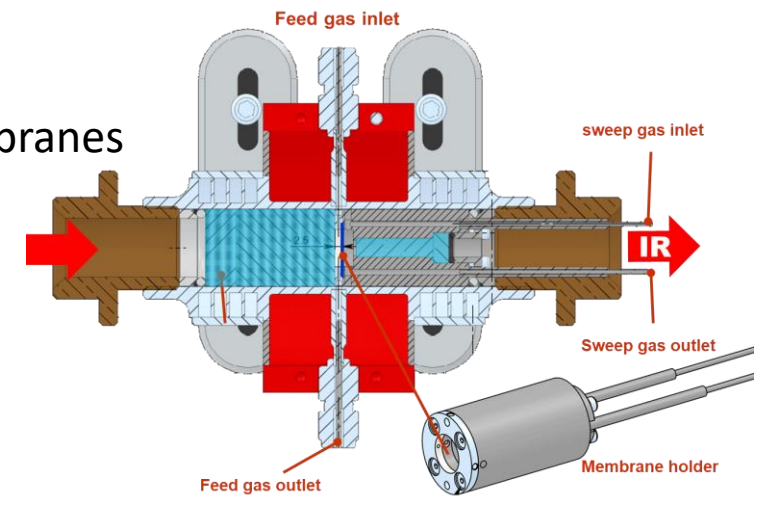
Operando cells

Sandwich cell
 “workhorse” Operando cell

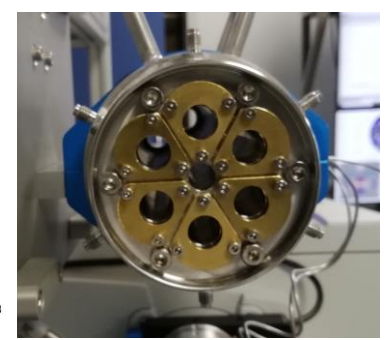
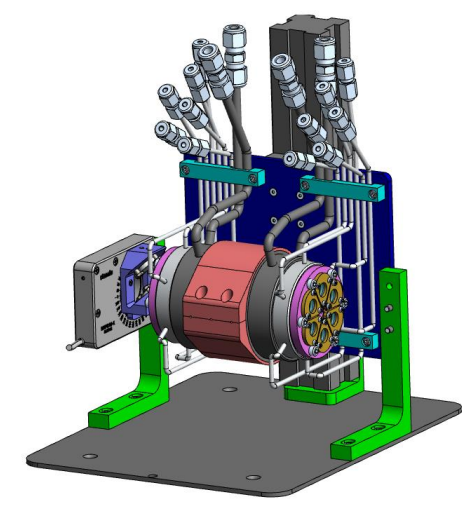
OPERATING CONDITIONS
 T & P ranges : 25 - 450°C & 1 - 30 atm
 Dead volume = ~ 0.42 cm³



Sandwich cell
 Adaptation to membranes



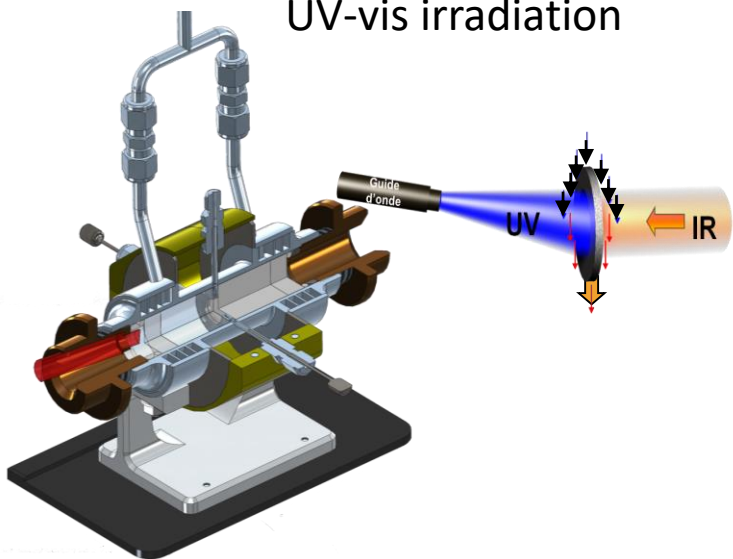
Revolv'IR
 “high-throughput” Operando



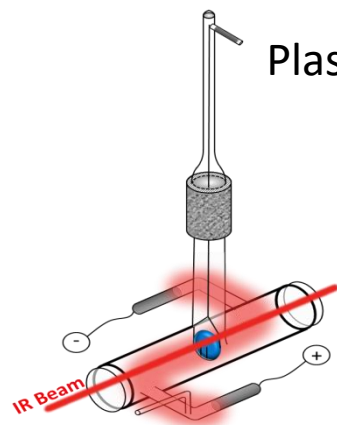


Operando cells for “special environments”

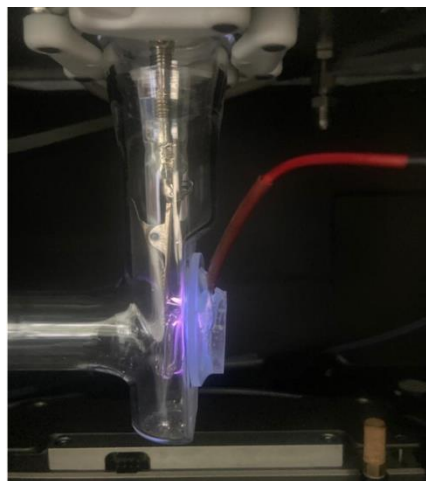
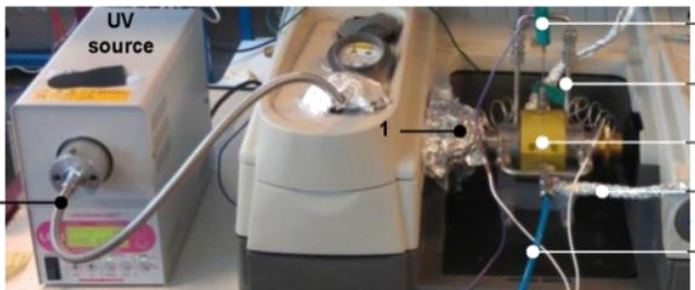
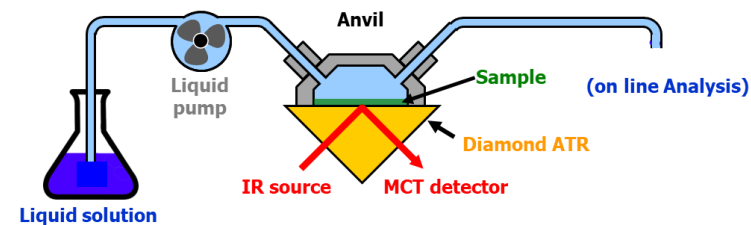
UV-vis irradiation



Plasma



Liquid phase



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

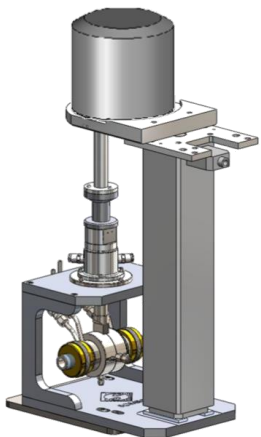
Van Thurnout et al. . 2022, *Catal. Sci. & Tech.*, under revision

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

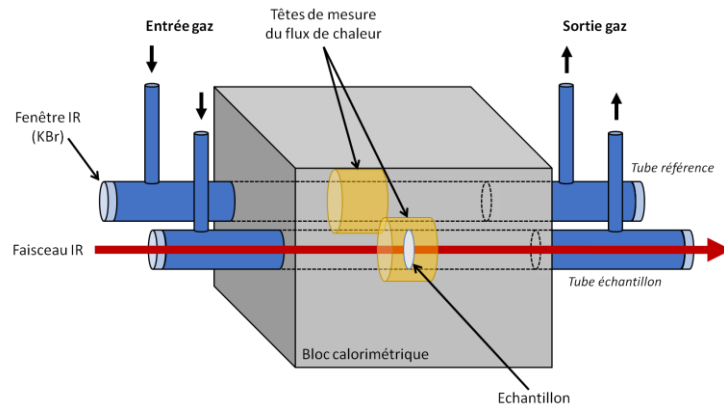


Couplings

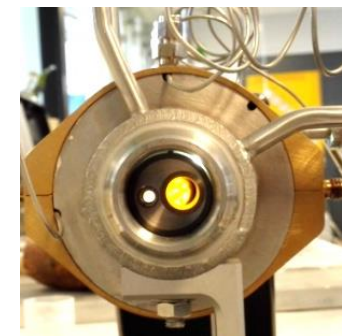
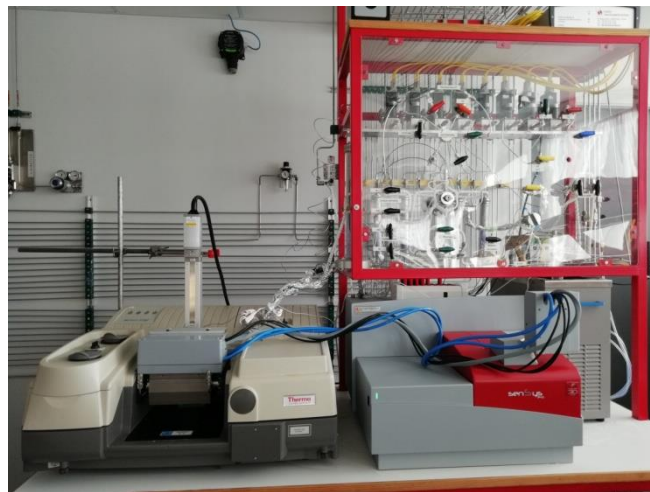
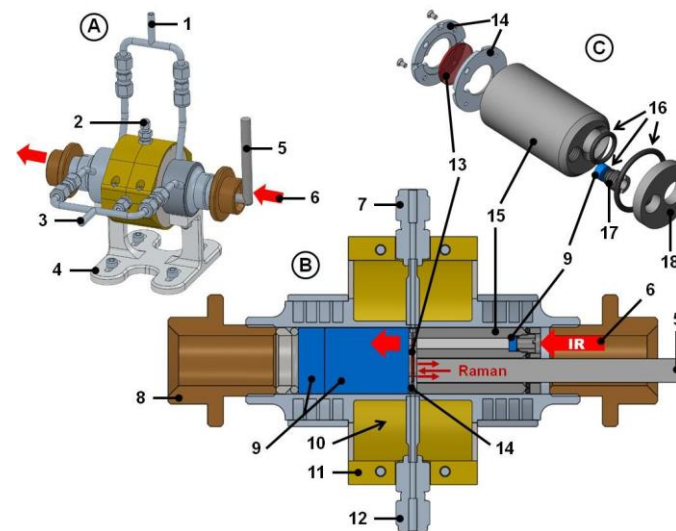
TGA-IR



DSC-IR



IR-Raman



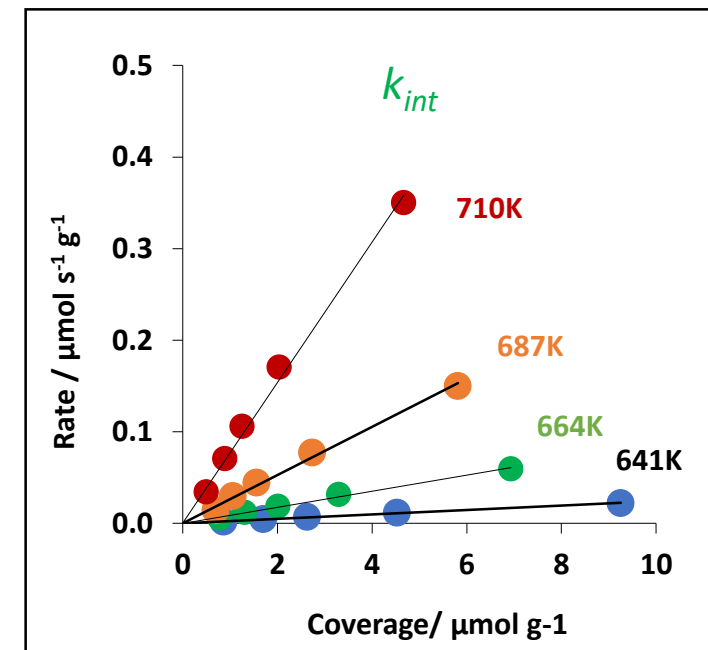
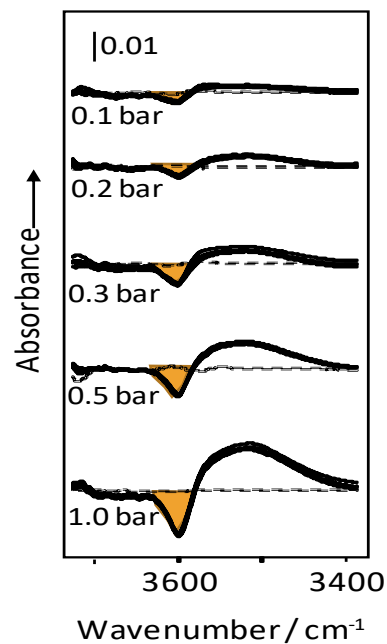
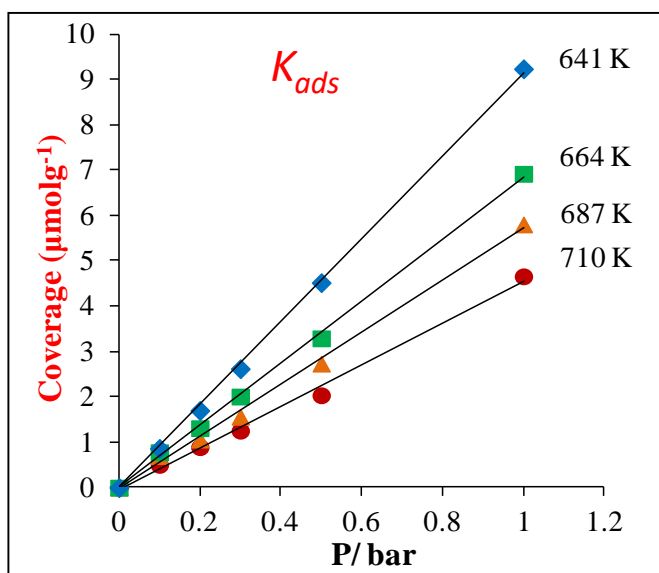
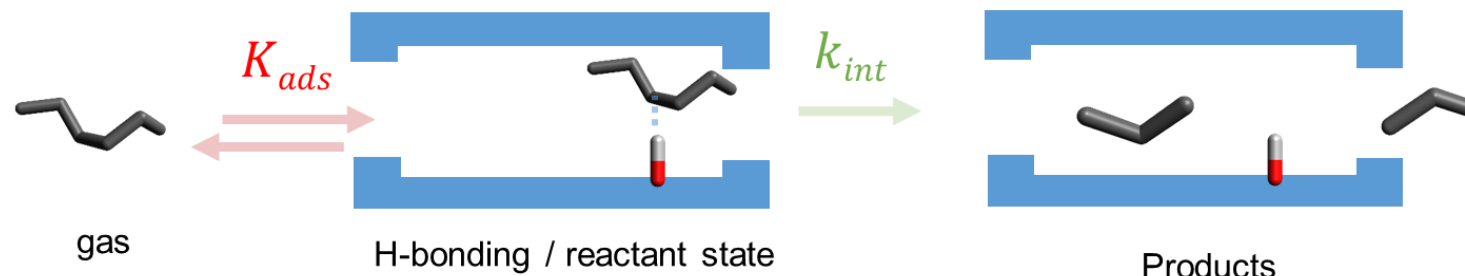
P. Bazin et al., Dalton Trans., 39 (2010) 8432

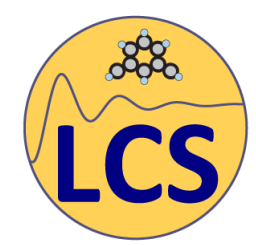
J. Ternero et al.,
Anal. Chem., 2020, 92, 5100–5106
Catal. Today, 387 (2022) 197-206



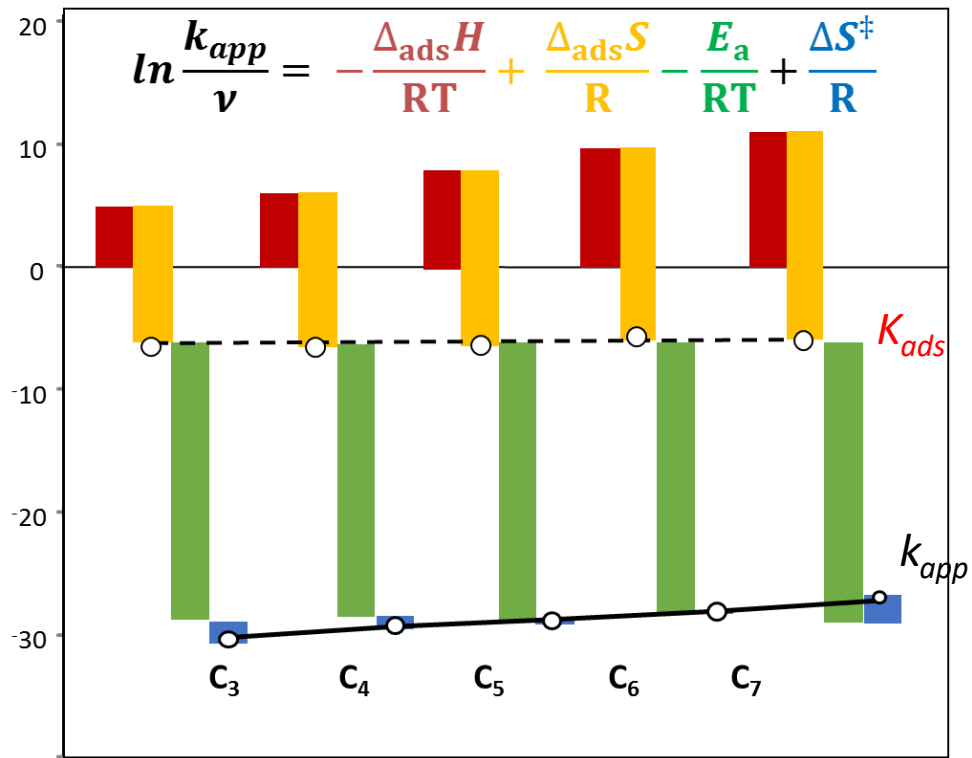
Structure-activity in alkane protolytic cracking in zeolites

Simple reaction but highly controversial explanations of SAR

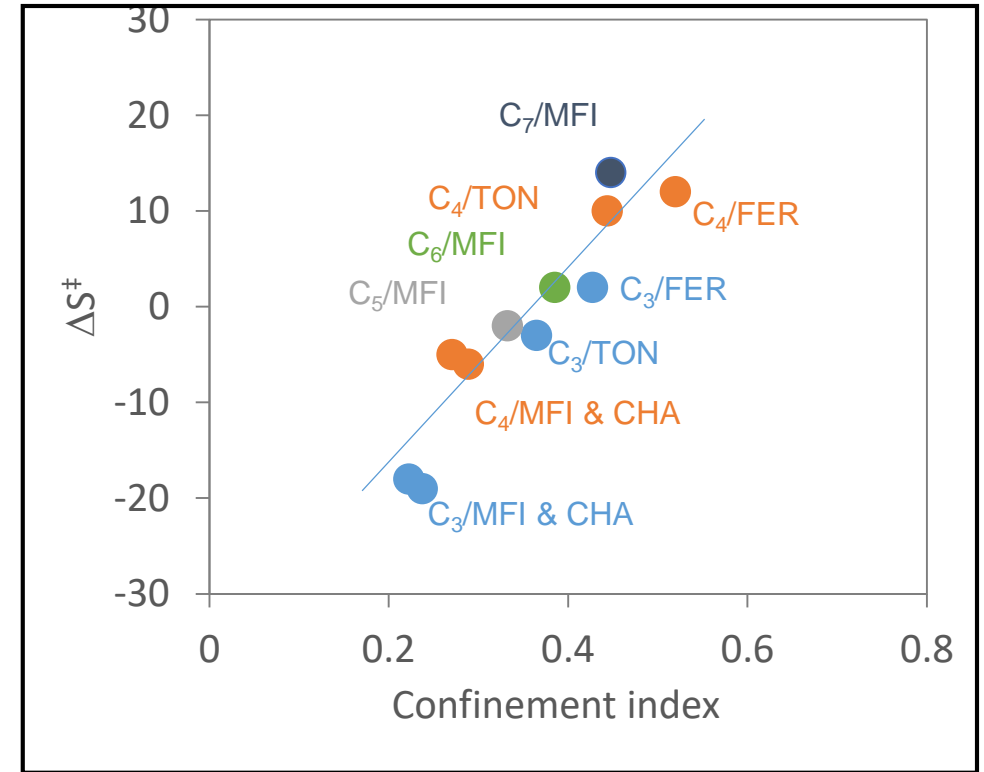




Structure-activity in alkane protolytic cracking in zeolites



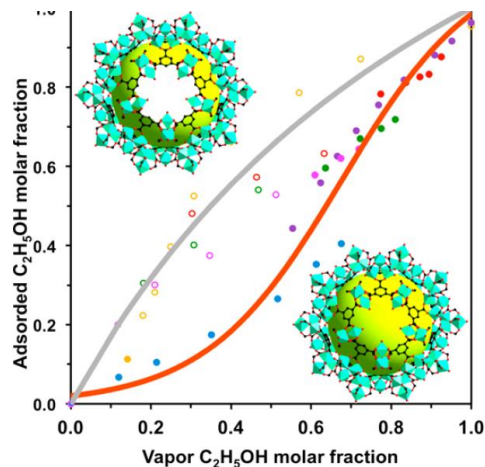
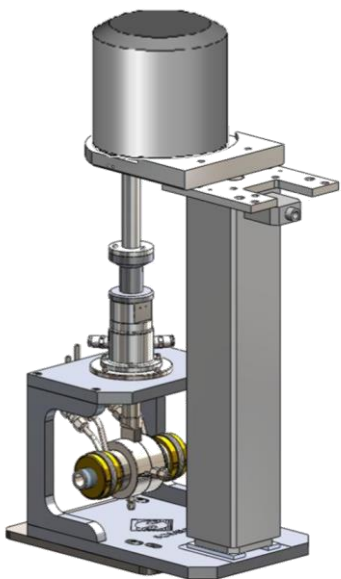
Activation entropy is the driving factor...



... and can be related to a structural descriptor



Adsorption of binary mixtures in porous materials



THE JOURNAL OF
PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCA

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

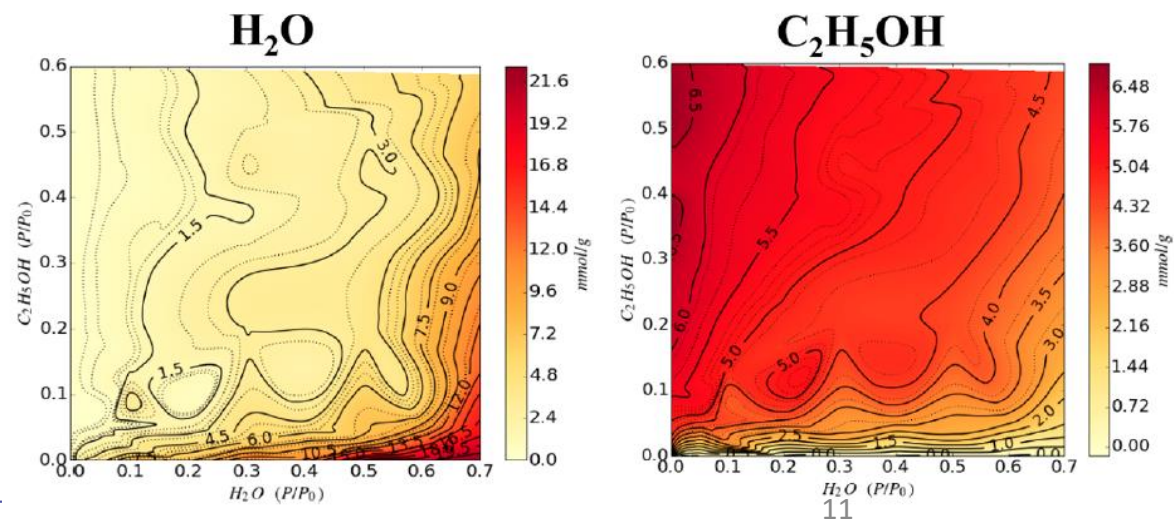
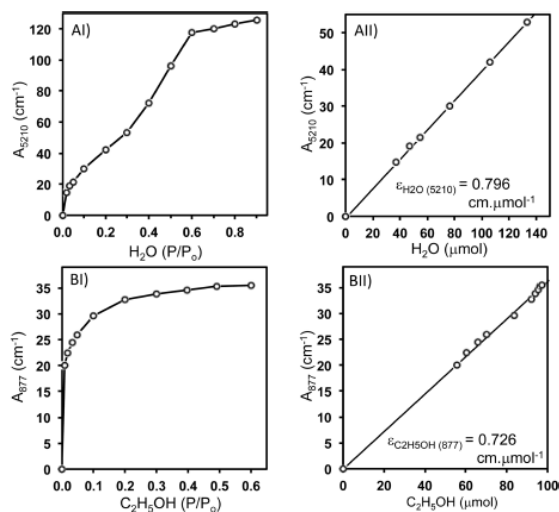
Mohamad El-Roz,^{*,†} Philippe Bazin,[†] Tadeja Birsa Čelič,[‡] Nataša Zabukovec Logar,^{‡,§} and Frederic Thibault-Starzyk[†]

[†]Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6, Boulevard du Maréchal Juin, 14050 Caen, France

[‡]Laboratory for Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

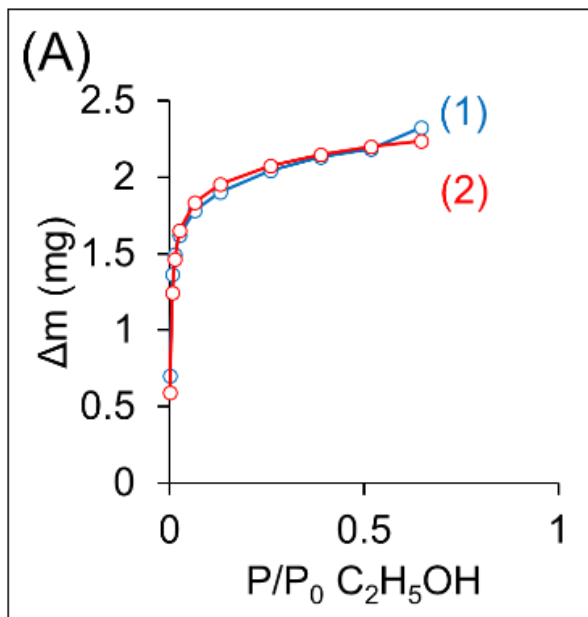
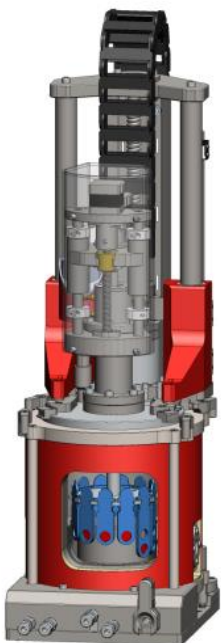
[§]University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

Preferential adsorption of ethanol even at low P_{H_2O}

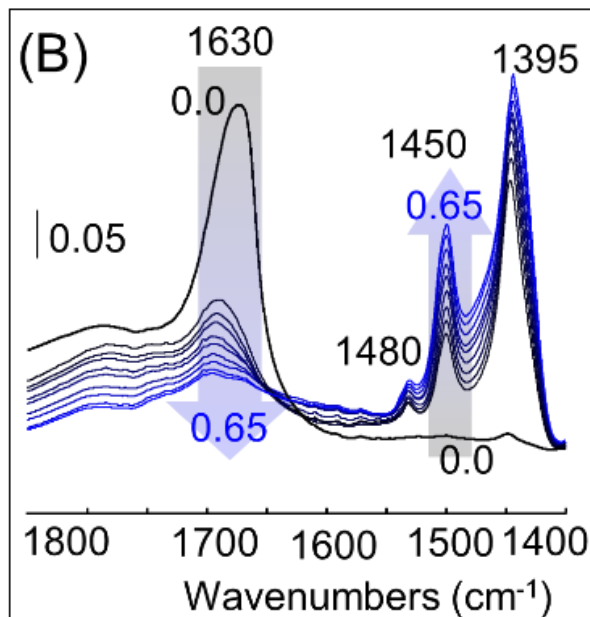




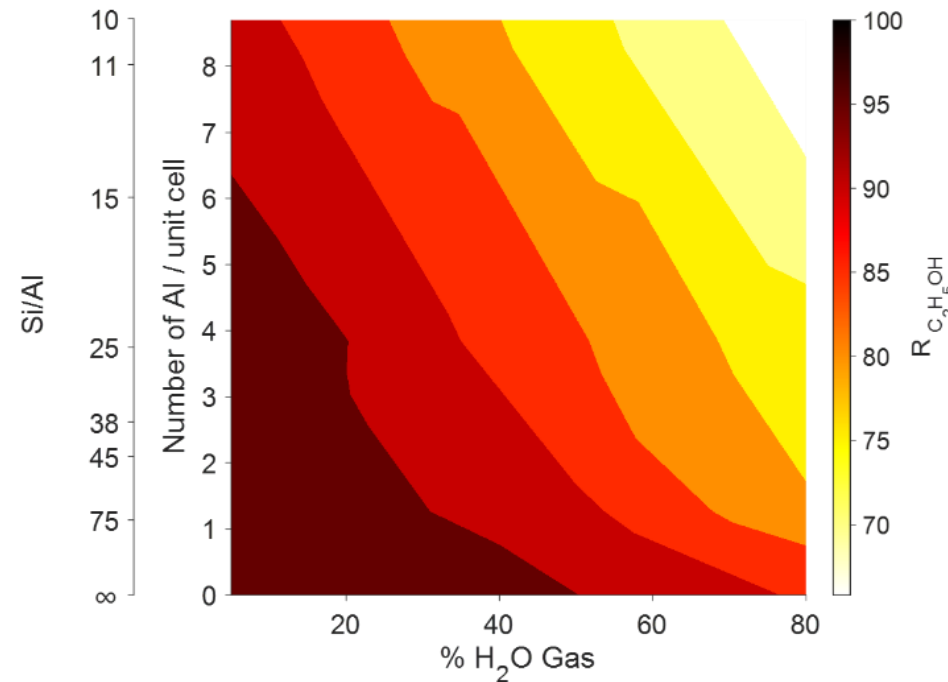
Adsorption of binary mixtures in porous materials



C₂H₅OH uptake at 0% H₂O
(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 ZrO₂ vs P

- All bands increase simultaneously
- Curve fitting not applicable

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

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

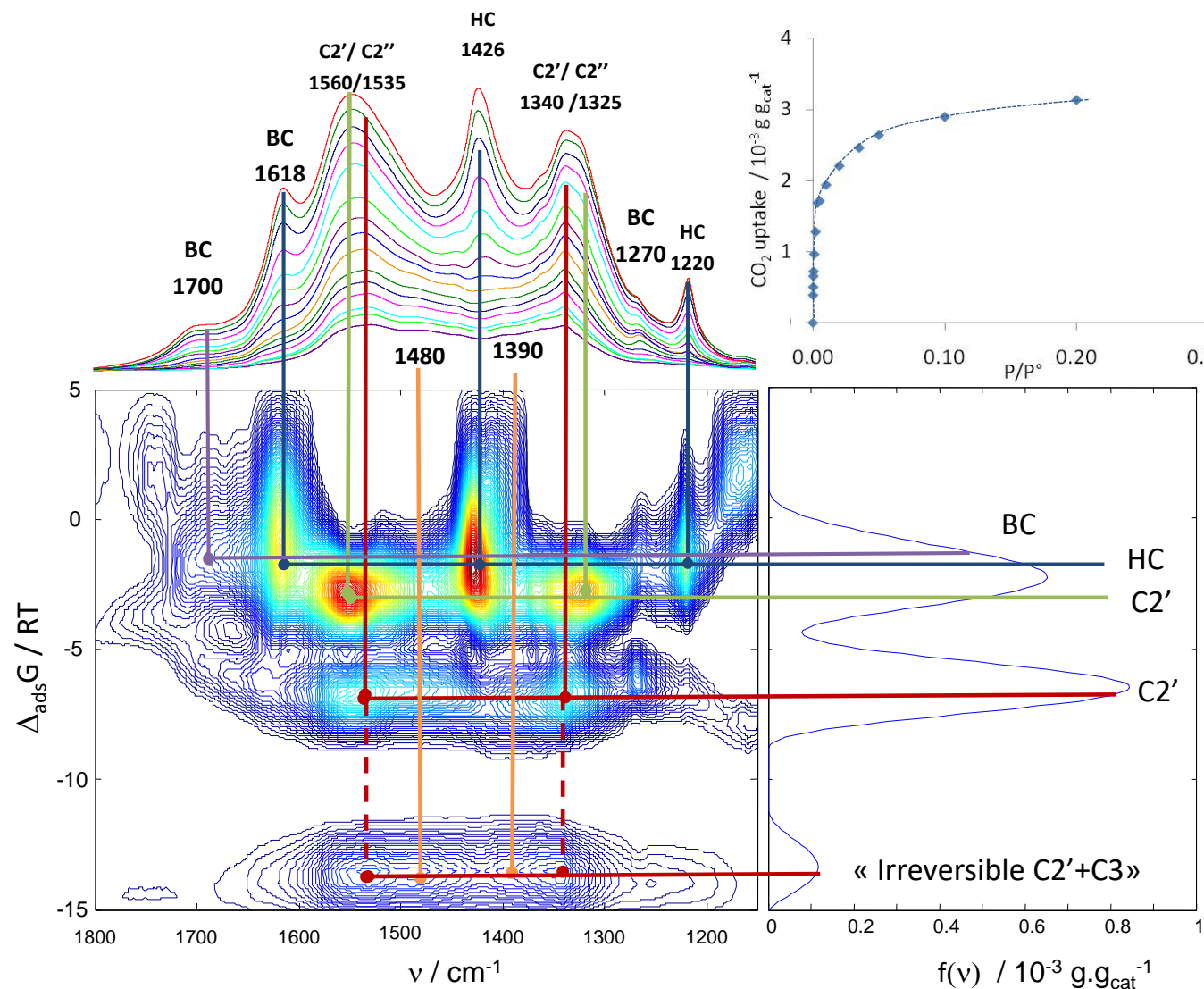
IR spectra

2D Distribution function

Resolves individual spectra on the energy scale.

⇒ Nature & Stability of distinct species.

⇒ Quantification with AGIR





Extension to other processes

$$p \quad q \quad \theta_i = K(p, q)$$

Adsorption

$$p \quad K_{ads} \quad \theta_i = \frac{K_{ads} p}{1 + K_{ads} p}$$

First order rxn, reactant

$$t \quad k \quad \theta_i = \exp(-kt)$$

First order rxn, product

$$t \quad k \quad \theta_i = 1 - \exp(-kt)$$

Internal diffusion

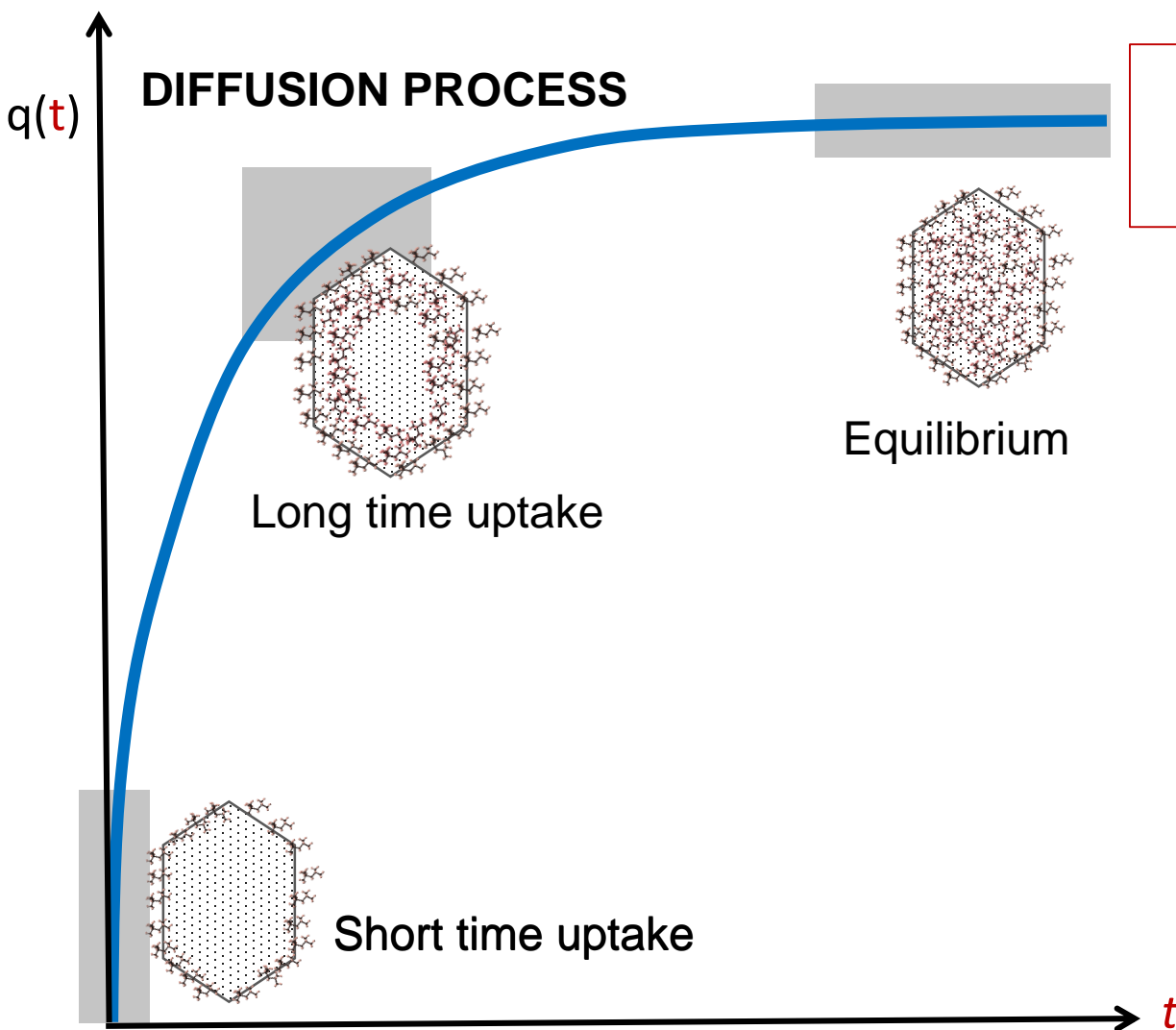
$$t \quad D/L^2 \quad \theta_i = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2}{9} \frac{D}{L^2} t\right)$$

TPD, first order

$$T \quad E \quad \theta_i = \exp\left[-\frac{v_0}{\beta} \left(T \exp\left(-\frac{E}{RT}\right) - T_0 \exp\left(-\frac{E}{RT_0}\right) - \frac{E}{R} \left(\text{expint}\left(\frac{E}{RT}\right) - \text{expint}\left(\frac{E}{RT_0}\right)\right)\right)\right]$$



Internal diffusion in zeolite-based materials



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

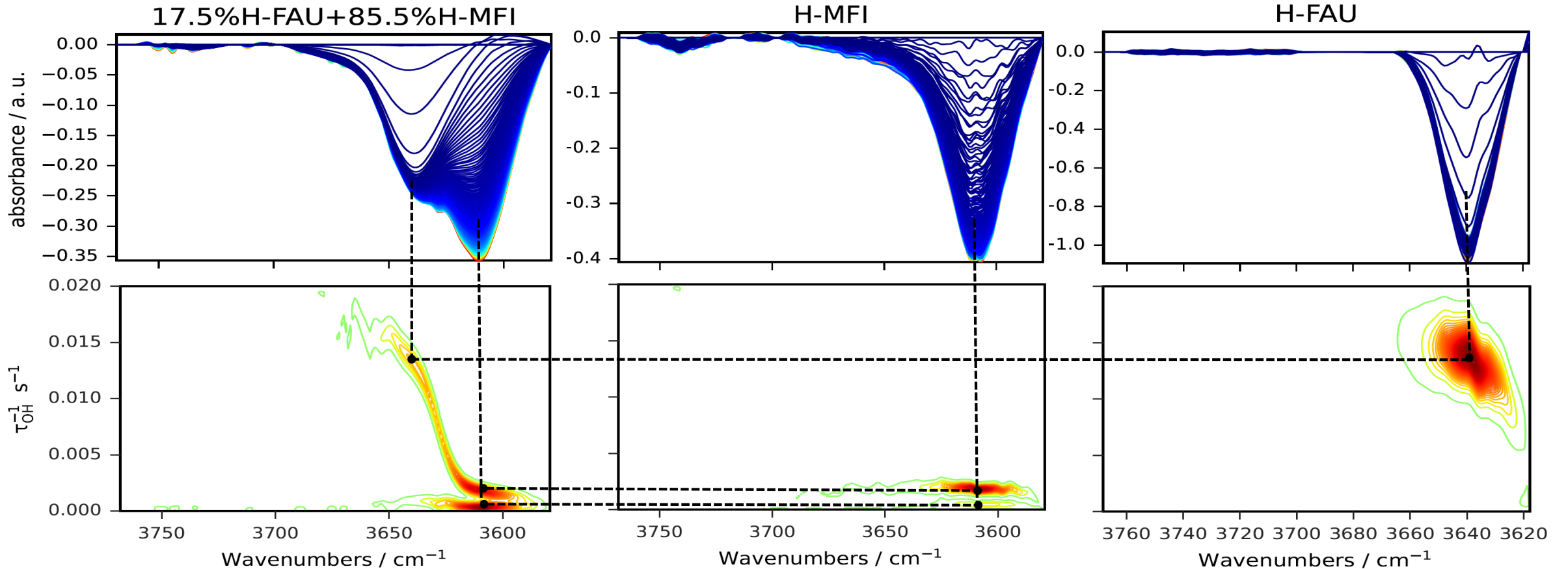
characteristic diffusion rate $\tau^{-1} = \frac{D_e}{L^2}$

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



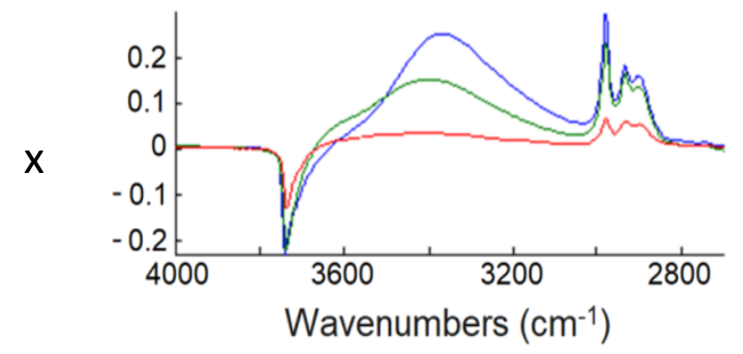
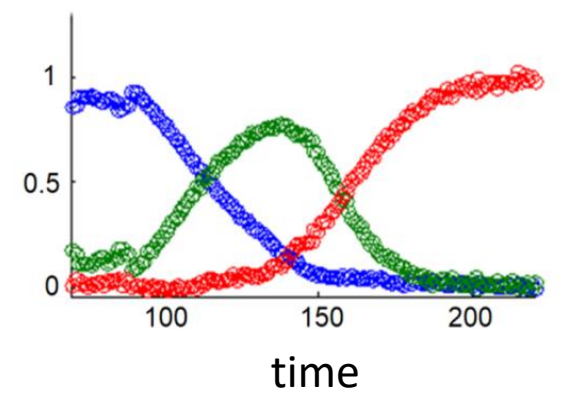
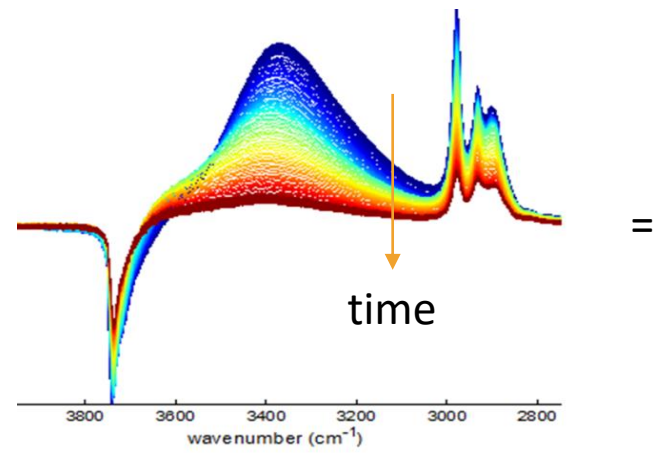
Ait Blal et al. 2022,. submitted



MCR-ALS to unravel complex transformation processes

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

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



The solution is not unique.
Getting chemically meaningful species requires adding constraints



Classical constraints and algorithm

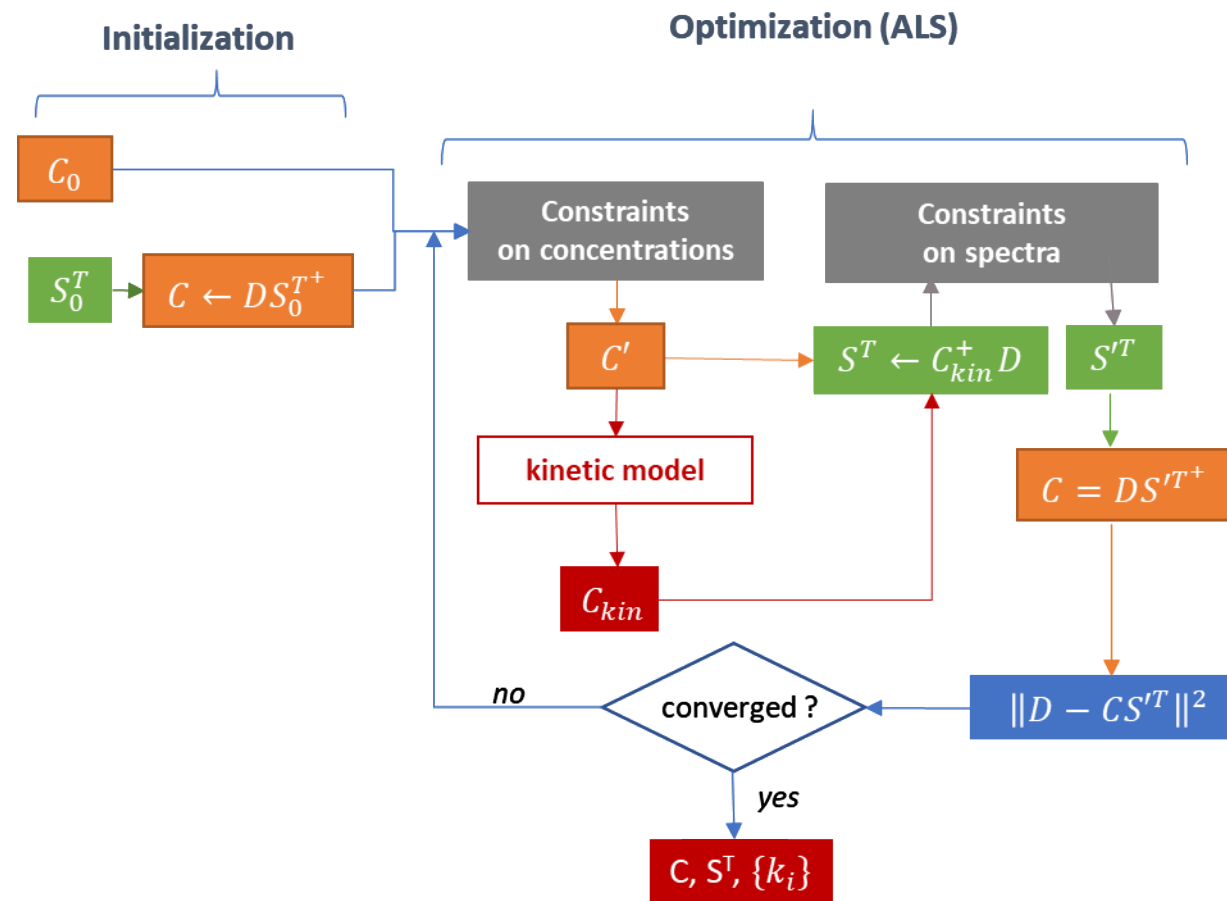
Constraints on C and/or S^T

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

« Hard » constraints on C and/or S^T

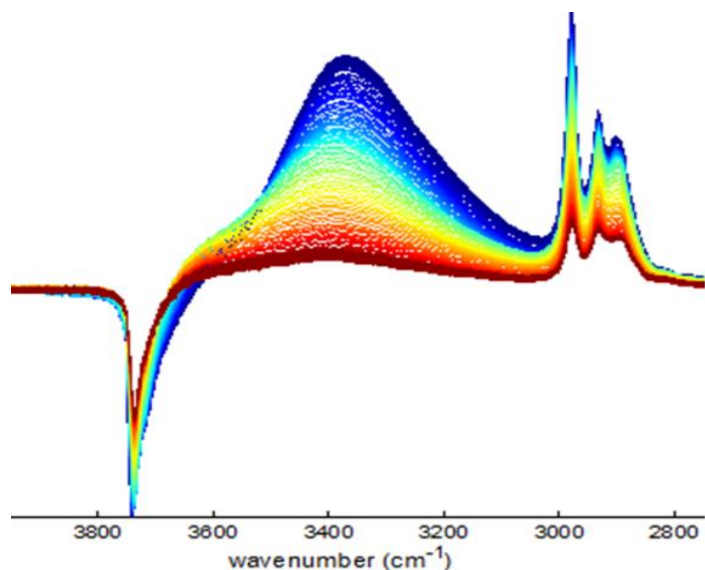
- part C or S^T a priori known
 - Spectrum of known species
 - Concentration profile (full or partial)

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. | $H_2O_{ads} \rightarrow H_2O_g$ | $H_2O \cdots HOSi \equiv \rightarrow HOSi \equiv + H_2O_{(g)}$ |

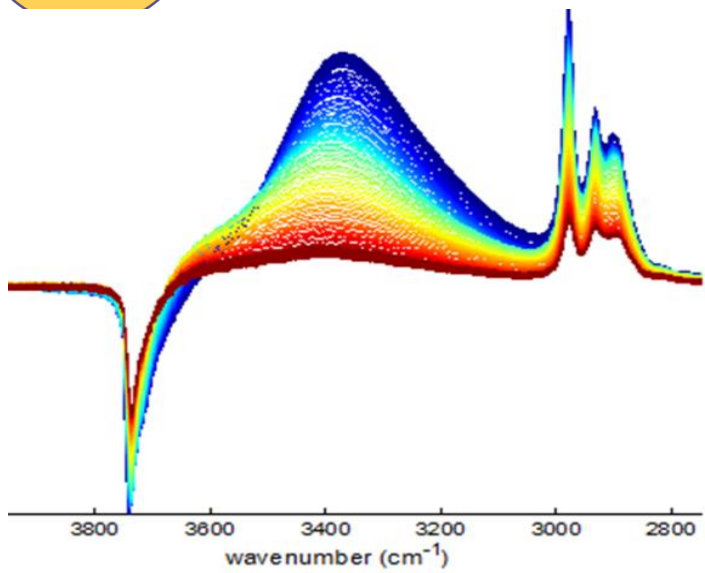
Single-site formal kinetics model

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**

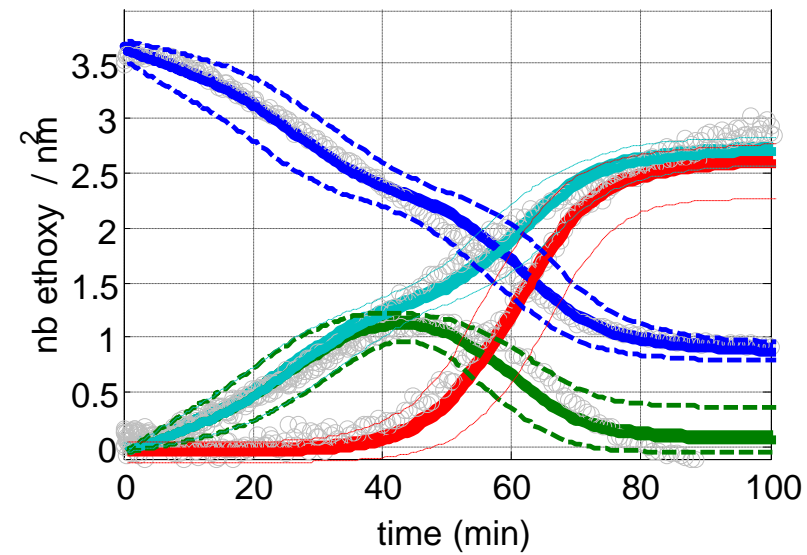


Example: Silane grafting on SiO₂

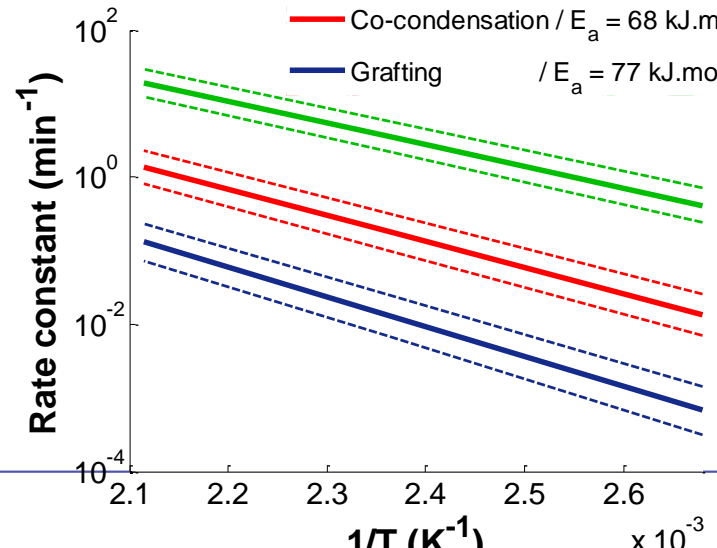


Rate constants and activation energies

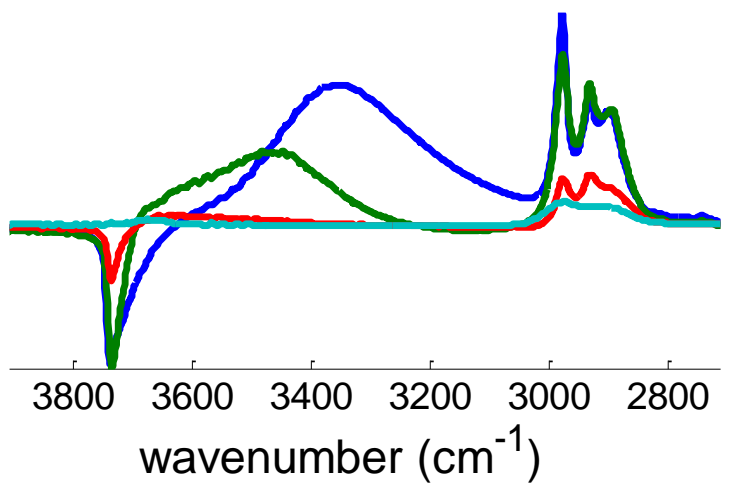
Concentration profiles



- Hydrolysis / $E_a = 57 \text{ kJ.mol}^{-1}$
- Co-condensation / $E_a = 68 \text{ kJ.mol}^{-1}$
- Grafting / $E_a = 77 \text{ kJ.mol}^{-1}$



Spectra of pure species

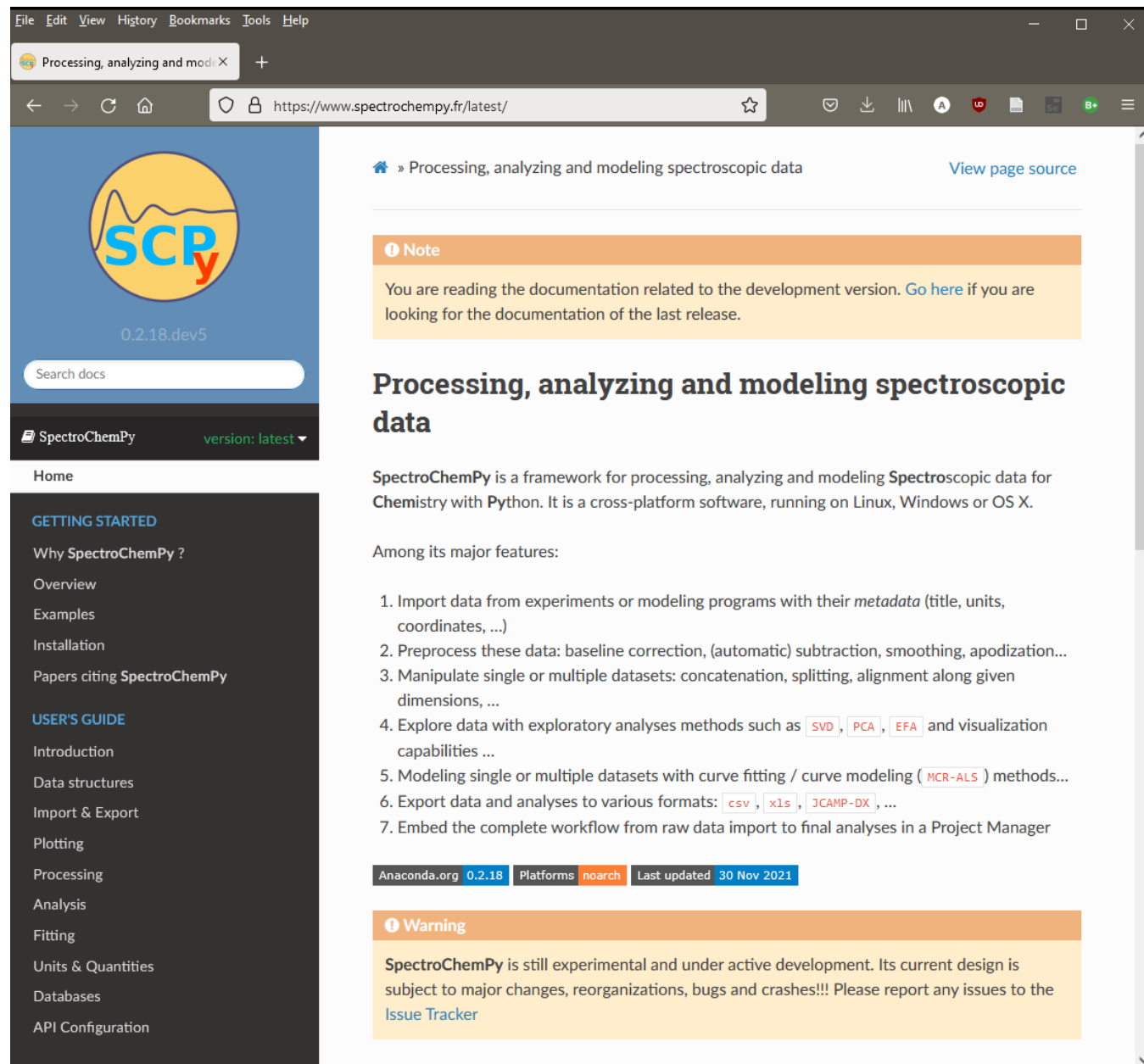


- A (surf) = **Physisorbed**
- B (surf) = **Hydrolysed**
- C (surf) = **grafted + co-condensed**

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

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)



The screenshot shows the SpectroChemPy website documentation page. The browser address bar shows the URL <https://www.spectrochempy.fr/latest/>. The page features a navigation menu on the left with sections like 'GETTING STARTED' and 'USER'S GUIDE'. The main content area includes a 'Note' box stating that the user is viewing the development version documentation, a title 'Processing, analyzing and modeling spectroscopic data', a brief description of SpectroChemPy as a cross-platform framework, a list of seven major features, and a 'Warning' box indicating that the software is still experimental and under active development.

Processing, analyzing and modeling spectroscopic data [View page source](#)

Note

You are reading the documentation related to the development version. [Go here](#) if you are looking for the documentation of the last release.

Processing, analyzing and modeling spectroscopic data

SpectroChemPy is a framework for processing, analyzing and modeling Spectroscopic data for Chemistry with Python. It is a cross-platform software, running on Linux, Windows or OS X.

Among its major features:

1. Import data from experiments or modeling programs with their *metadata* (title, units, coordinates, ...)
2. Preprocess these data: baseline correction, (automatic) subtraction, smoothing, apodization...
3. Manipulate single or multiple datasets: concatenation, splitting, alignment along given dimensions, ...
4. Explore data with exploratory analyses methods such as `SVD`, `PCA`, `EFA` and visualization capabilities ...
5. Modeling single or multiple datasets with curve fitting / curve modeling (`MCR-ALS`) methods...
6. Export data and analyses to various formats: `csv`, `xls`, `JCAMP-DX`, ...
7. Embed the complete workflow from raw data import to final analyses in a Project Manager

Anaconda.org `0.2.18` Platforms `noarch` Last updated `30 Nov 2021`

Warning

SpectroChemPy is still experimental and under active development. Its current design is subject to major changes, reorganizations, bugs and crashes!!! Please report any issues to the [Issue Tracker](#)



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**

