Project 8

Measuring Zeolitic Diffusion by the Frequency Response Technique

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Goals

- Explore the diffusivity in molecular sieves as function of
  - Pore size and connectivity
    - AFI (uni-dimensional channels)
    - Silicalite-1, Ferrierite (two intersecting channels)
    - LTA, NaX (three-dimensional network)
  - Pressure
  - Temperature
- Explore the diffusivity in the presence of more than one sorbing component as function of
  - Pore size and connectivity
  - Pressure
  - Temperature

Means

- Frequency Response technique accessed *via* pressure variations
- Determination of averaged coverages by IR spectroscopy and TGA

Frequency response technique

- Response of a closed system to a periodic perturbation

Volume modulation → Pressure response

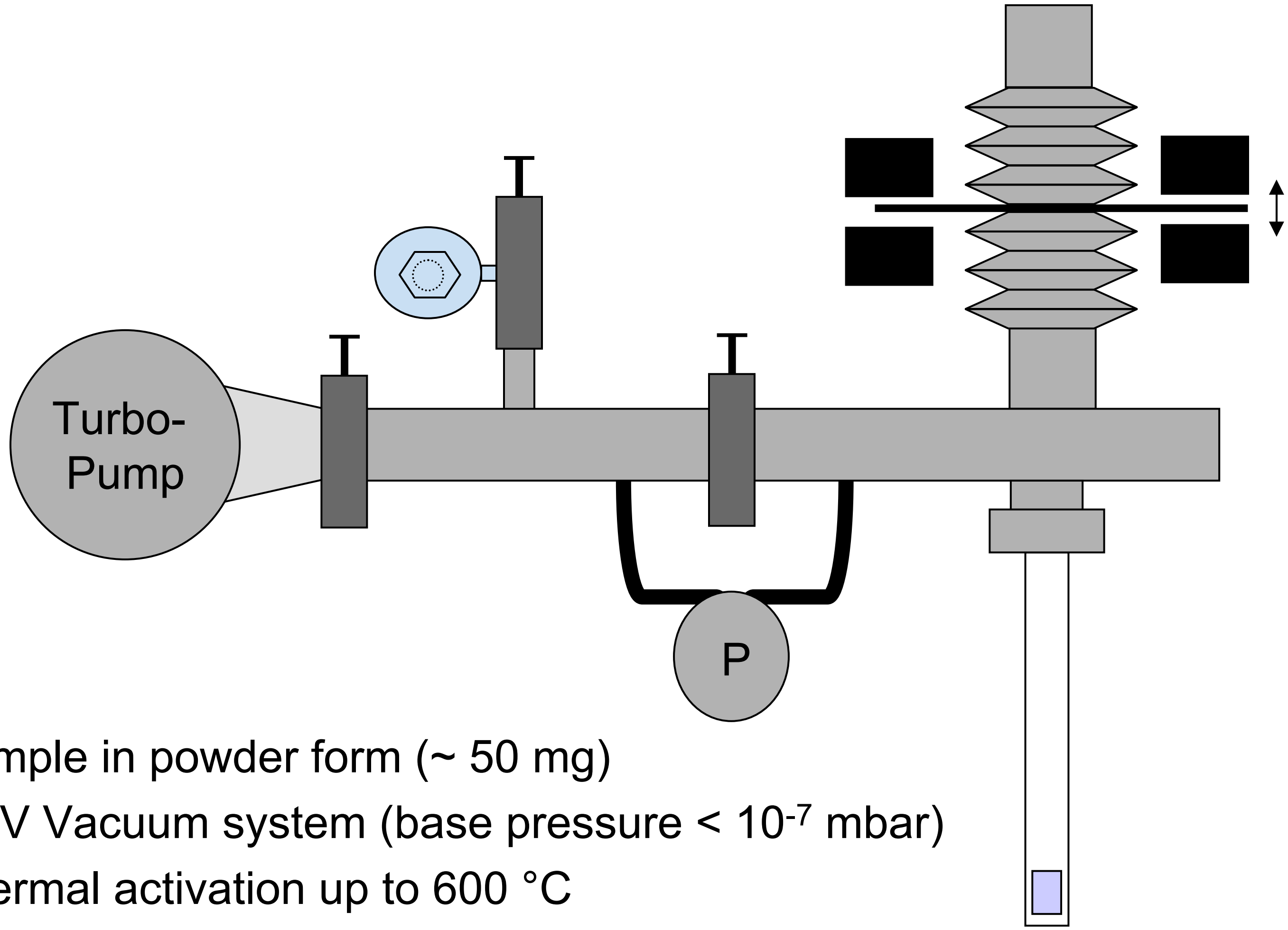
  - **Empty system**: the pressure modulation varies at the same frequency as the volume perturbation (180° out of phase)
  - **Porous sample**: change in the phase and the amplitude of the pressure response to volume modulation is observed

- Measuring the pressure response as function of the frequency of the pressure perturbation

→ Determination of diffusion coefficients

Experimental setup

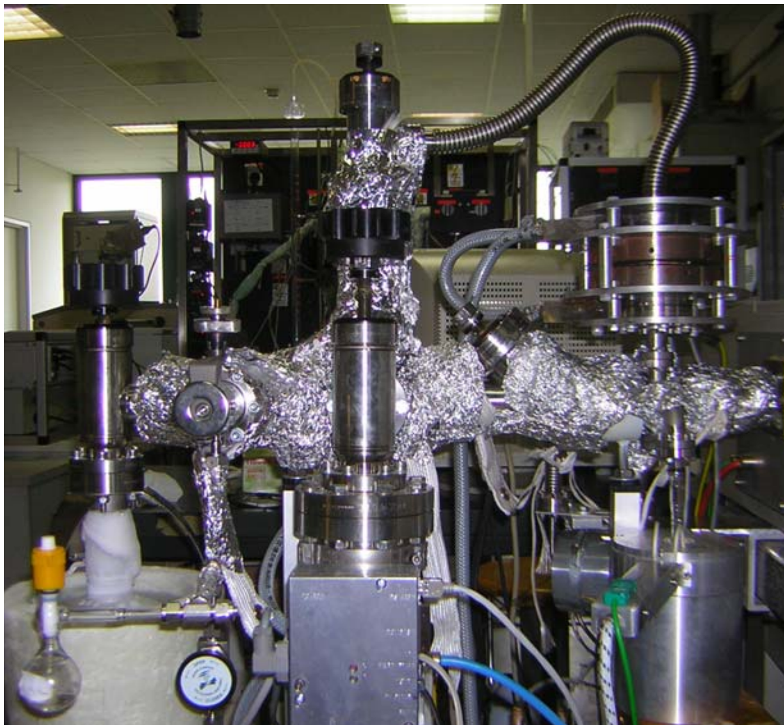
Square-wave volume modulation

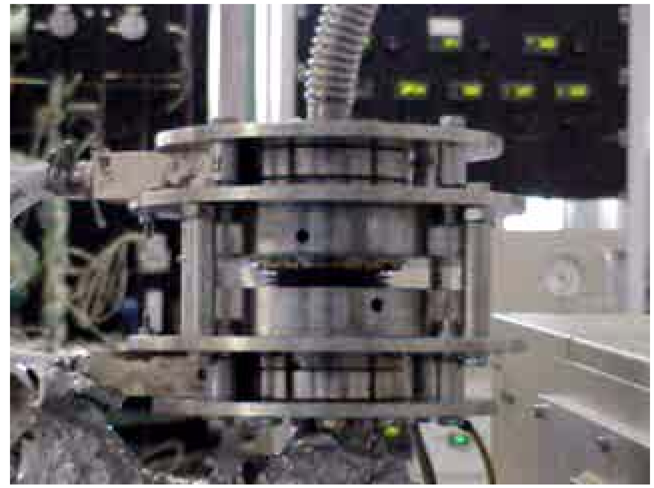


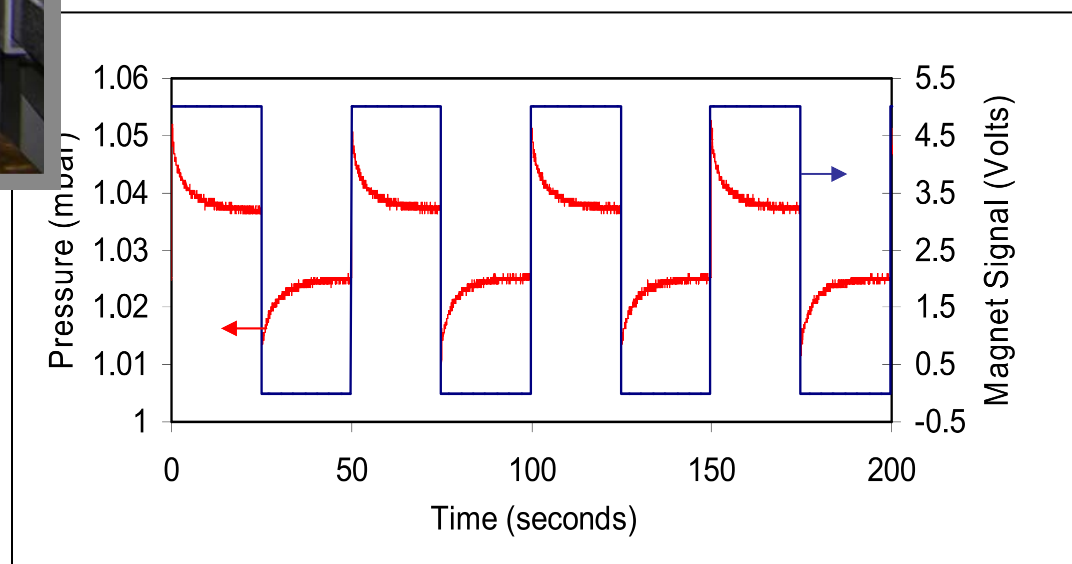
- Sample in powder form (~ 50 mg)
- UHV Vacuum system (base pressure < 10^{-7} mbar)
- Thermal activation up to 600 °C
- Magnetically driven separator plate, UHV bellows
- Frequency range 0.001 – 5 Hz
- High precision differential pressure gauge (MKS-Baratron)

Frequency response Method

Square-wave volume modulation







Frequency response method

Experimental data

p_B/p_Z = amplitude ratio

$\phi_Z - \phi_B$ = phase lag

Theoretical model

$\delta_c,\ \delta_s = f(f, r, D)$

$K = (RT_0/V_e)(dB_e/dP_e)$

$$(p_B/p_Z)\cos(\phi_Z - \phi_B) - 1 = K\delta_c$$

$$(p_B/p_Z)\sin(\phi_Z - \phi_B) = K\delta_s$$

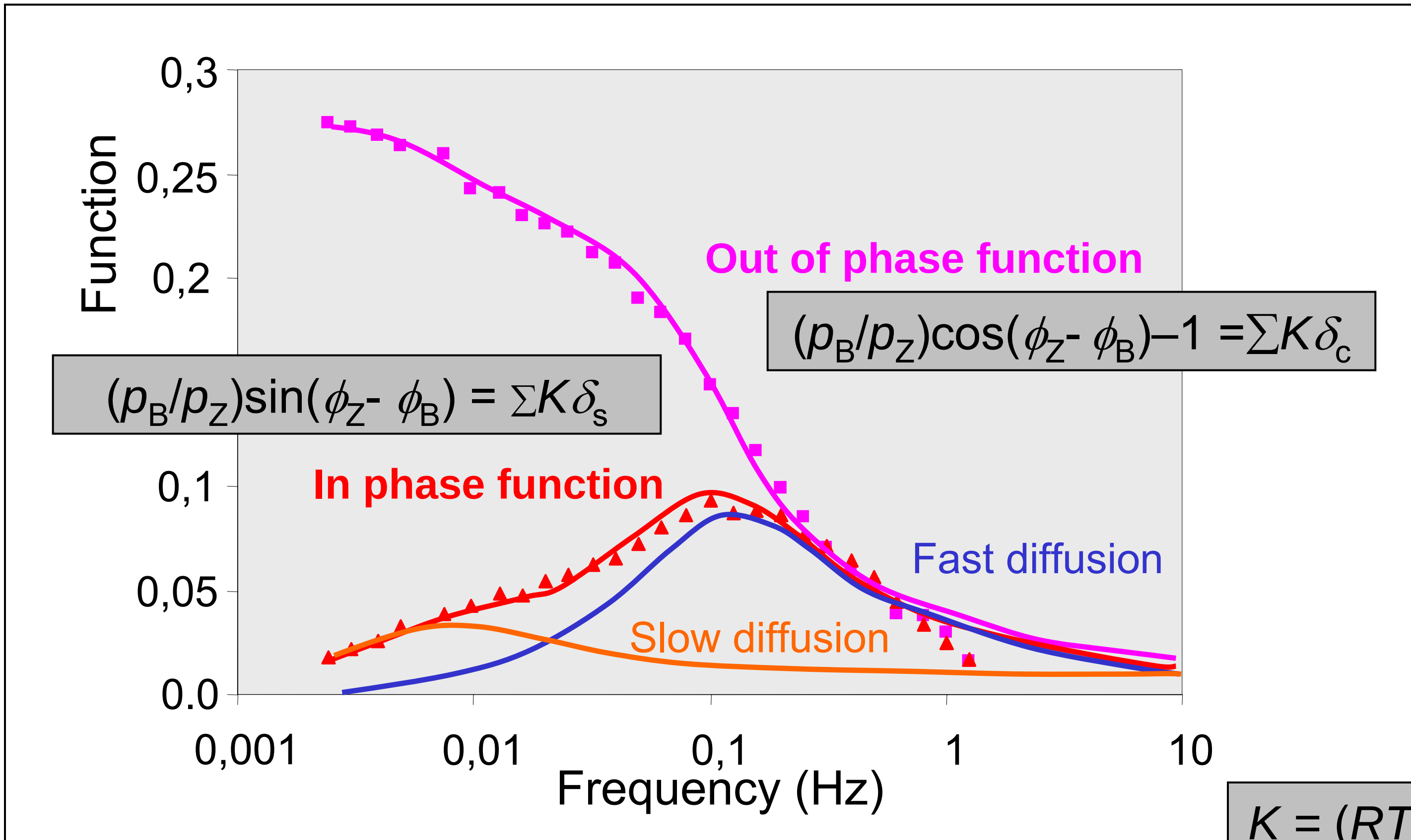
- Planar sheet model

$$\delta_{1c} = (1/\eta)(\sinh\eta + \sin\eta)/(\cosh\eta + \cos\eta) \qquad \eta = (\omega L^2/D)^{1/2}$$

$$\delta_{1s} = (1/\eta)(\sinh\eta - \sin\eta)/(\cosh\eta + \cos\eta) \qquad \omega = 2\pi f$$

- More complex models
  - Spherical particles
  - Two (or more) independent diffusion processes
  - Non-isothermal behavior
  - Diffusion rearrangement

Frequency response method



$$K = (RT_0/V_e)(dB_e/dP_e)$$

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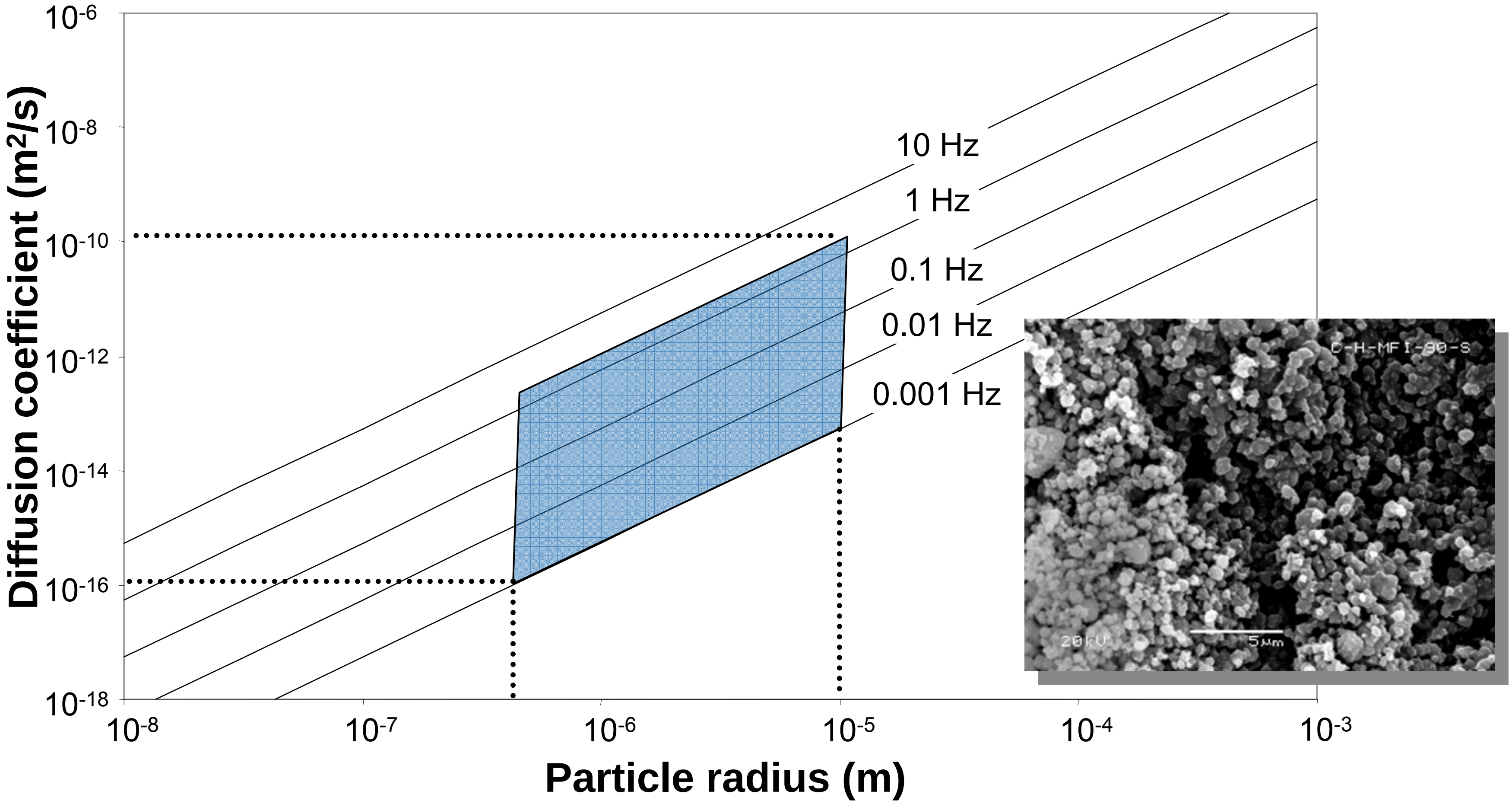
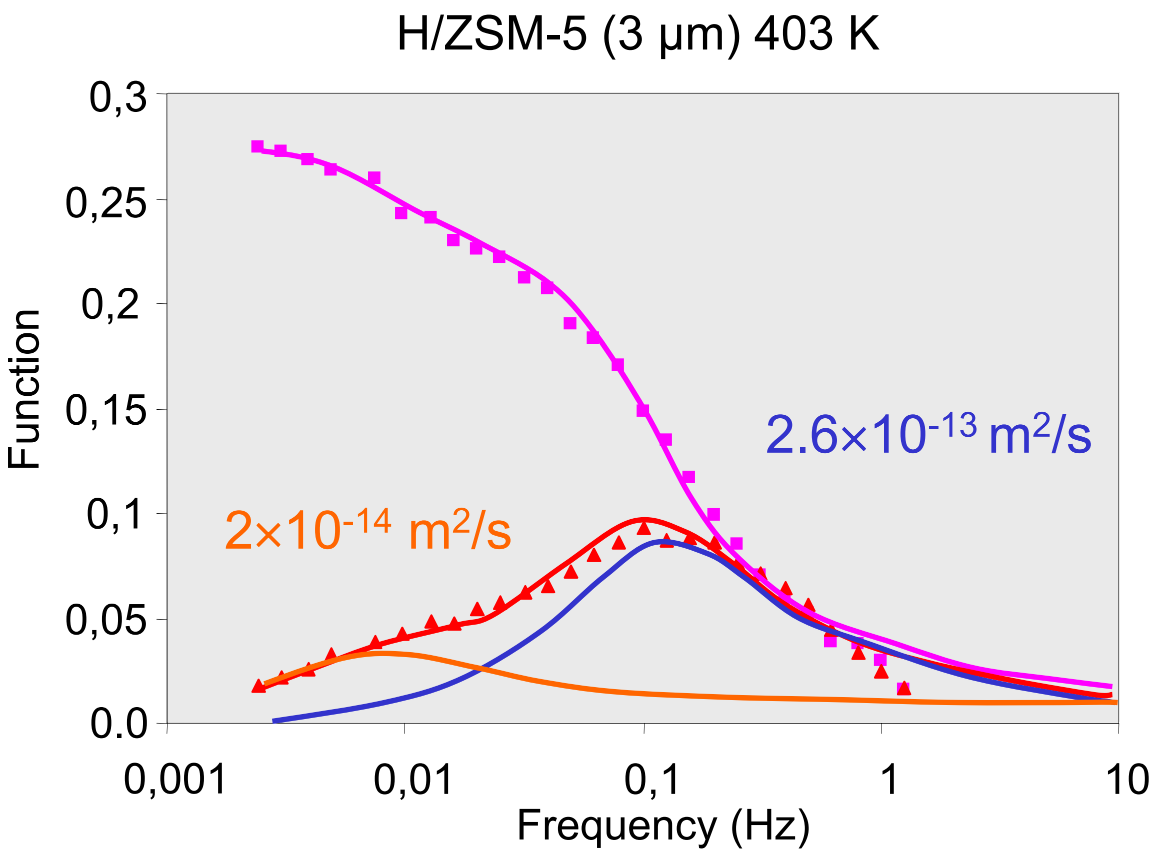
Relationship between frequency range, particle size and diffusion coefficient

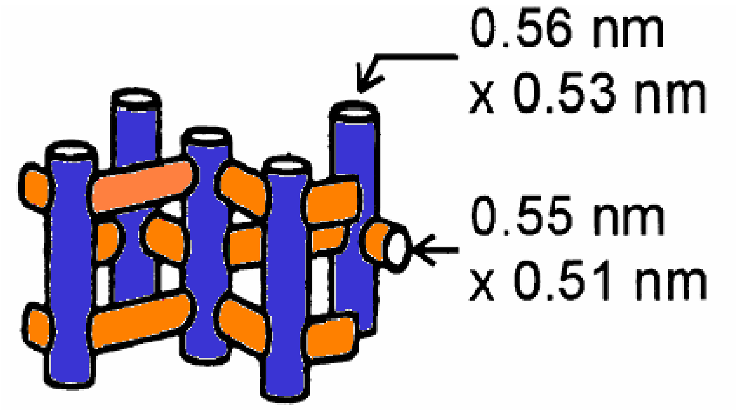


Advantages of the frequency response method

- Small perturbation to the sorption equilibrium
  - Concentration of the sorbed phase remains almost constant
  - Determination of diffusion coefficients as function of coverage
- Compression and expansion cycles
  - Adsorption and desorption pressure response
  - Differences in the diffusion mechanisms for the two processes
- Investigation of multiple diffusion processes
  - Separation of processes differing by half order of magnitude of D
- Using higher harmonics to study faster processes
  - Larger diffusion coefficients can be measured

Diffusion of toluene in H/ZSM-5

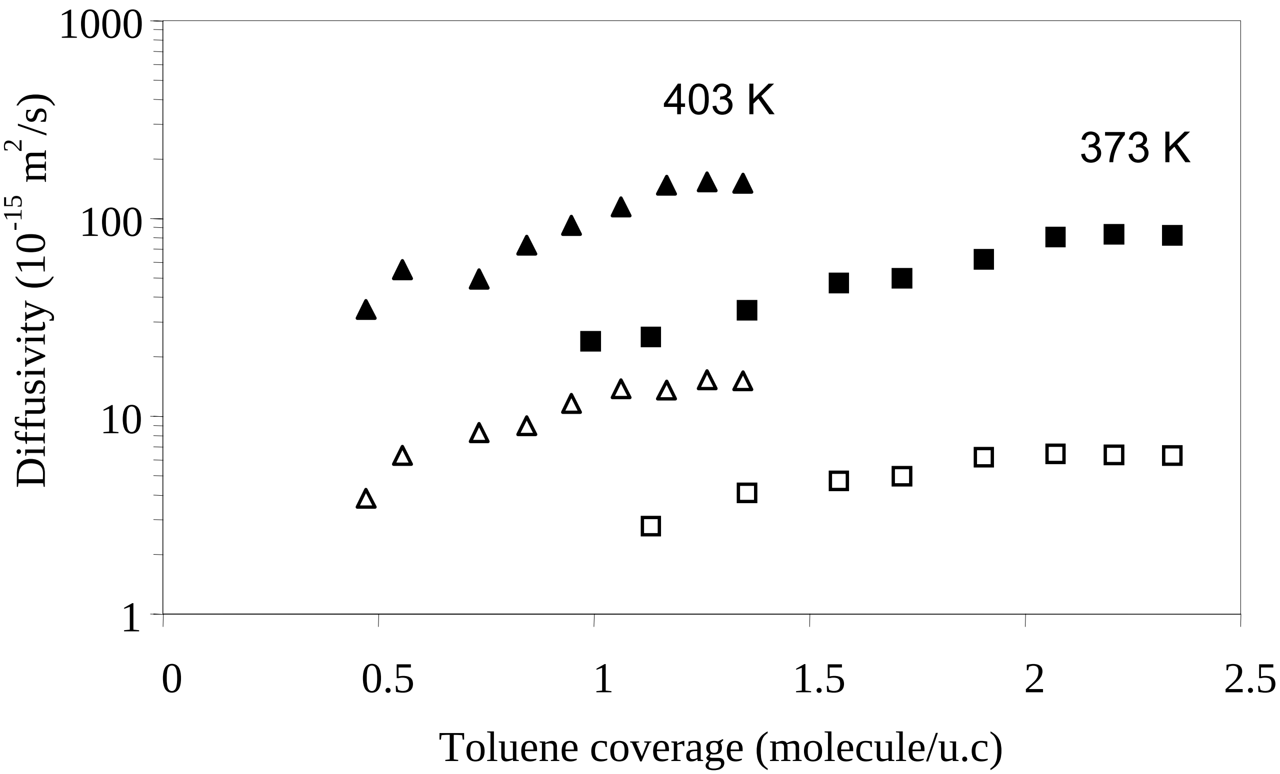




ZSM-5

Application of the frequency response method

Diffusion coefficients as function of coverage

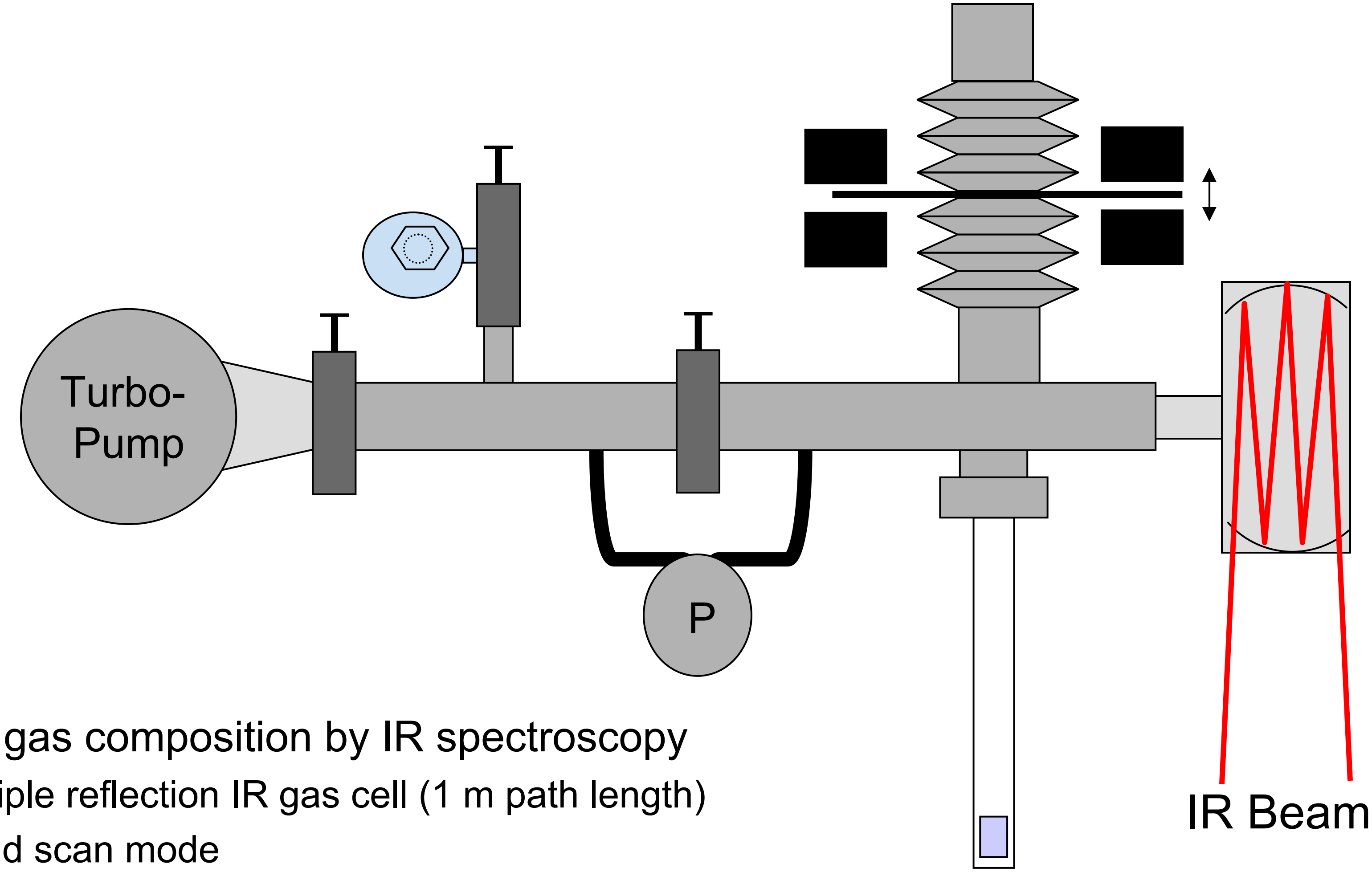


Work programme

- Diffusion in non uni-dimensional pore systems
  - Study sorption of benzene and alkanes in
    - AFI (uni-dimensional channels)
    - Silicalite-1, Ferrierite (two intersecting channels)
    - LTA, NaX (three-dimensional network)
  - effects of pore diameter, channel intersections and transport barriers
  - Link with other techniques within the project
- Multi-component diffusion in zeolites
  - Develop multi component detection of two (or more) molecules in the gas phase using IR spectroscopy
  - Study sorption of
    - Alkyl substituted aromatic molecules
    - n- and iso-alkanes (deuterated molecules)
  - Describe multi-component diffusion pathways and molecular passages
  - Differentiate between single-file and normal diffusion (passages possible)

Square-wave volume modulation

Multi component detection by IR spectroscopy



Analysis of gas composition by IR spectroscopy

- Multiple reflection IR gas cell (1 m path length)
- Rapid scan mode
- Vacuum IR spectrometer (high S/N)

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