Package of Research Projects **"Diffusion in Zeolites"**

by CNRS (France), DFG (Germany), EPSRC (United Kingdom), NSF (USA)

Extension for the Period from 2006-2009

Project 6

PFG NMR Studies of Zeolitic Diffusion

Petrik Galvosas

Jörg Kärger

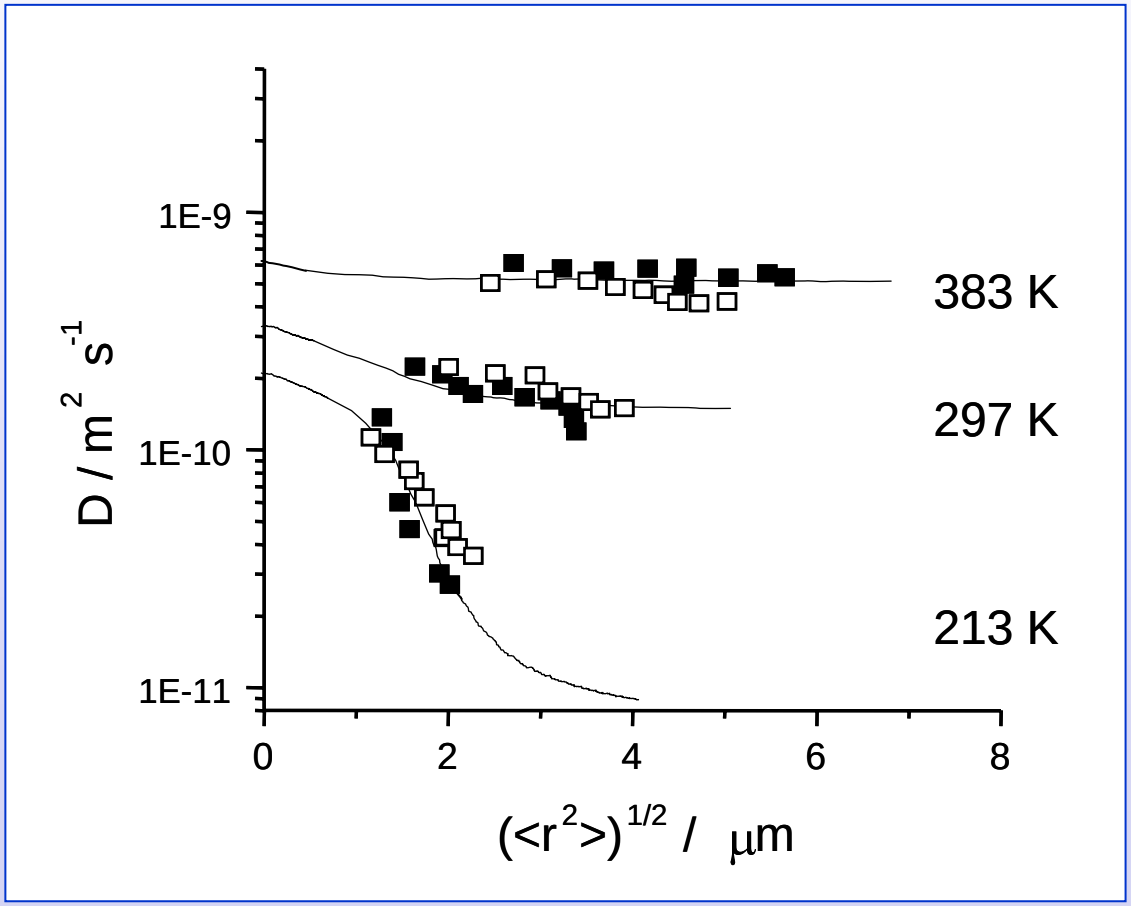
Margarita Krutyeva

Cordula Bärbel Krause

Marcel Gratz

Intracrystalline Diffusion

Comparison of the PFG NMR results with the results of MC simulations



n-Butane / Silicalite-1

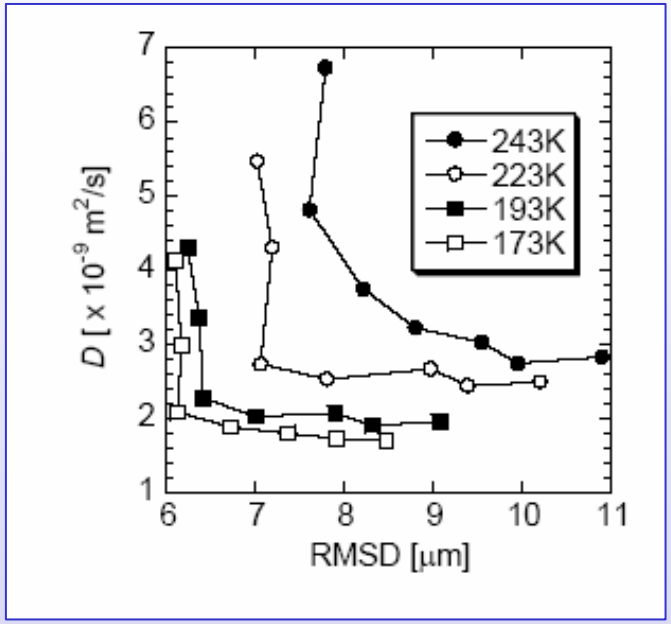
two sets of measurement with different samples

$p_y = 1$ $p_x = 0.32$
$p_z = 0.067$

$(E_b - E_d)$ = 21.5 kJ/mol
N = 3000 (×1nm)

Gas Diffusion in Polycrystalline MFI-type Zeolite Membranes

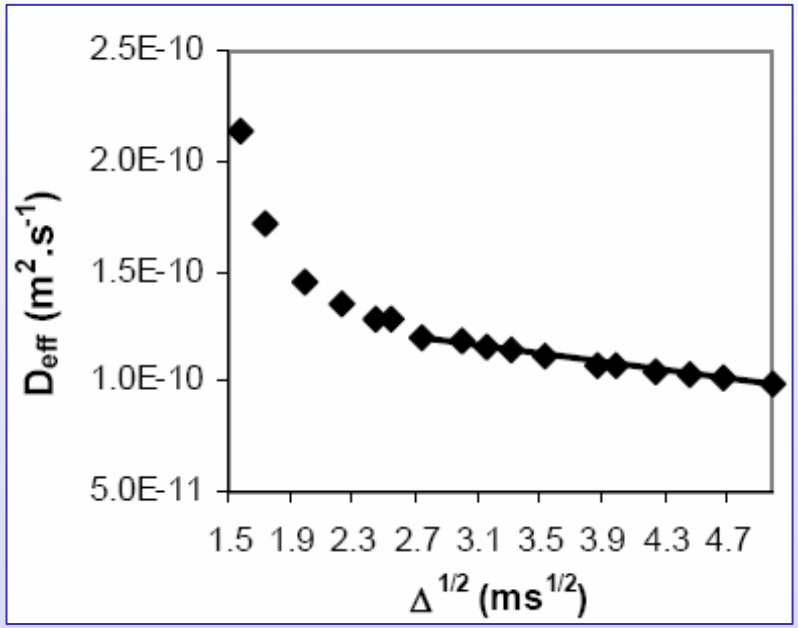
H. Takaba, A. Yamamoto, K. Hayamizu, S. Nakao



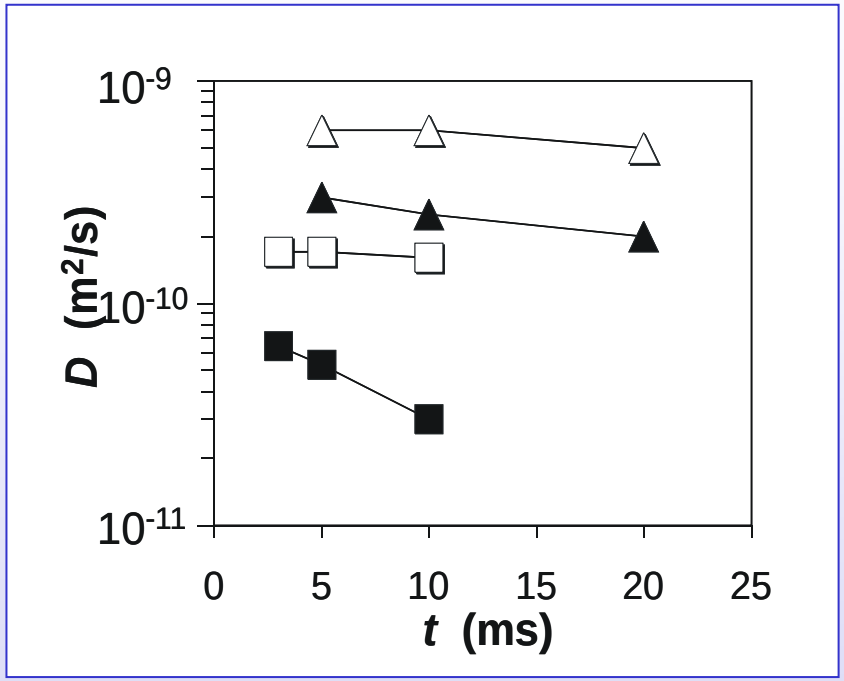
The relationship of the estimated
diffusion coefficients of methane and the RMSD.

Evidence for Subdomaines in Large Crystals of NaX Zeolite

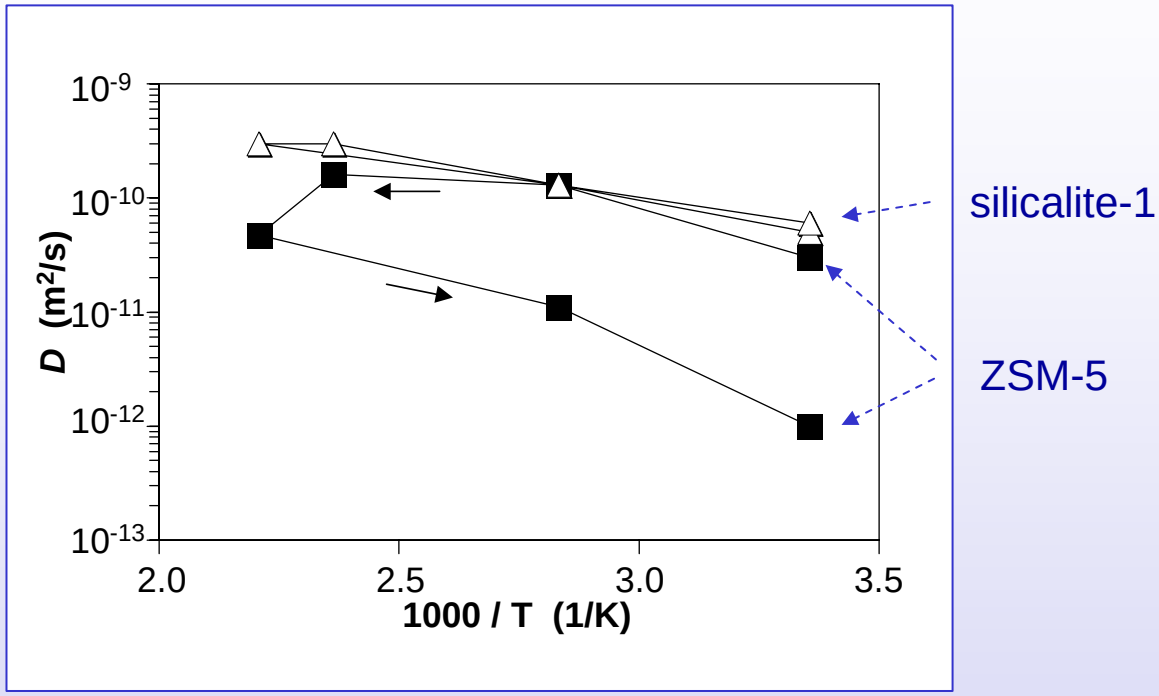
Z. Adem, F. Guenneau, M.-A. Springuel-Huet, A. Gédéon



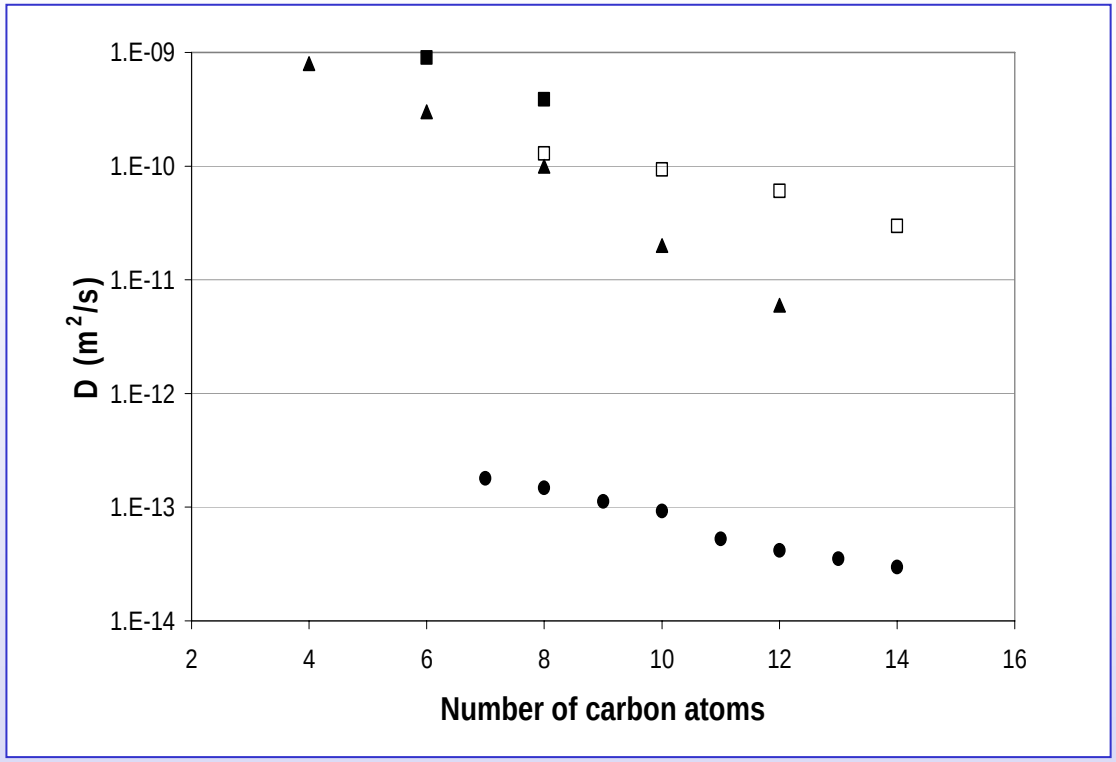
Effective diffusivity of *n*-hexane in zeolite NaX at 293 K as a function of observation time.



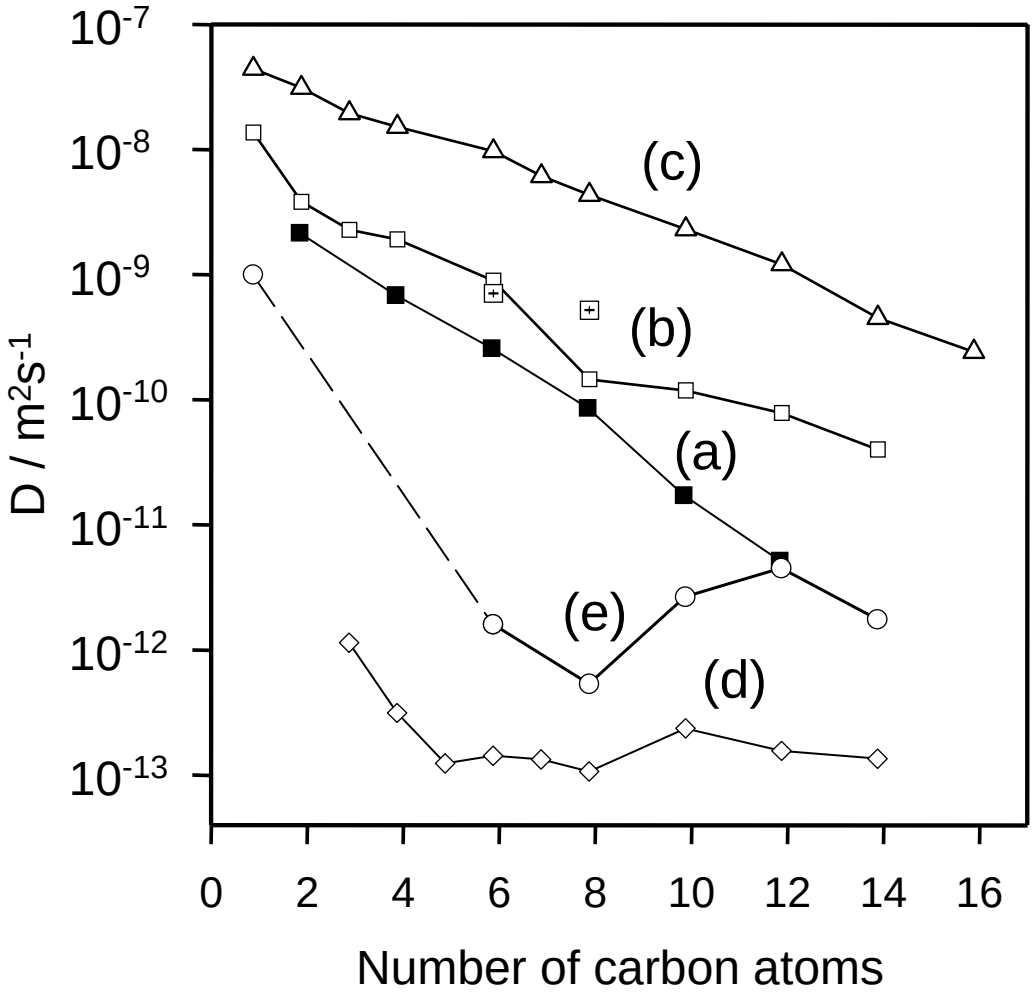
Self-diffusion coefficients of n-butane in silicalite-1 (triangles) and of *n*-hexane in ZSM-5 (squares) at 298 K (filled symbols) and 353 K (open symbols), measured by PFG NMR as a function of the observation time.



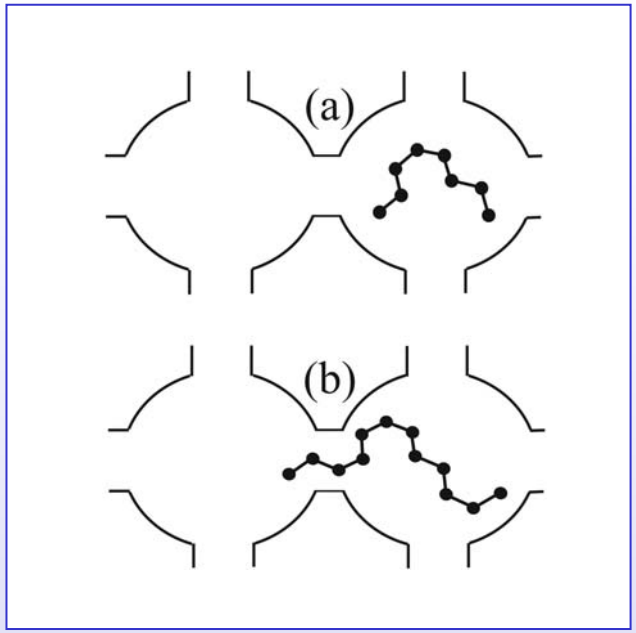
Arrhenius representation of the guest diffusivities measured by PFG NMR within a (closed) sample containing MFI-type zeolites (△: silicalite-1, ■: ZSM-5) loaded with *n*-hexane at a concentration corresponding to 1 molecule per channel intersection, and their reproducibility after temperature enhancement and reduction. The observation time was 10 ms, the measuring error was smaller than 10 %.



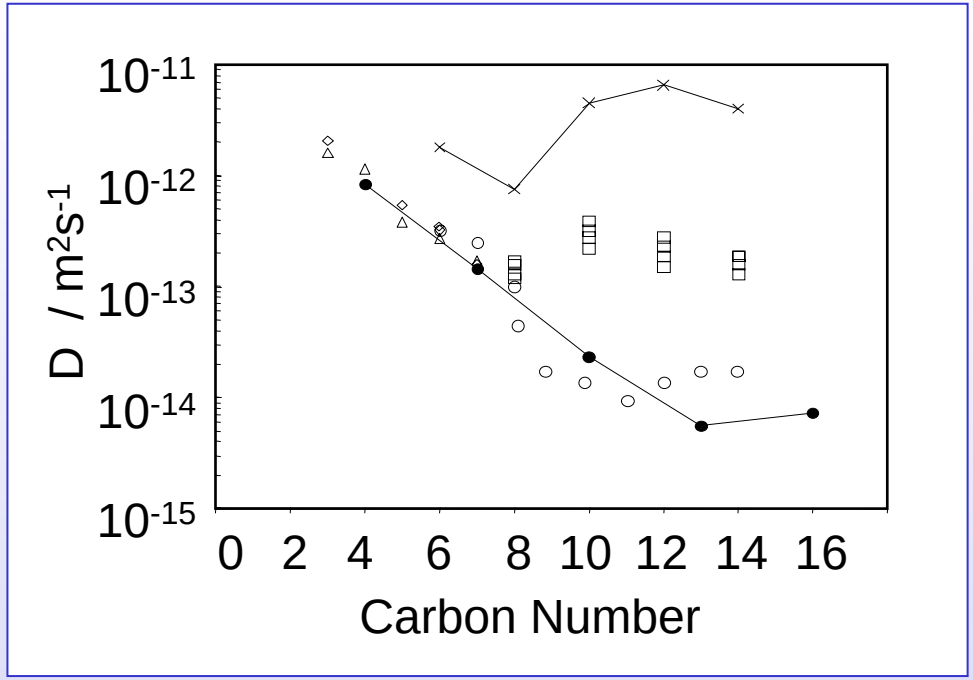
n-alkanes in MFI at a loading corresponding to 6 carbons per channel crossing.
Comparison of experimental results at 423K.
■ QENS new data; □ QENS; ▲ PFG-NMR ; ● ZLC.



Chain-length dependence of the self-diffusivities of *n*-alkanes in **(a)** silicalite-1 determined by PFG NMR at 423 K and in **(b)** Na-ZSM-5 determined by QENS at 475 K (the dotted squares correspond to the new measurements in silicalite-1) and comparison with previous PFG NMR self-diffusion measurements in **(c)** NaX at 475 K and in **(d)** NaCaA at 443 K and **(e)** neutron spin echo transport diffusion measurements in NaCaA at 475 K.



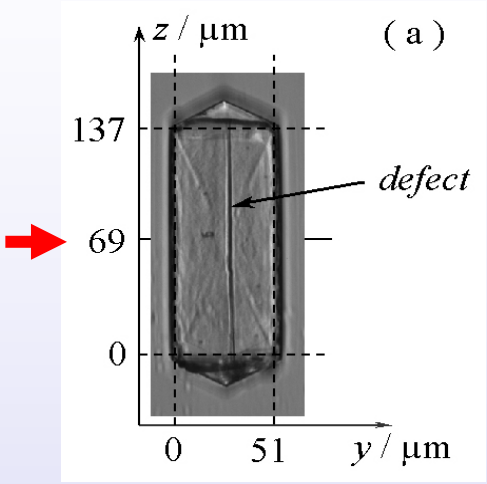
Schematic representation of the configuration of two *n*-alkanes within the hole network of a zeolite: *n*-octane fits well into a cage (a), but one end of *n*-dodecane sits in a window between two cages (b).



n-alkanes in NaCaA:
Variation of diffusivity with carbon number (at 473K).
NSE **x**
ZLC ● and o
PFG NMR data at 1 molecule/cage Δ and □, and 2 molecules/cage ◊ .

Package of Research Projects **"Diffusion in Zeolites"**
by CNRS (France), DFG (Germany), EPSRC (United Kingdom), NSF (USA)
Extension for the Period from 2006-2009

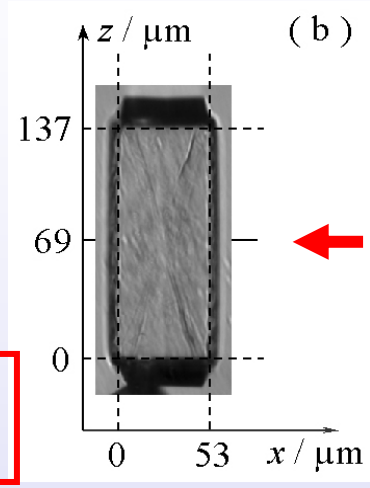
Influence of defects on the external crystal surface on the isobutane uptake into MFI-type zeolite

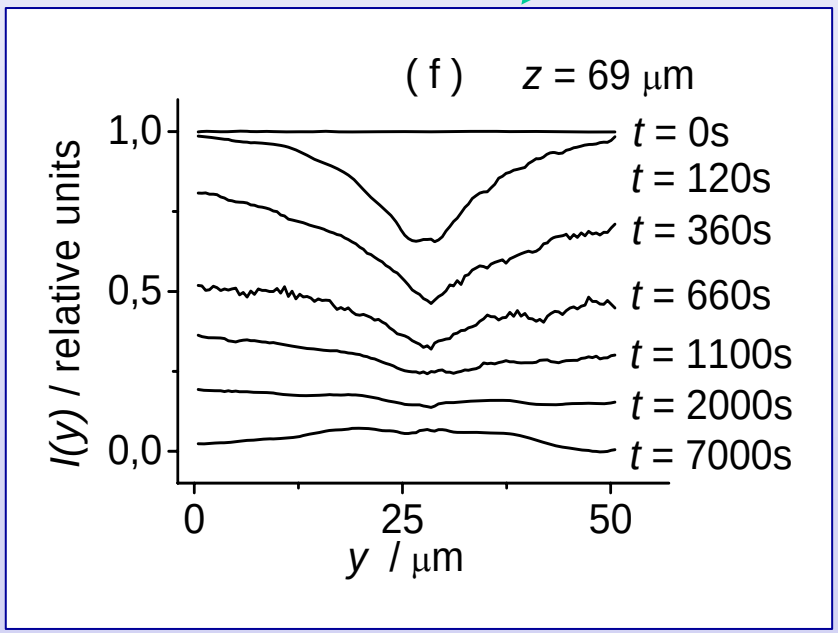


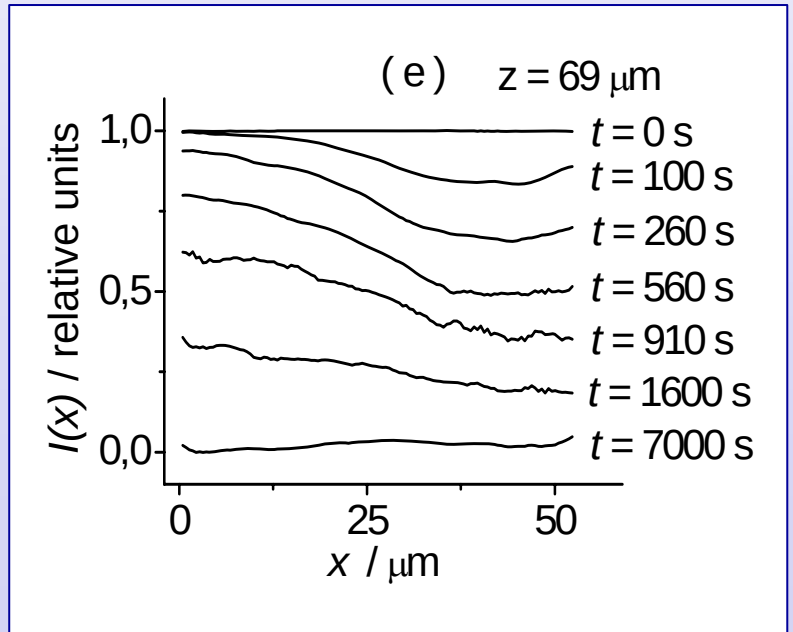
The non-etched sample (strong surface barriers)

Faster desorption in the middle part of the crystals than near crystal edges: desorption through the crack surface

Faster desorption in the crystal part with the crack



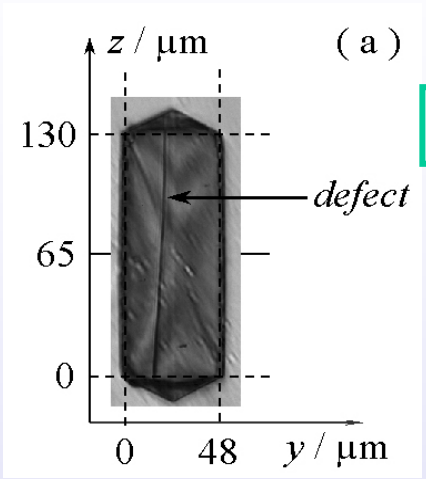


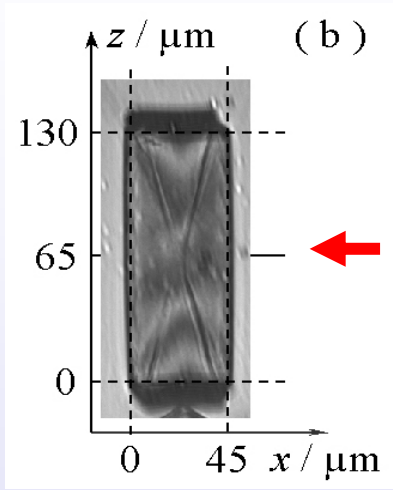


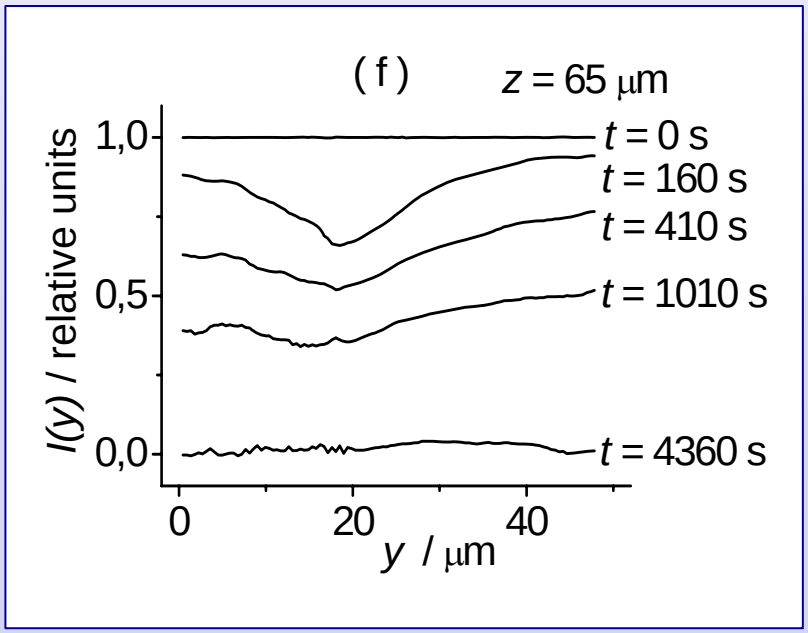
The etched sample (mild surface barriers)

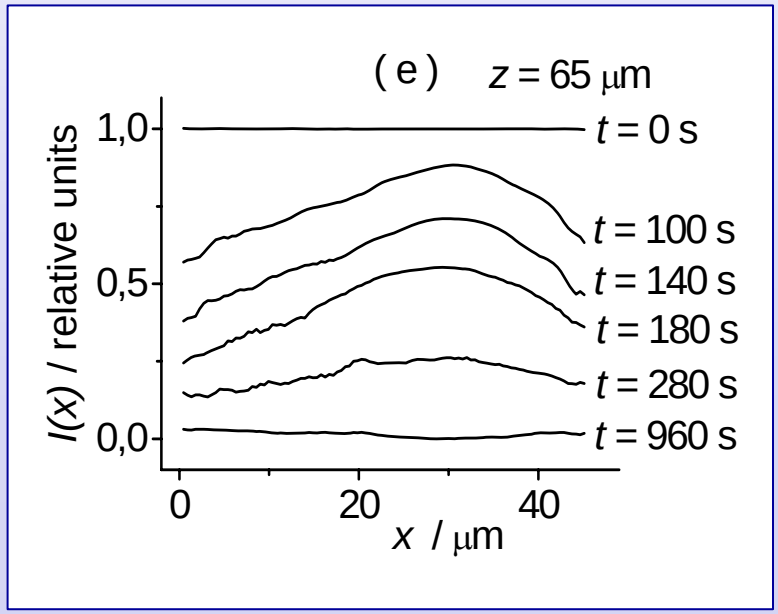
Desorption through the crack surface

(i) Both the diffusivity and permeability of transport barriers determine the rate of desorption
(ii) Faster desorption in the crystal part with the crack







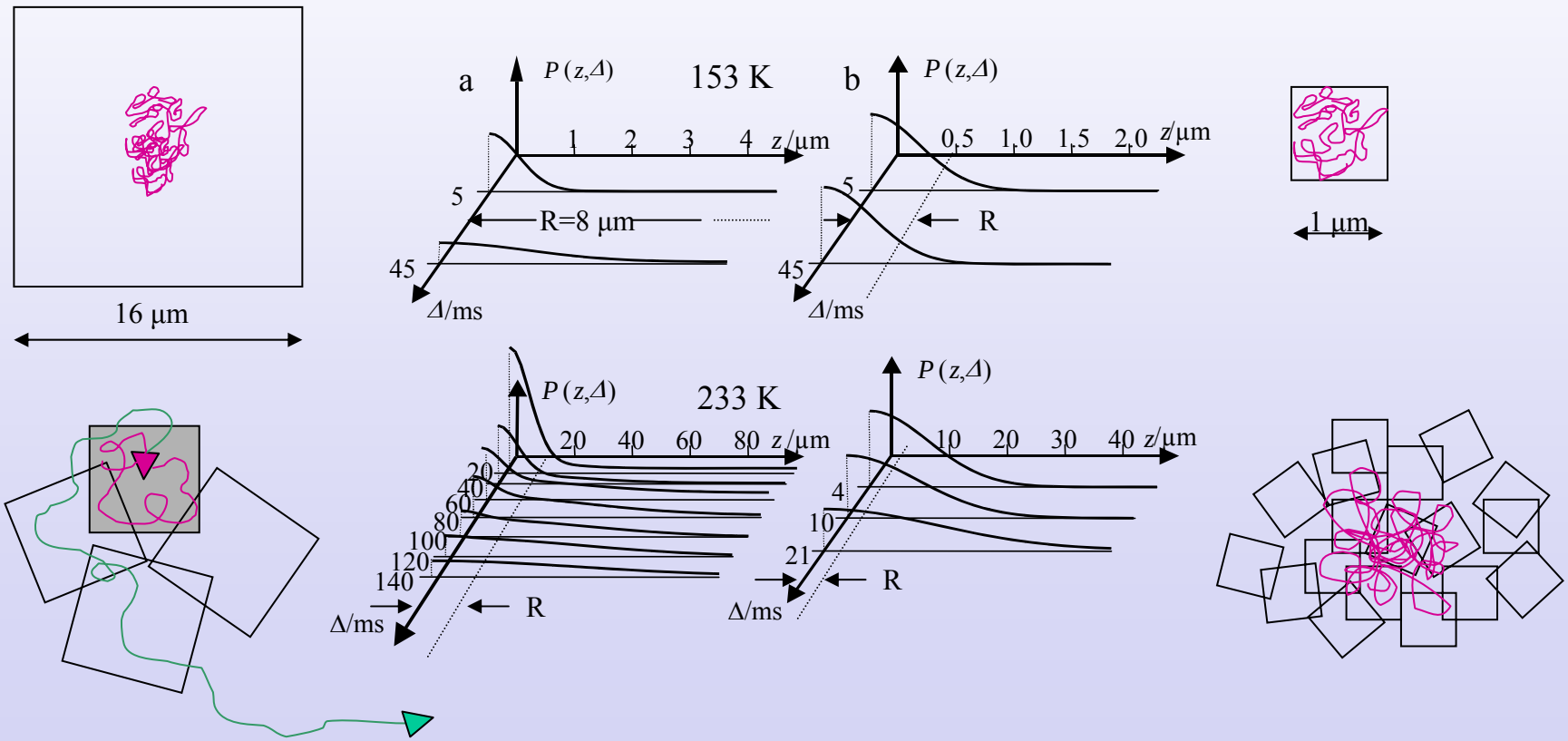


Package of Research Projects **"Diffusion in Zeolites"**
by CNRS (France), DFG (Germany), EPSRC (United Kingdom), NSF (USA)
Extension for the Period from 2006-2009

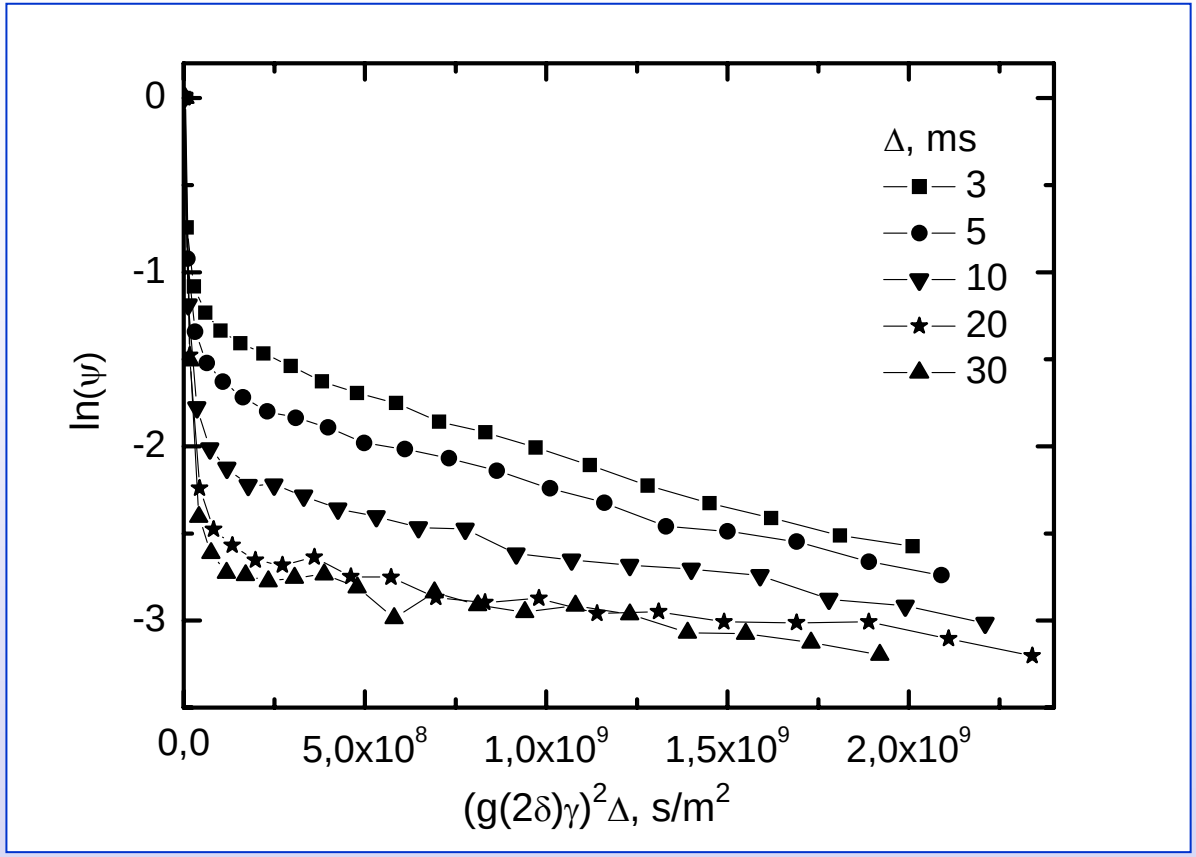
Molecular transport in pores does not necessarily lead to normal diffusion.

Pulsed Field Gradient (PFG) NMR provides **PROPAGATOR** and hence easy means to ascertain normal diffusion

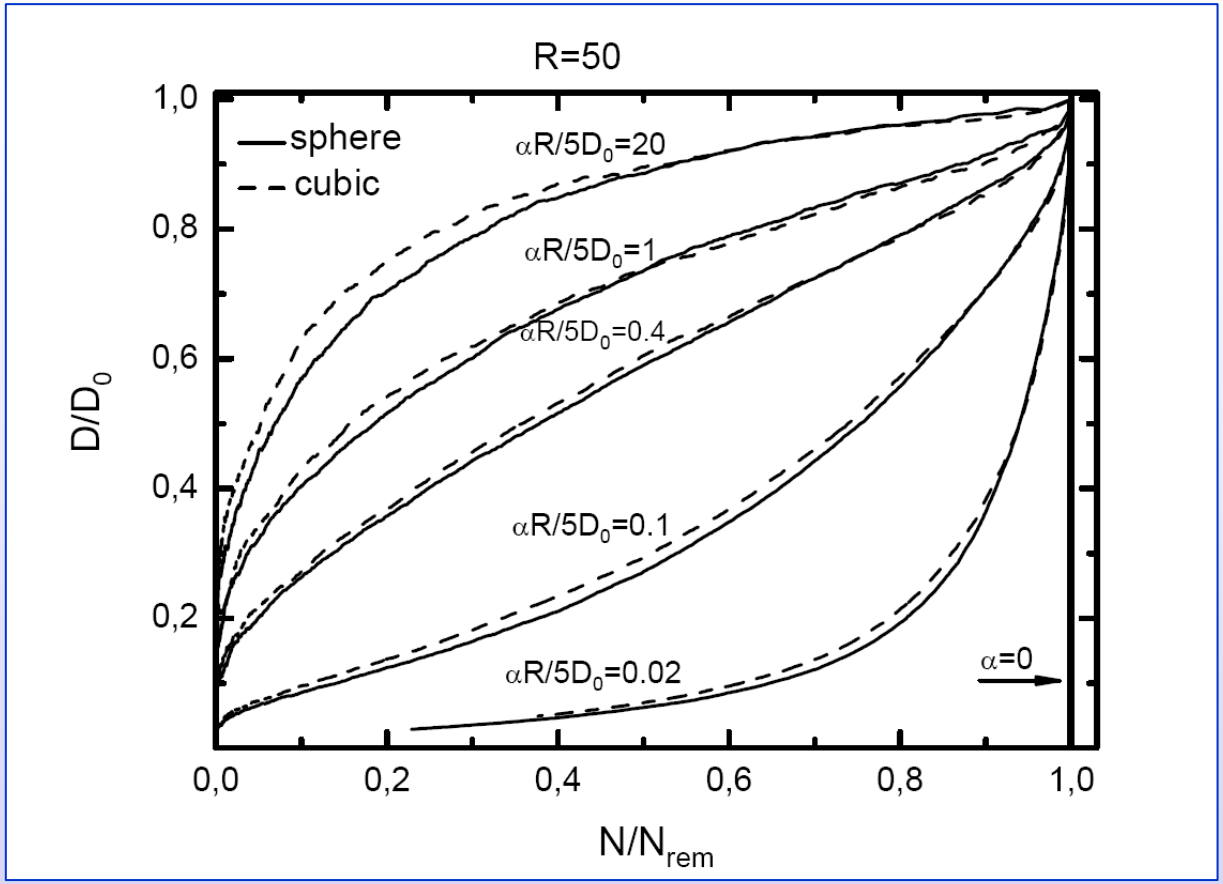
Mean Propagator for Ethane in NaCaA Crystallites of Different Size



complementary to single-particle tracking



PFG NMR Spin-echo attenuation of methane in zeolite NaCaA at 25°C for different observation times Δ.

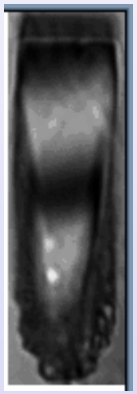


Correlating the effective diffusivity of restricted diffusion with the corresponding relative tracer exchange for different ratios $\alpha R/5D_0$ (reflecting the contribution of diffusion- and barrier-control to the overall process).

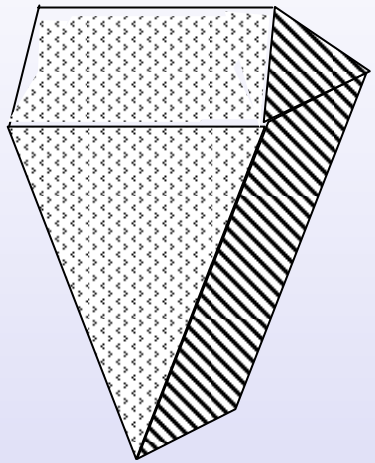
Package of Research Projects **"Diffusion in Zeolites"**
by CNRS (France), DFG (Germany), EPSRC (United Kingdom), NSF (USA)
Extension for the Period from 2006-2009

Silicalite(-1) fragments

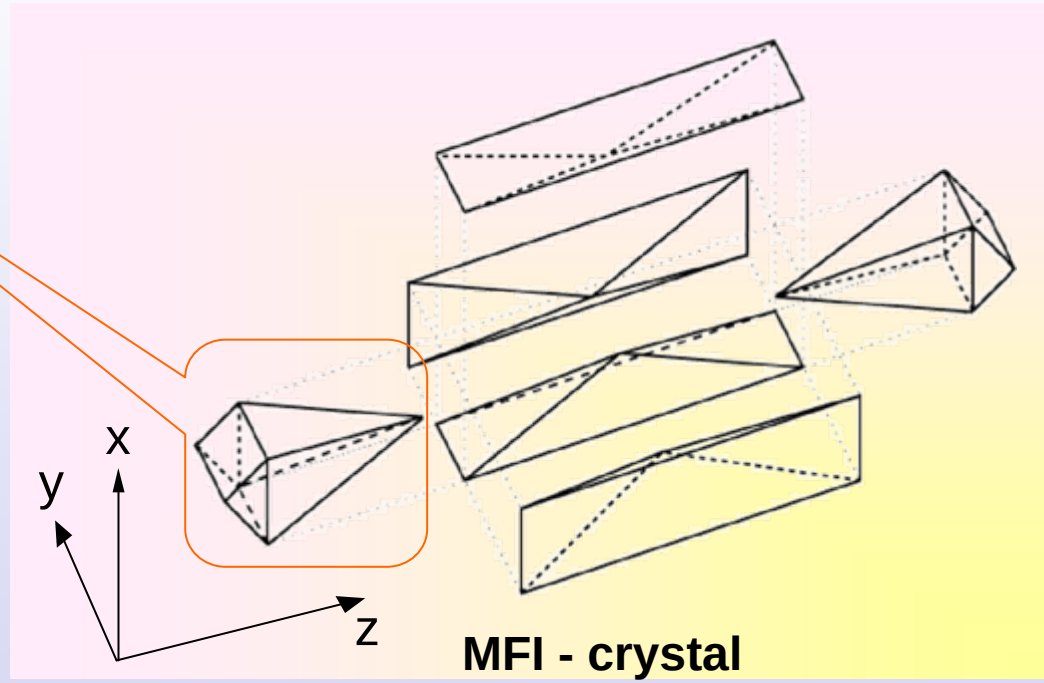
Adsorption-desorption with isobutane



"side 1"



"side 2"



MFI - crystal
(Geus et al., 1994)

Crystal_6:

- **adsorption 0-1mbar ⇒ adsorption 1-2mbar ⇒ desorption 2-1 mbar ⇒ desorption 1-0mbar**
- **1st, 2nd, 3rd, 4th cycle**

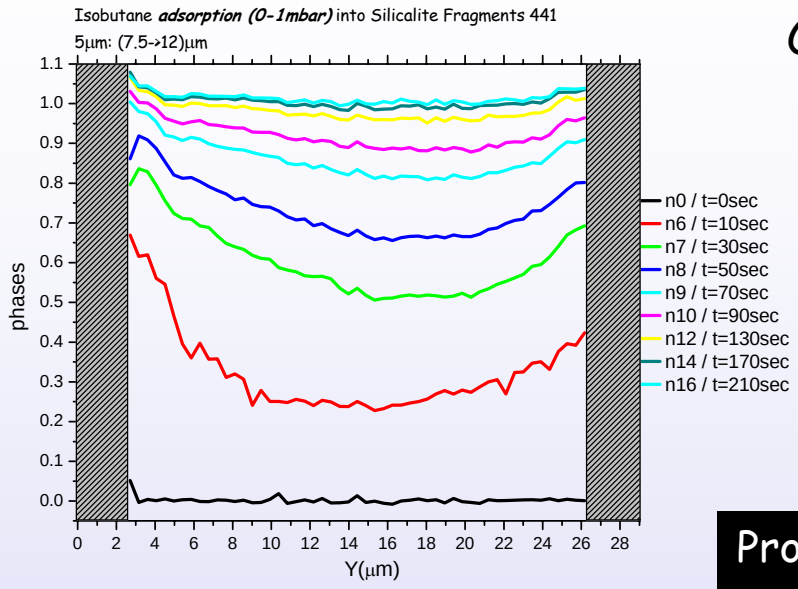
Package of Research Projects **"Diffusion in Zeolites"**

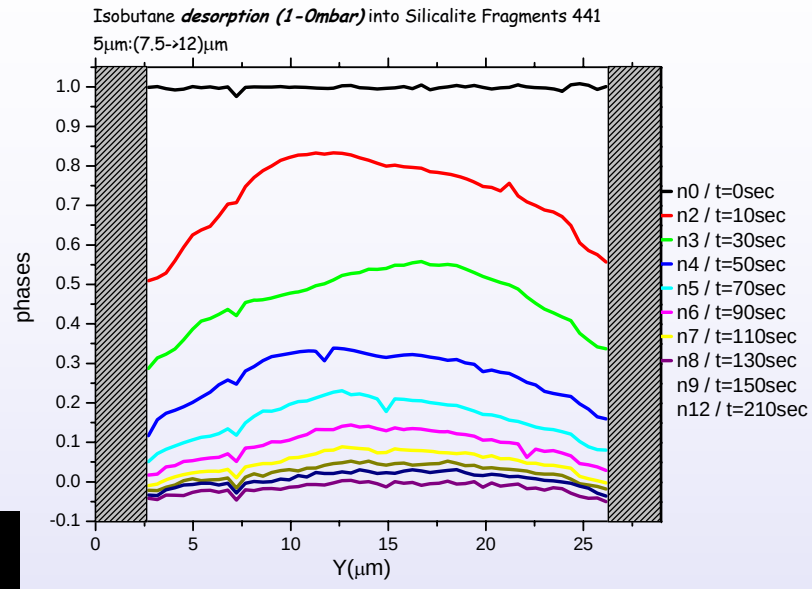
by CNRS (France), DFG (Germany), EPSRC (United Kingdom), NSF (USA)

Extension for the Period from 2006-2009

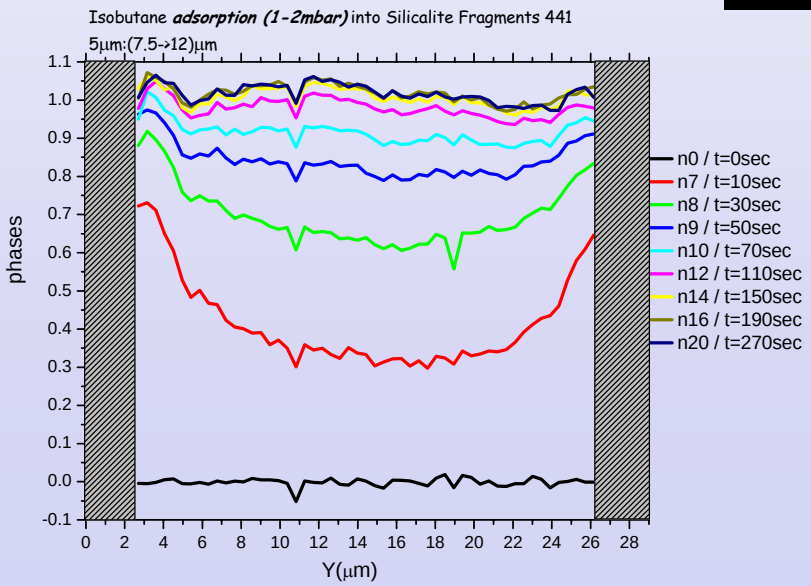
Crystal_6

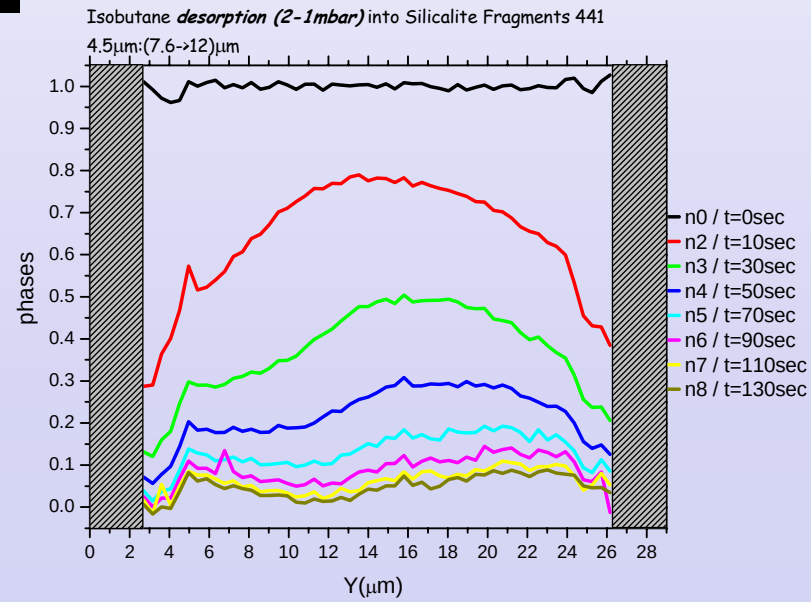
15.09.06





Profiles along y
1st cycle





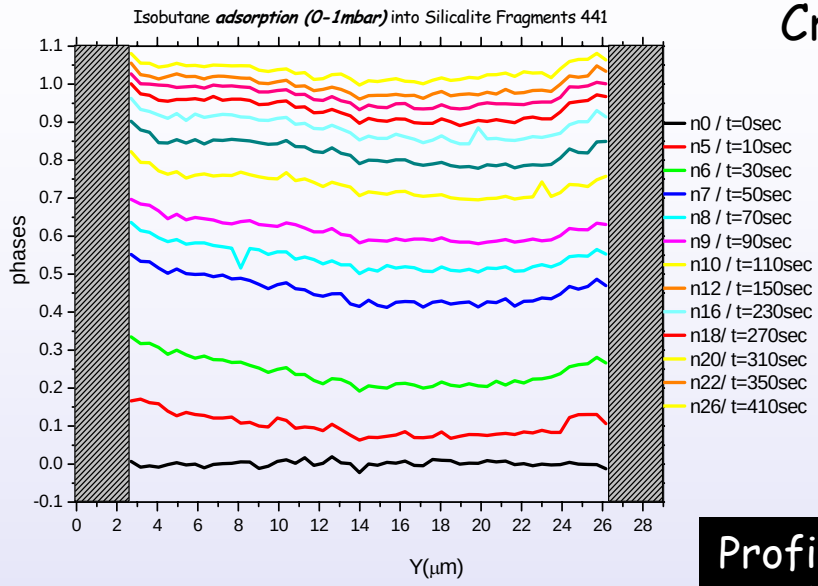
Package of Research Projects **"Diffusion in Zeolites"**

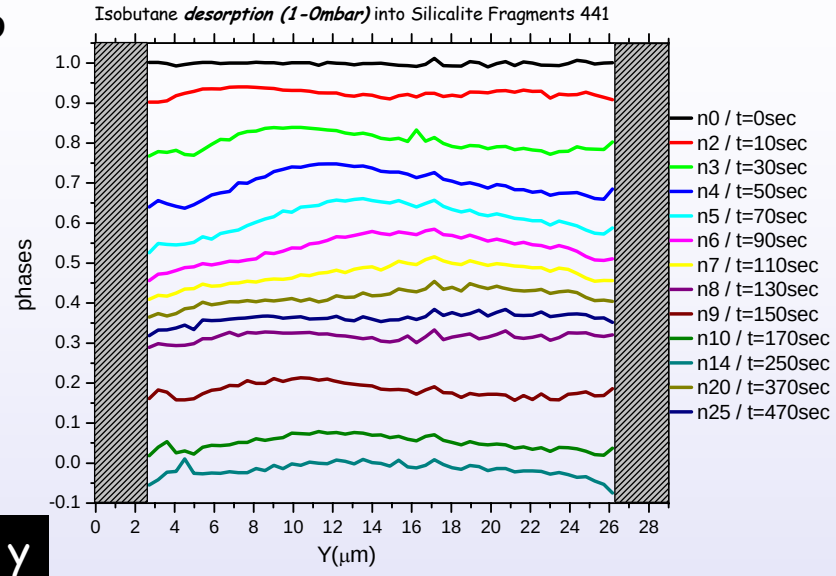
by CNRS (France), DFG (Germany), EPSRC (United Kingdom), NSF (USA)

Extension for the Period from 2006-2009

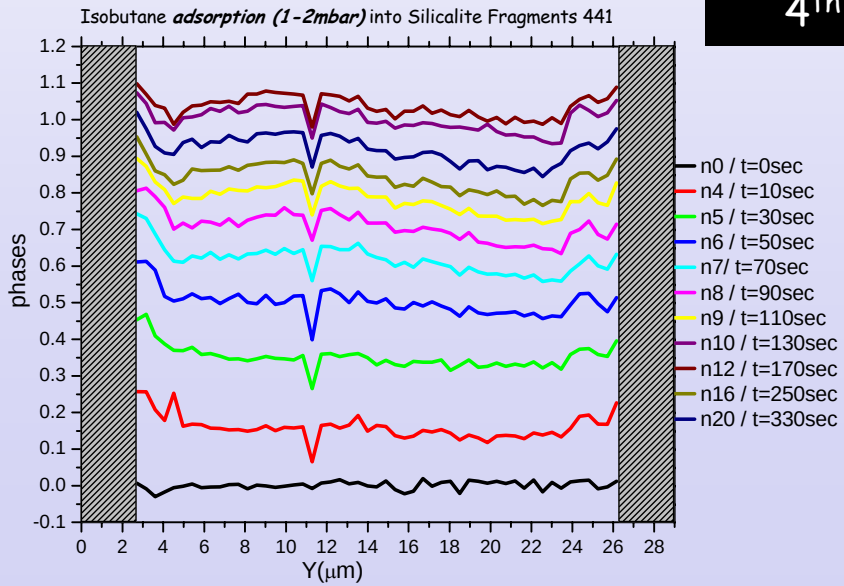
Crystal_6

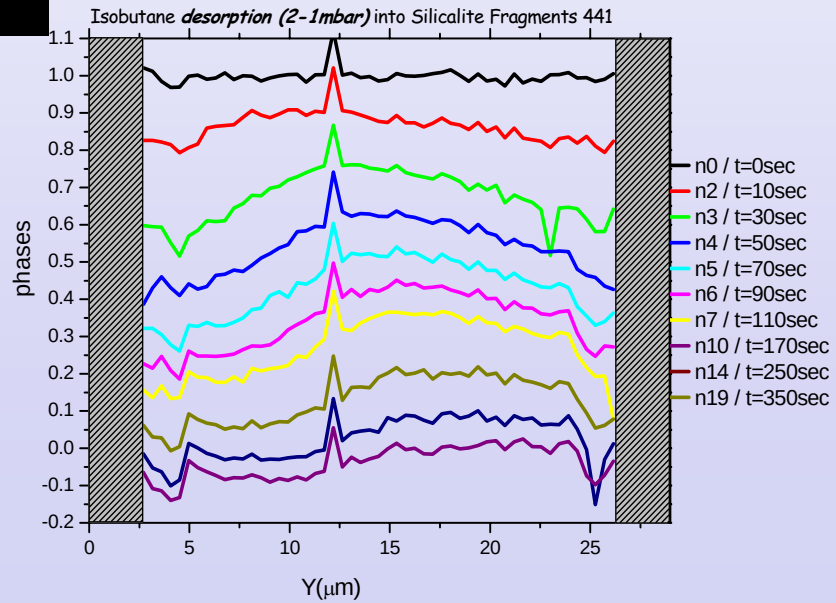
15.09.06





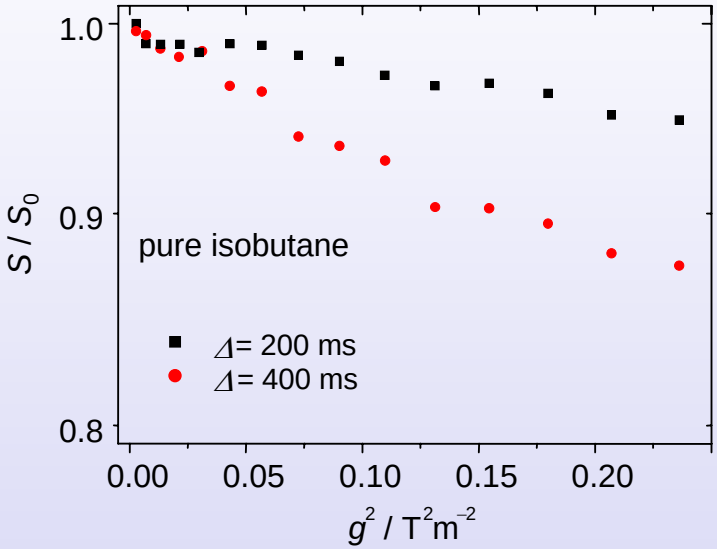
Profiles along y
4th cycle

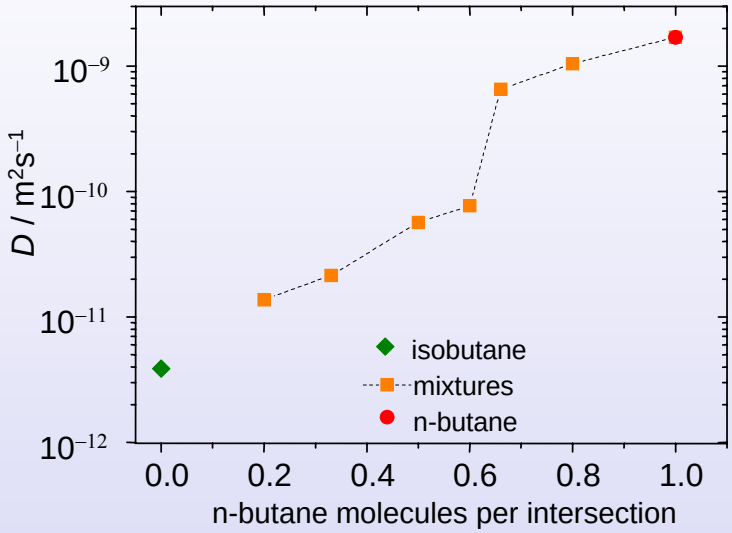


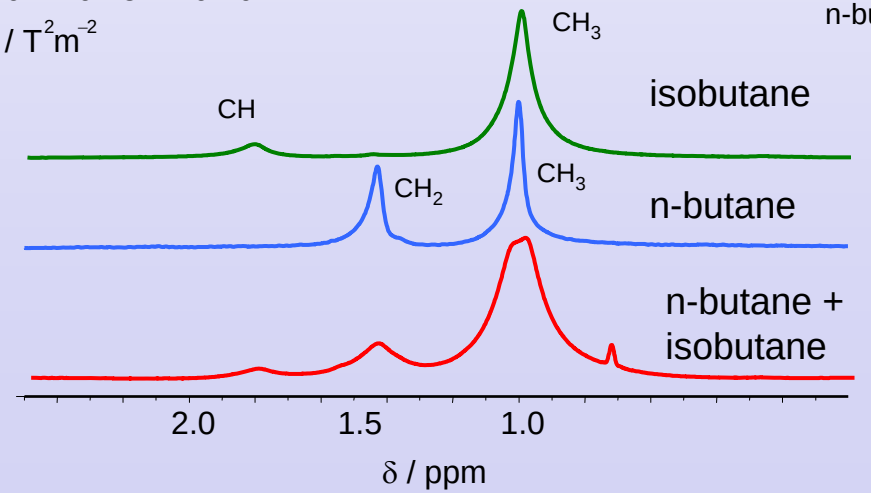


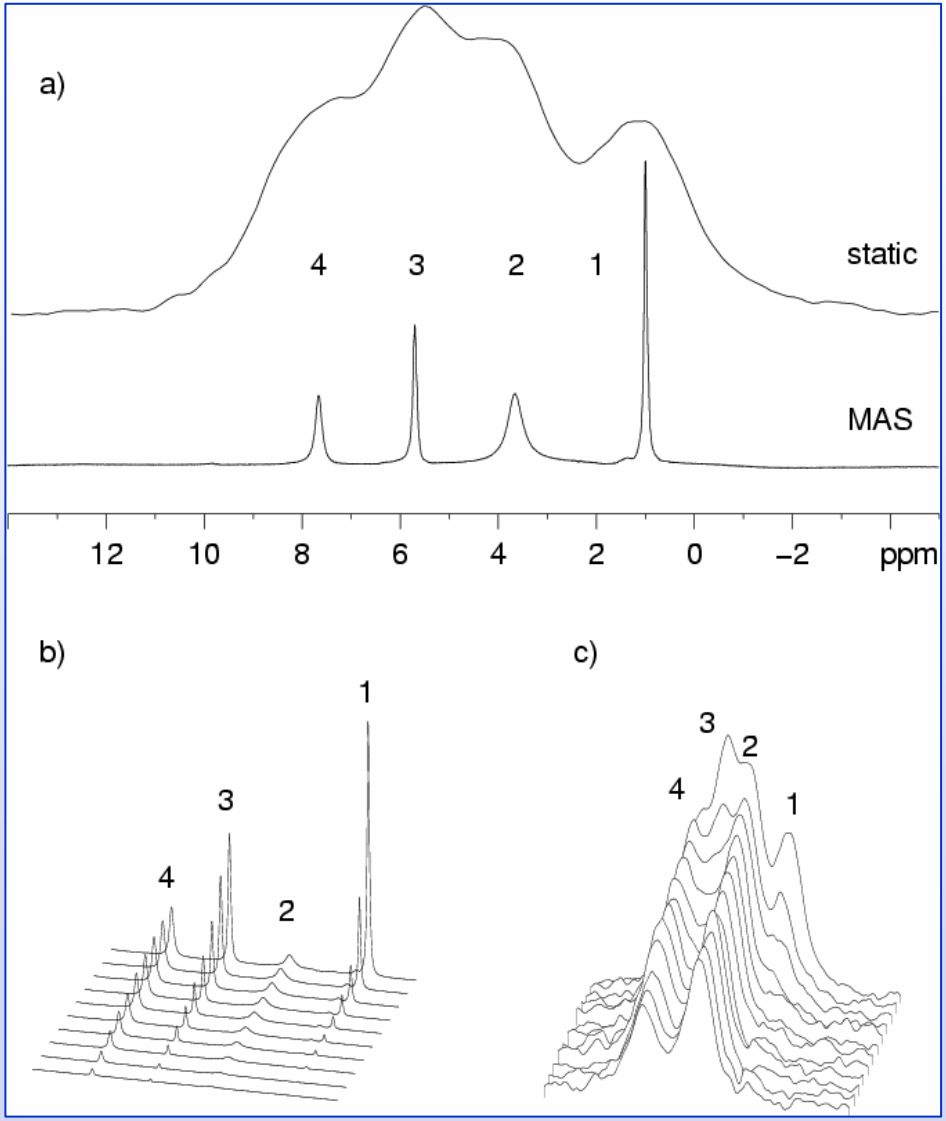
(MAS) PFG NMR

MAS PFG diffusometry for isobutane, n-butane, and mixtures in silicalite-1









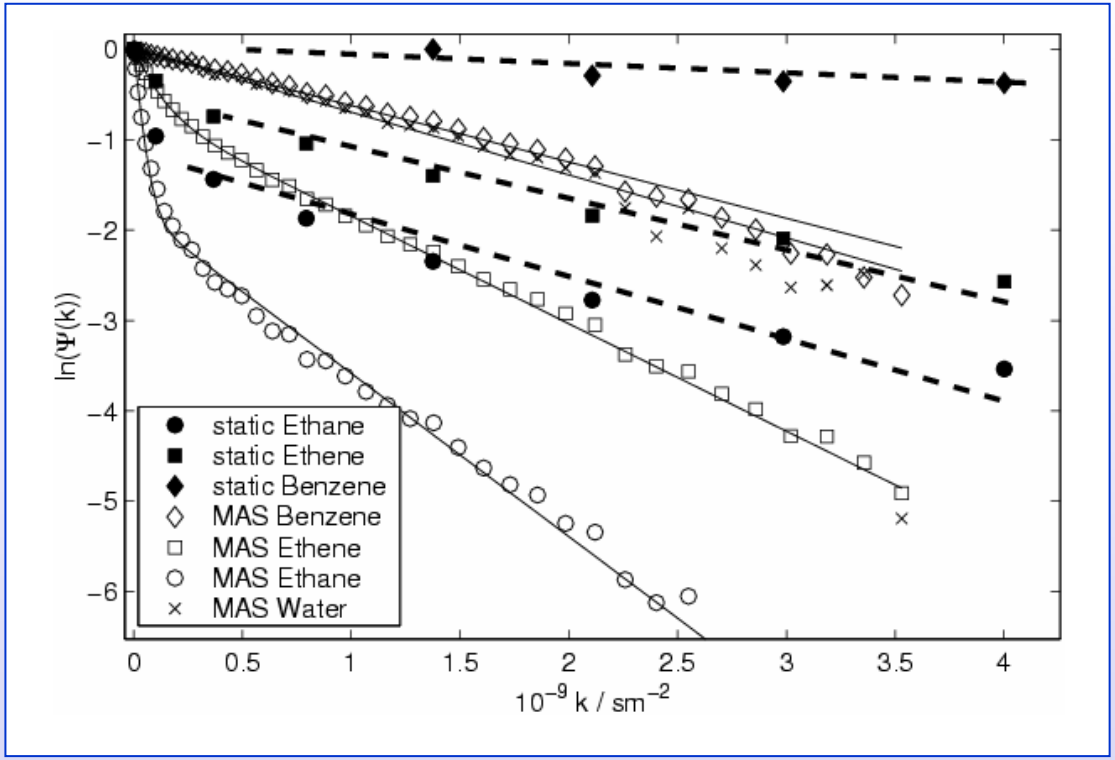
(MAS) PFG NMR

(a) ^{1}H-NMR spectra of ethane (signal 1), ethene (signal 3), water (signal 2) and benzene (signal 4) adsorbed in zeolite NaX.

(b) and (c) Attenuation of the observed spectra with increasing gradient intensity for a separation Δ of 10ms (static PFG NMR, (c)) and 20ms (MAS PFG NMR, (b)), respectively. The different spectra correspond to different *k*.

Observation at 400 MHz static (top) and with MAS (bottom), respectively.

(MAS) PFG NMR



Semi-logarithmic plot of the spin-echo attenuation of the several components observed using MAS and static PFG NMR experiments, respectively.

The lines were calculated using equ. $\Psi=\exp(-k\,D_i)$ fitted by least-squares optimisation. Broken straight lines are guides for the eyes of the attenuation data obtained for benzene, ethylene and ethane by static PFG NMR.