Cage Structures and Clathrates

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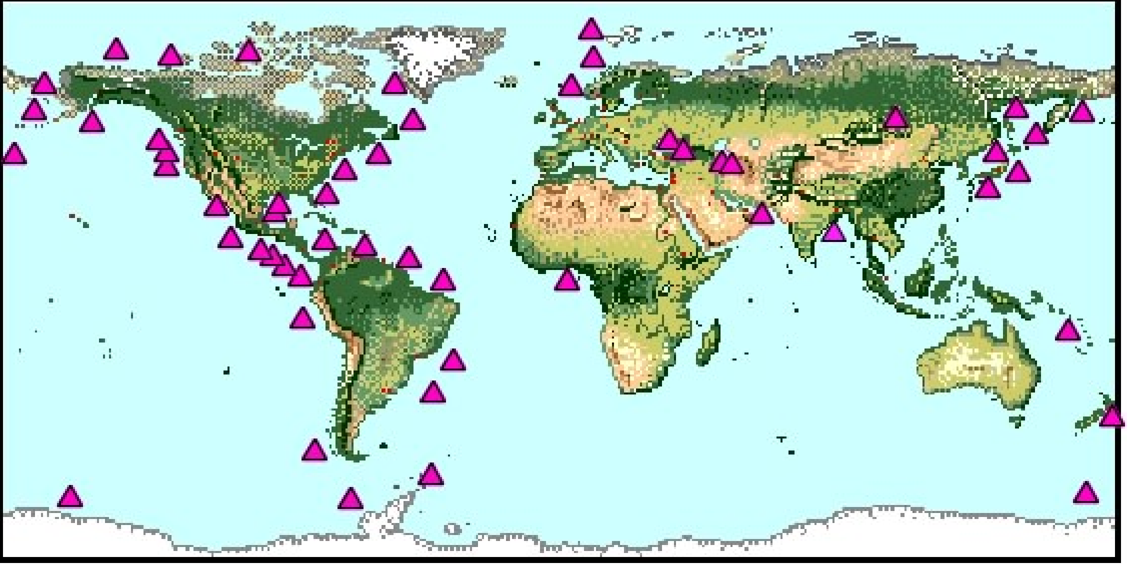
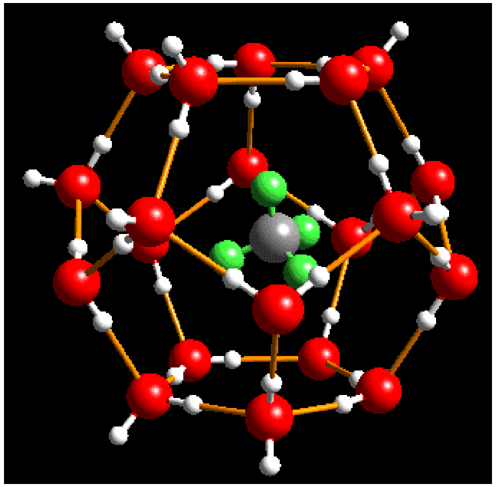
Introduction on clathrates & zeolites

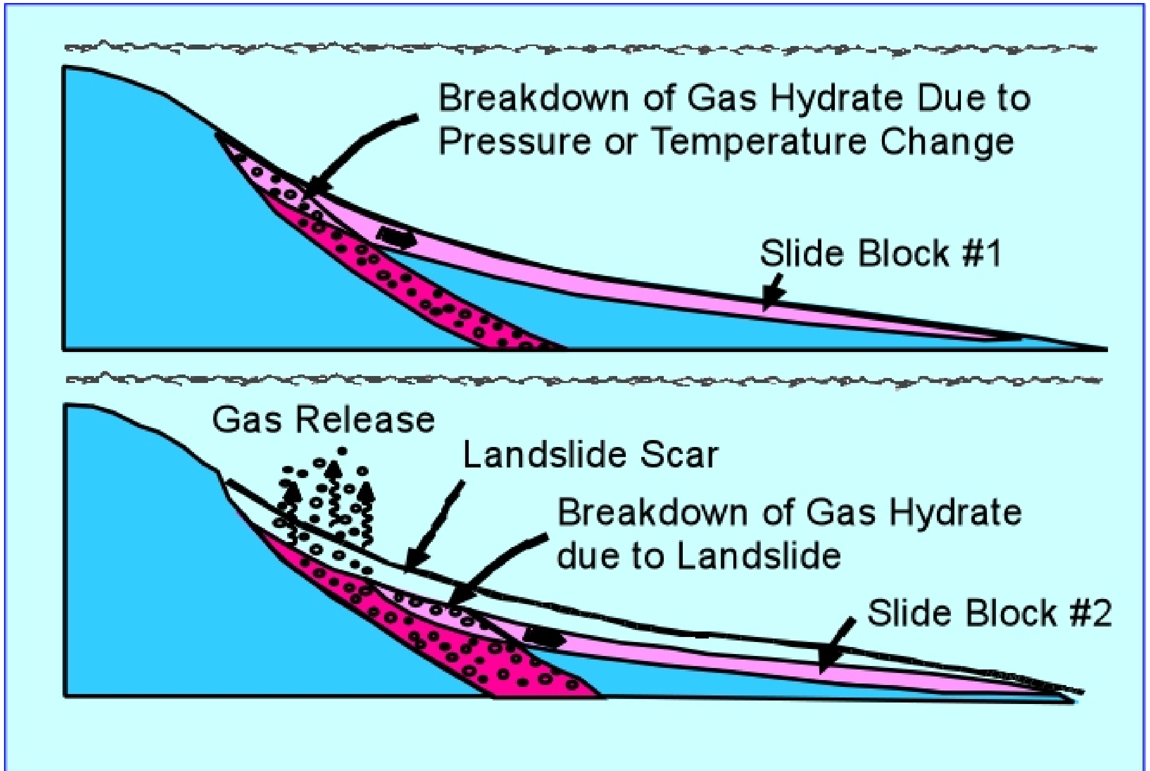
Applications of zeolites: adsorption & diffusion effects

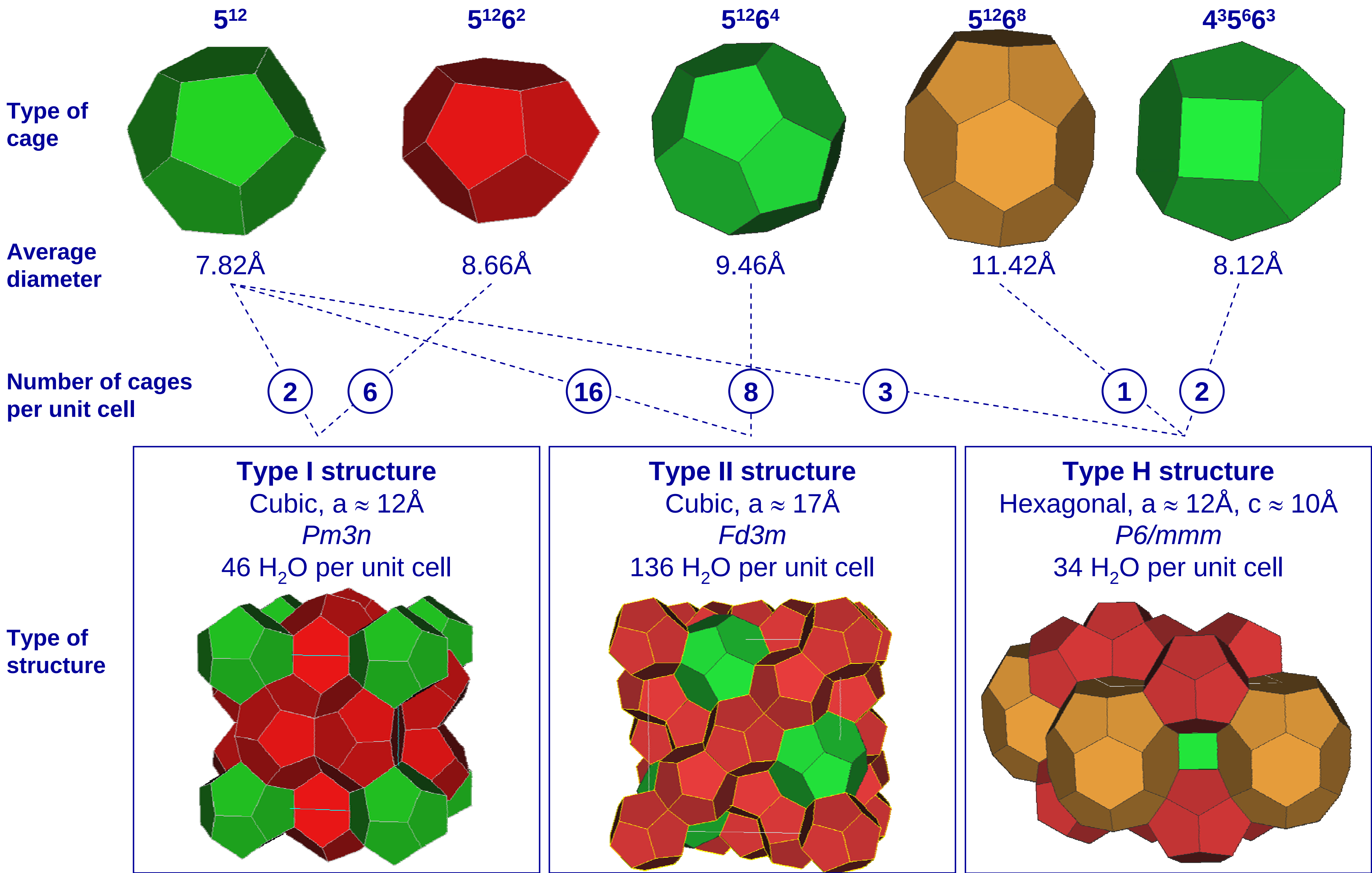
Different molecular motions:

- vibrations: N_2 / LiLSX, benzene/NaY, H_2O / H-ZSM-5, gas hydrates
- rotations: xylenes/FAU
- translations: jump diffusion models
  - ≠ methods for measuring D
  - 1D / 3D
  - alcanes/MFI, xylenes/FAU, benzene/MFI, FAU
  - ≠ types of diffusivities
  - D_2 / NaX, CF_4 / silicalite, S(Q)
  - linear alcanes / 5A
  - comparisons with simulations

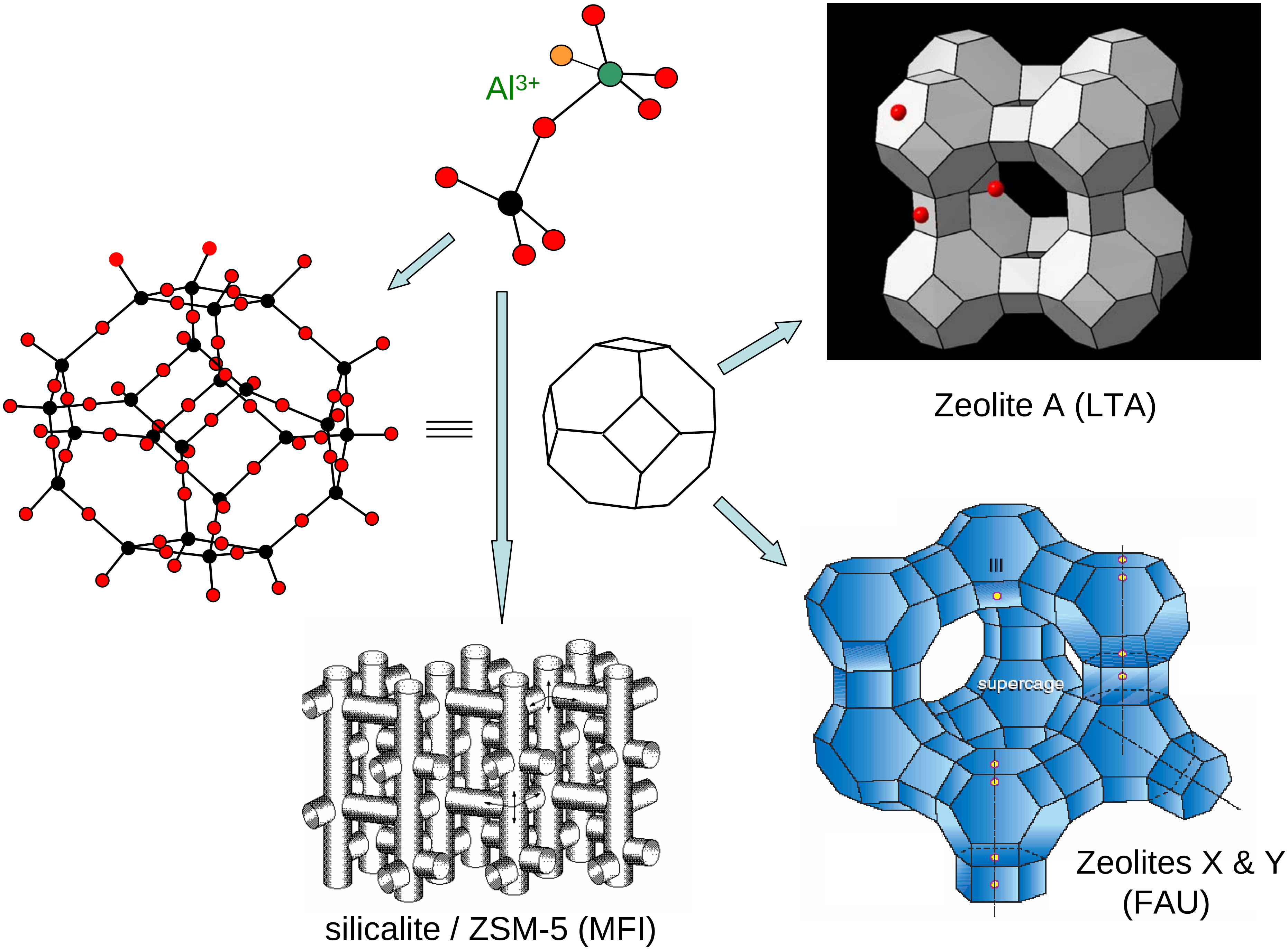





Breakdown of Gas Hydrate Due to
Pressure or Temperature Change
Slide Block #1
Gas Release
Landslide Scar
Breakdown of Gas Hydrate
due to Landslide
Slide Block #2



5^{12}
$5^{12}6^{2}$
$5^{12}6^{4}$
$5^{12}6^{8}$
$4^{3}5^{6}6^{3}$
Type of cage
Average diameter
7.82Å
8.66Å
9.46Å
11.42Å
8.12Å
Number of cages per unit cell
2
6
16
8
3
1
2
Type I structure
Cubic, a ≈ 12Å
Pm3n
46 H_2O per unit cell
Type II structure
Cubic, a ≈ 17Å
Fd3m
136 H_2O per unit cell
Type H structure
Hexagonal, a ≈ 12Å, c ≈ 10Å
P6/mmm
34 H_2O per unit cell
Type of structure


Al3+
Zeolite A (LTA)
III
supercage
silicalite / ZSM-5 (MFI)
Zeolites X & Y
(FAU)

Synthetic zeolites

Catalytic cracking:

Crude oil $\longrightarrow$ fuel components

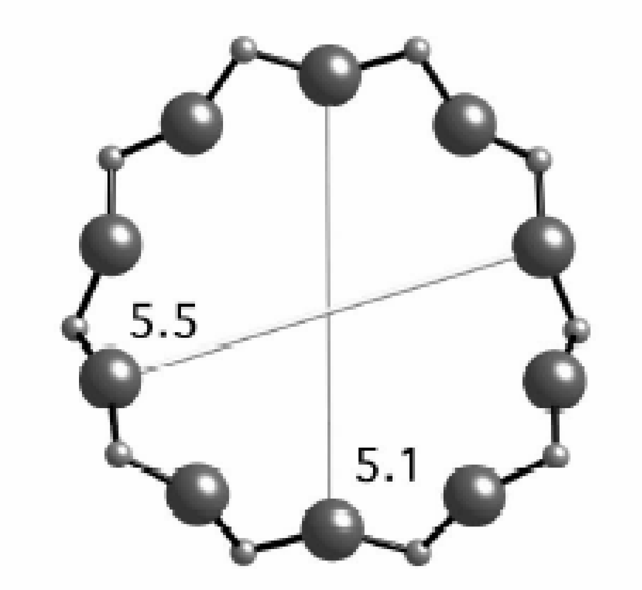
Hydrocracking:
High Mw fractions + H_2 $\rightarrow$ lower Mw fuels

Petrochemicals processing
MTO, LAB…

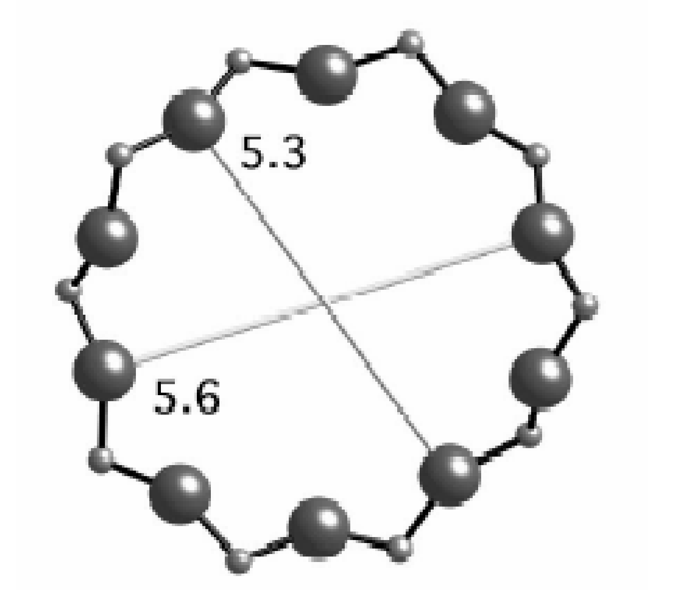
Gas separation

Purification

Typical cycle time: 1 – 2 years



MFI

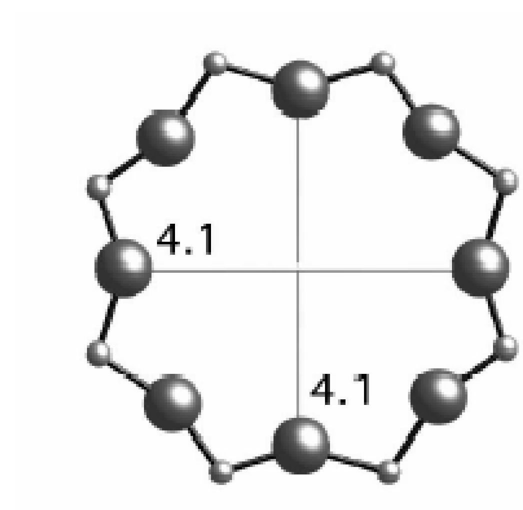


10-ring viewed along [100]

10-ring viewed along [010]

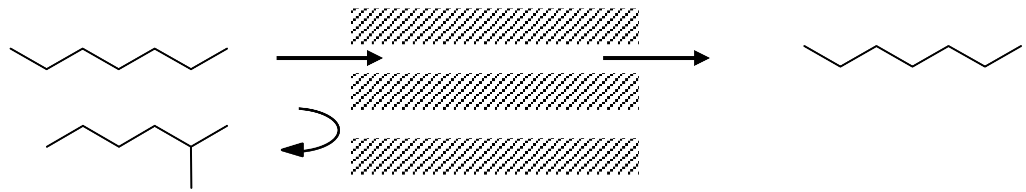
LTA

8-ring viewed along <100>



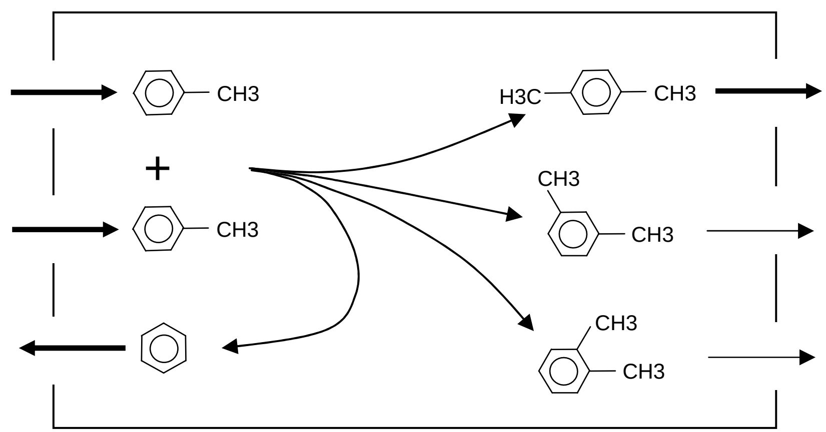
catalysis-separation / zeolites

Reactant selectivity

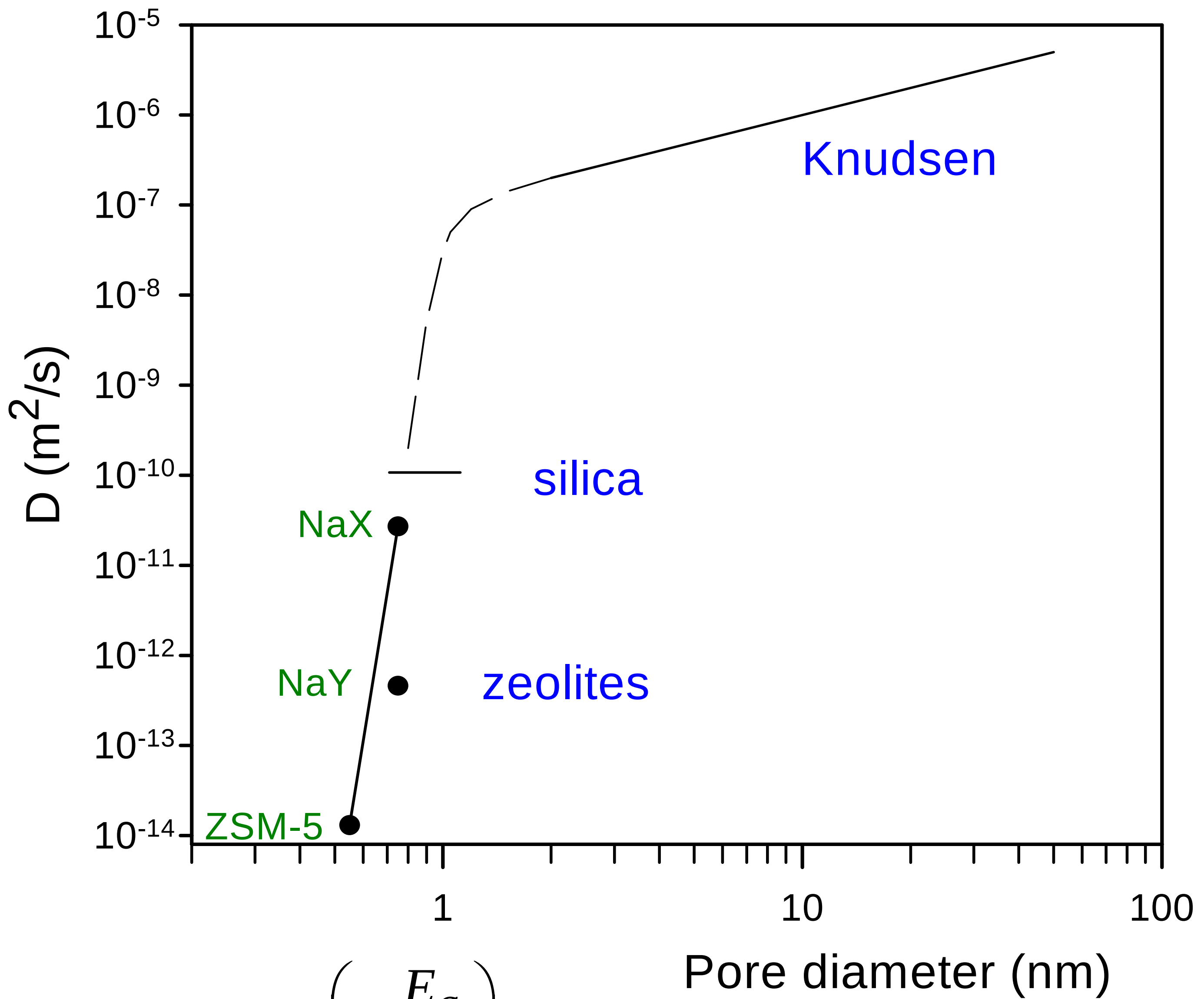


Diffusion effects

Product selectivity

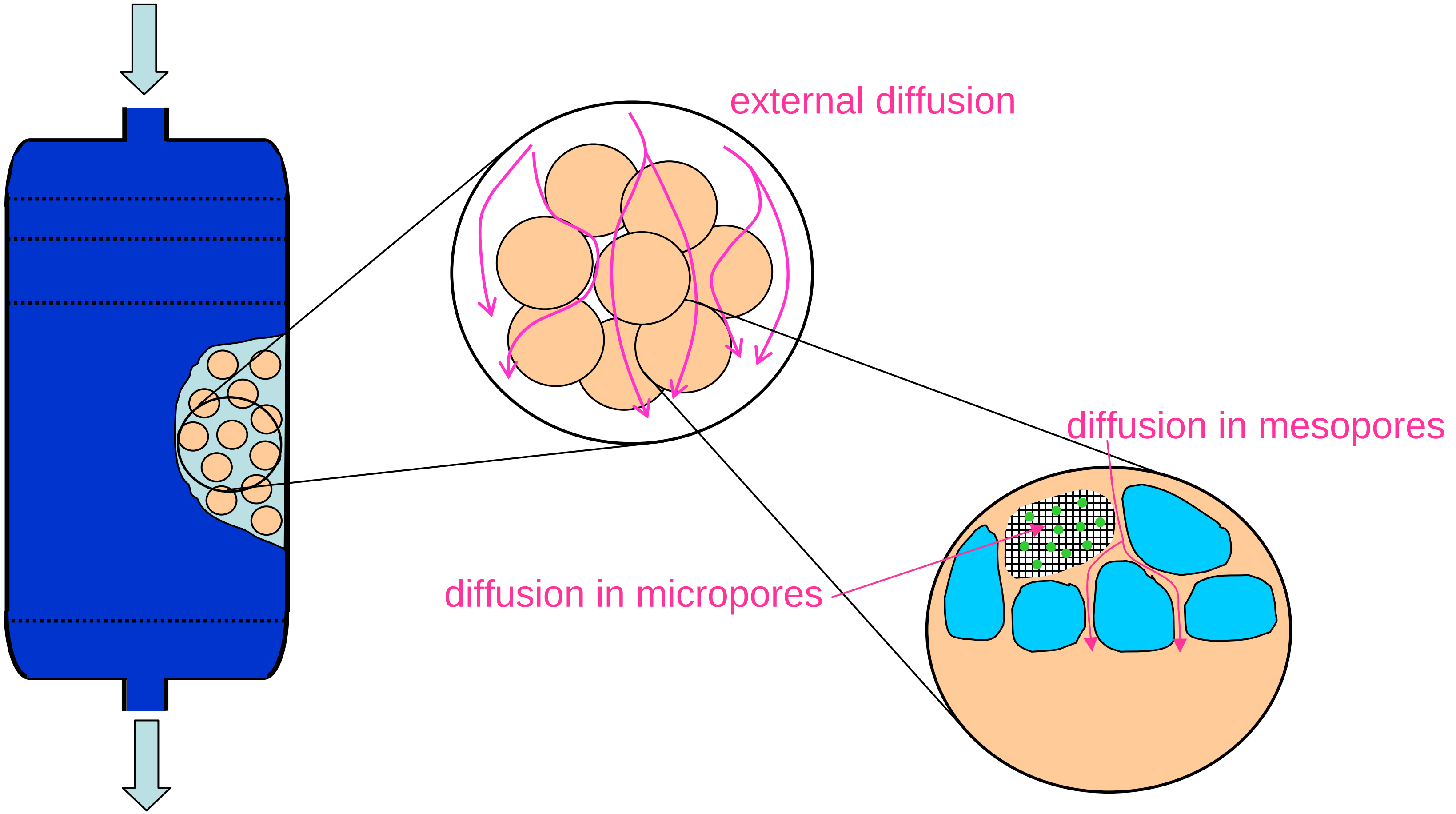


Benzene (300 K)

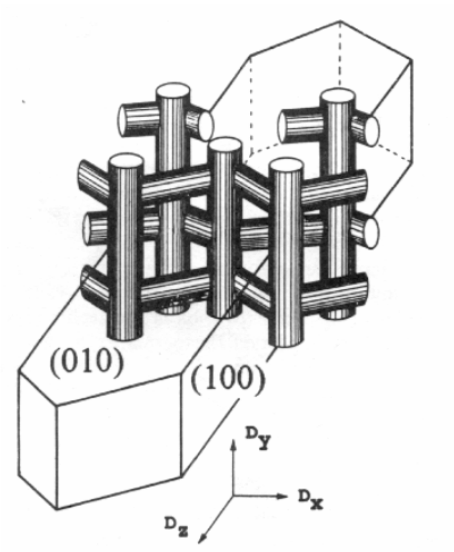


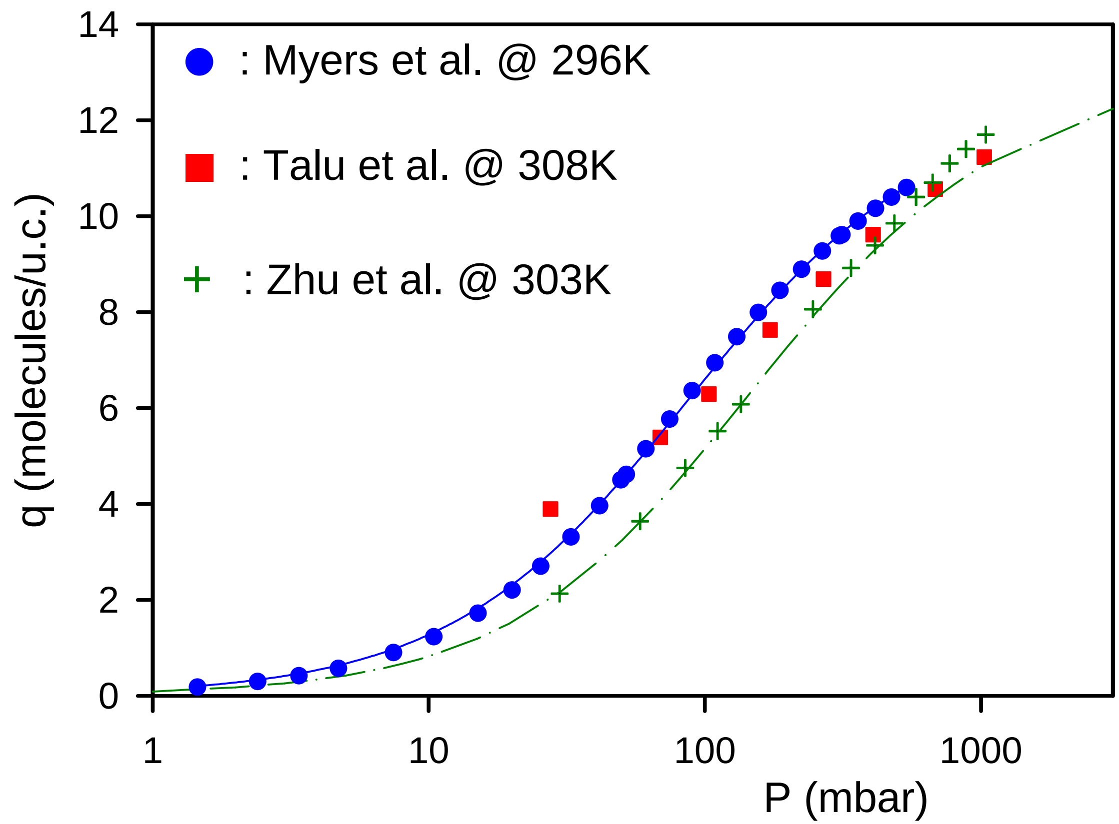
$$D = D_\infty \exp\left(-\frac{E_a}{RT}\right)$$

Transport phenomena in packed-bed reactor



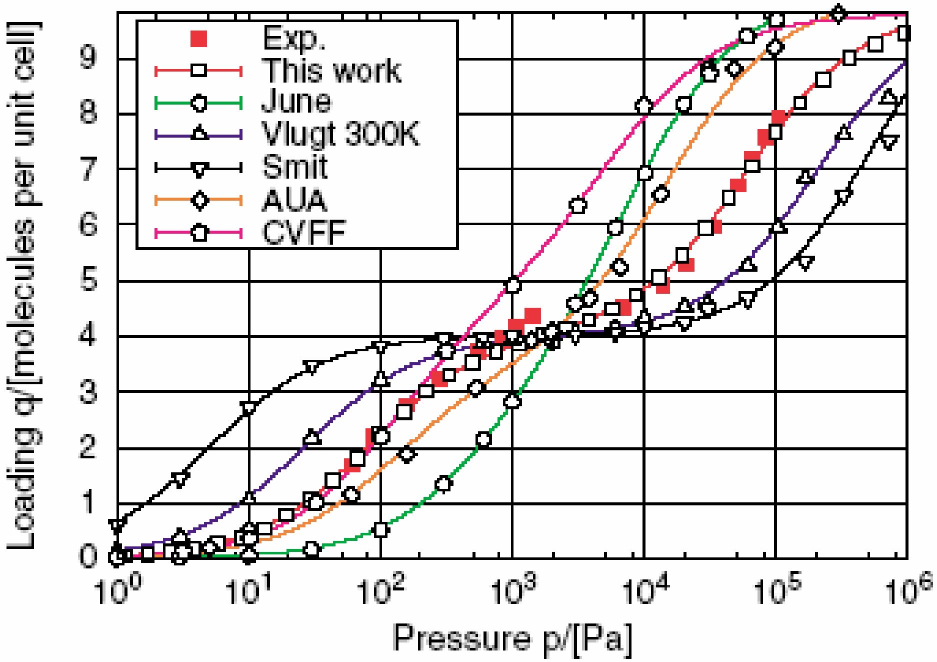
ethane in silicalite





Langmuir: $q = \dfrac{q_S KP}{1 + KP}$

Van't Hoff: $K = \exp\left(-\dfrac{\Delta G}{RT}\right) = \exp\left(-\dfrac{\Delta H}{RT}\right)\exp\left(\dfrac{\Delta S}{R}\right)$



Isotherms of 2-methylpropane at 308 K in silicalite-1 compared to various computational models.

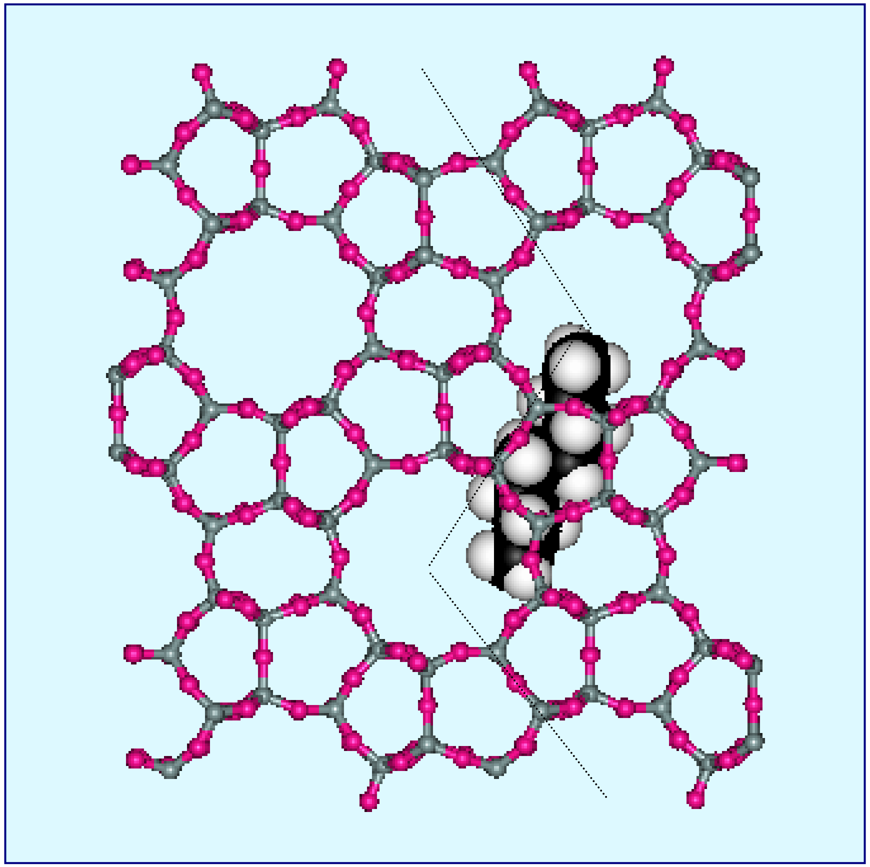
PRL 93 (2004) 88302

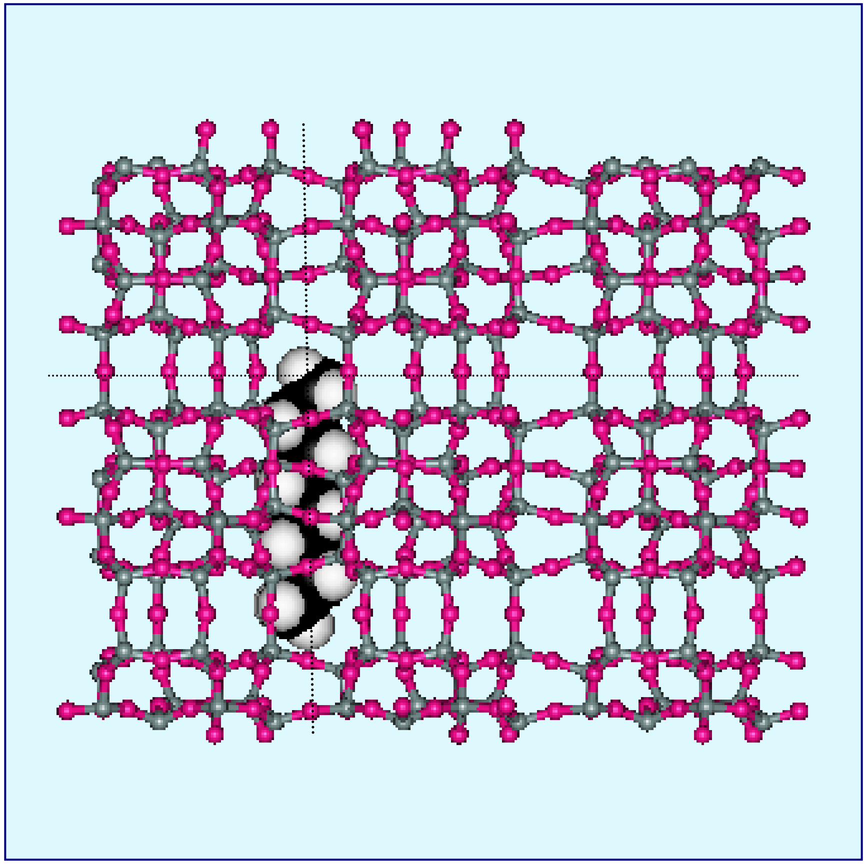
FF calculations (LJ parameters), CBMC technique

(mainly for siliceous zeolites, for aliphatic hydrocarbons)

A new FF has to be tested by adsorption or diffusion experiments

n-alcanes in silicalite



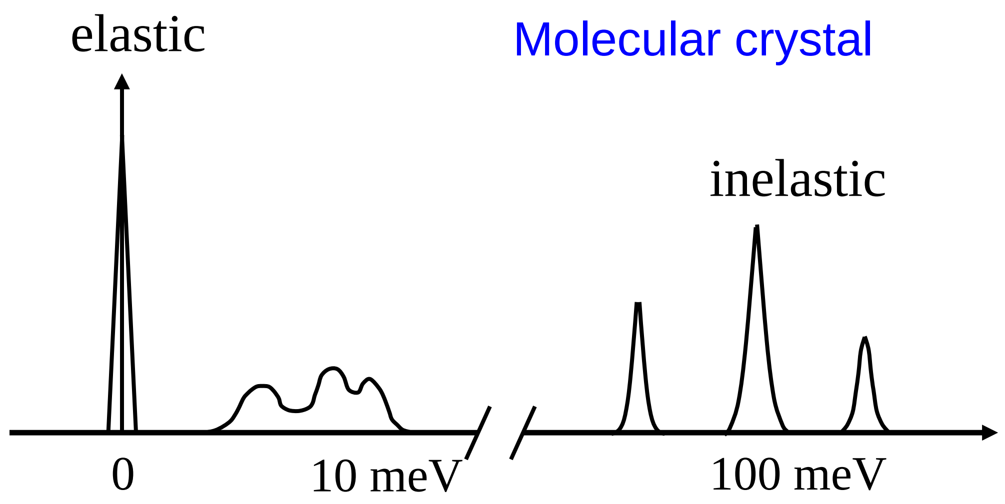


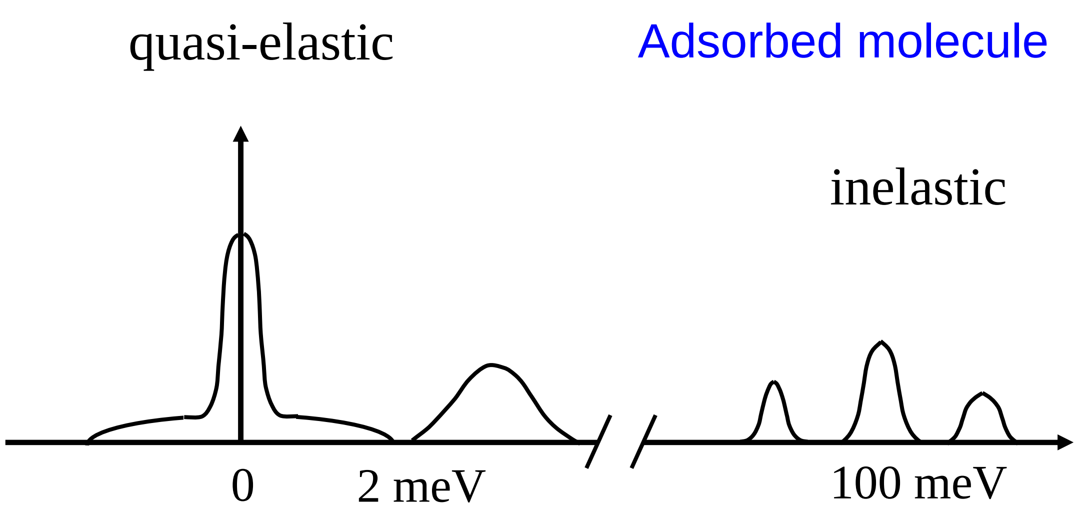
n-heptane:

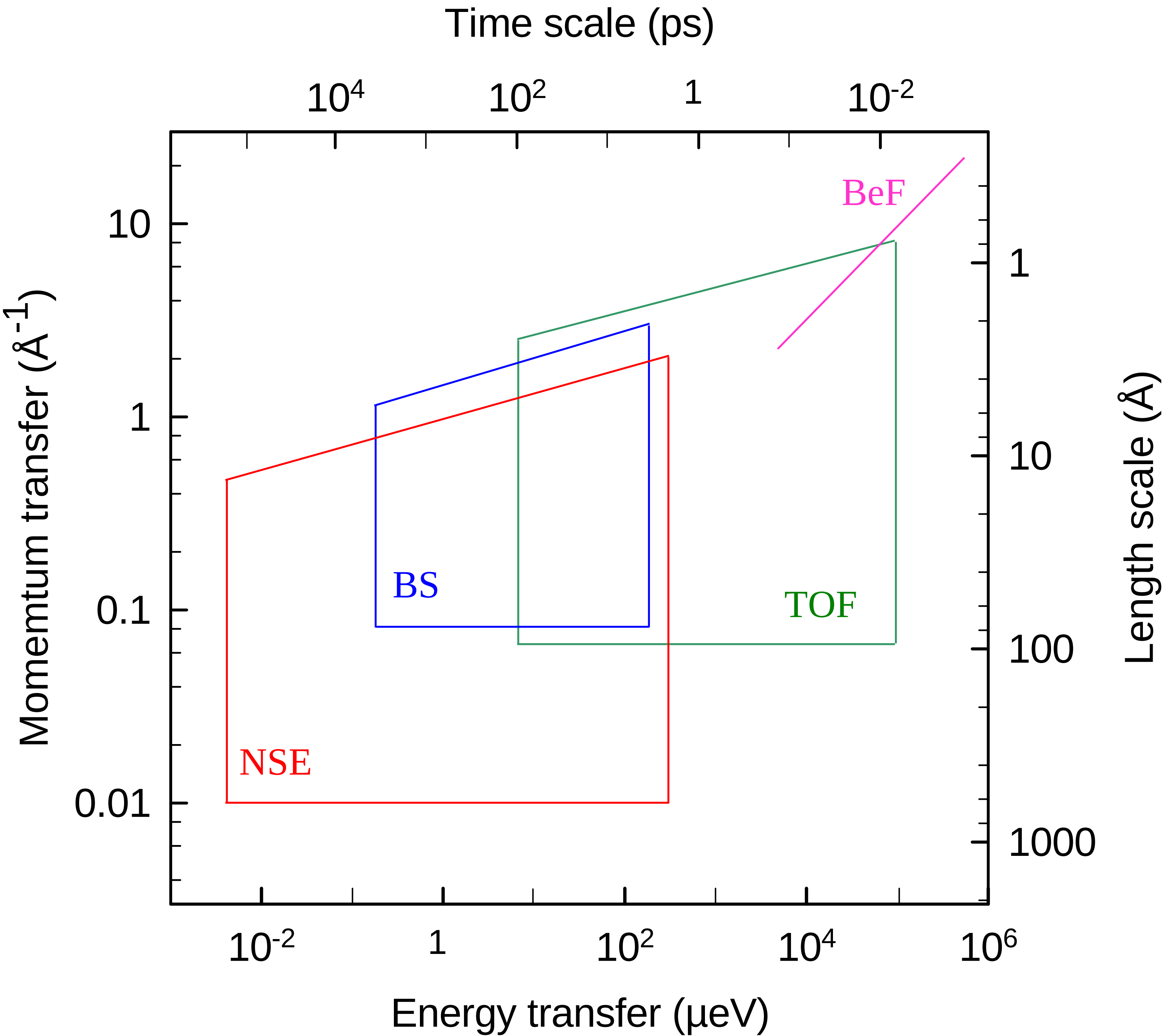
$\Delta H(1)$ = -84.3 kJ/mol , $\Delta H(2)$ = -87.7 kJ/mol

$\Delta S(1)$ = -131 J/K.mol , $\Delta S(2)$ = -211 J/K.mol

Dynamics of molecular systems





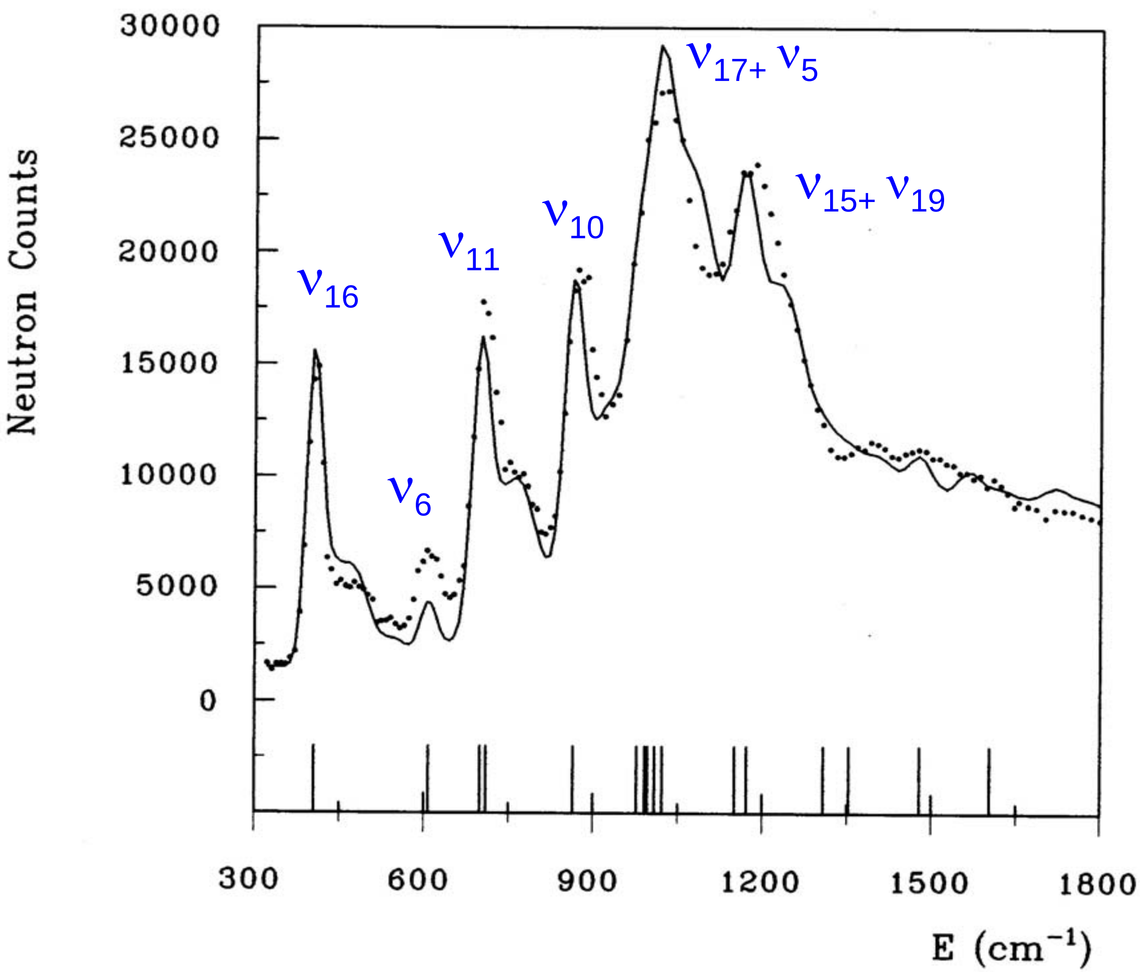


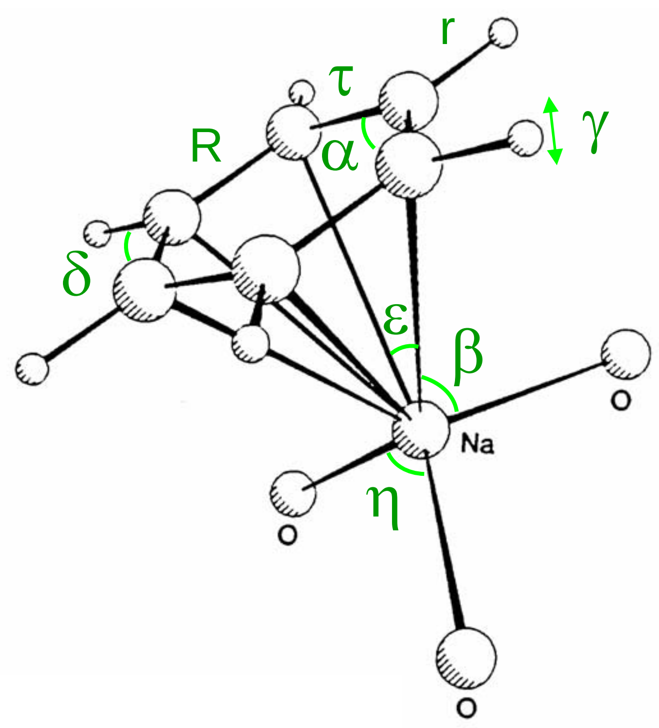
Time scale (ps)
10^4
10^2
1
10^-2
10
1
0.1
0.01
Momentum transfer (Å^-1)
1
10
100
1000
Length scale (Å)
BeF
TOF
BS
NSE
10^-2
1
10^2
10^4
10^6
Energy transfer (μeV)

Usual approximation for a molecule:

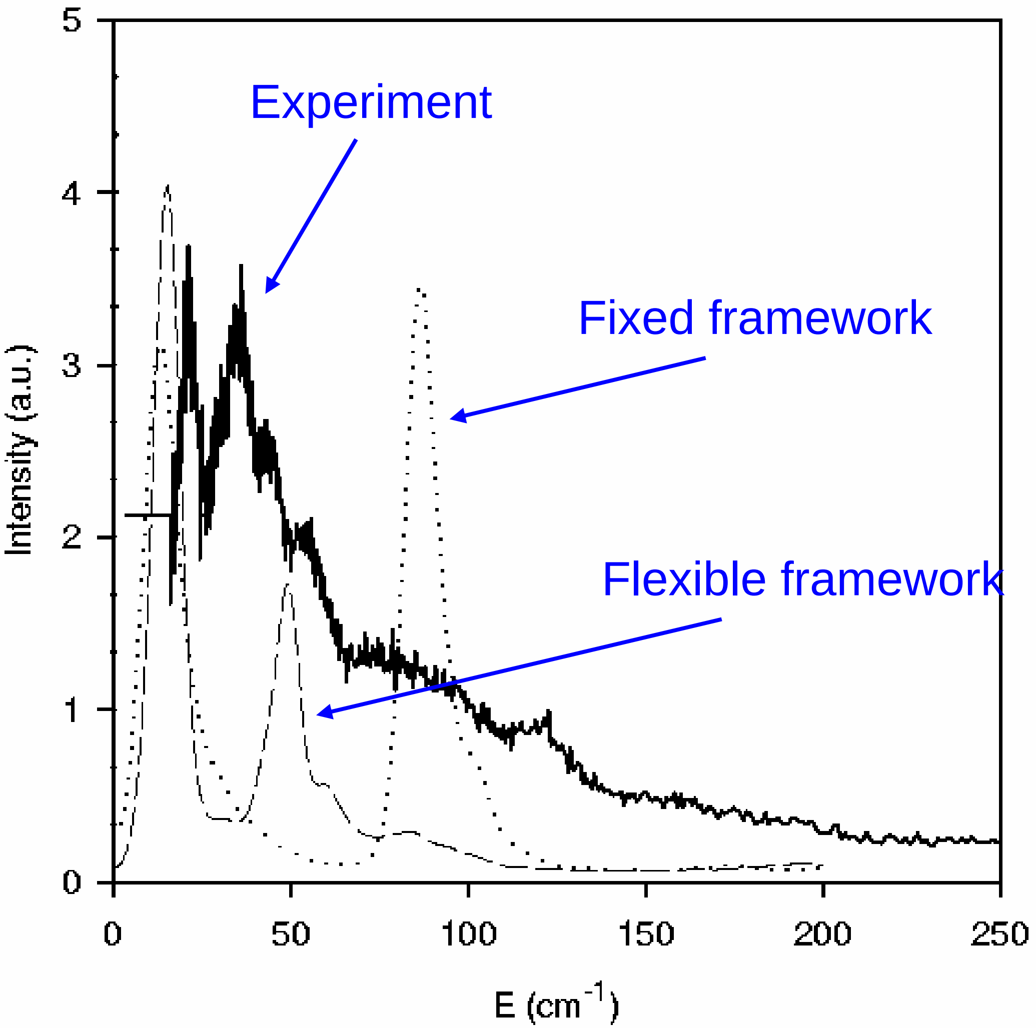
$$S_{tot}(\mathbf{Q},\omega) = S^{trans}(\mathbf{Q},\omega) \otimes S^{rot}(\mathbf{Q},\omega) \otimes S^{vib}(\mathbf{Q},\omega)$$

benzene / NaY (1 molecule / supercage ; T = 20 K)

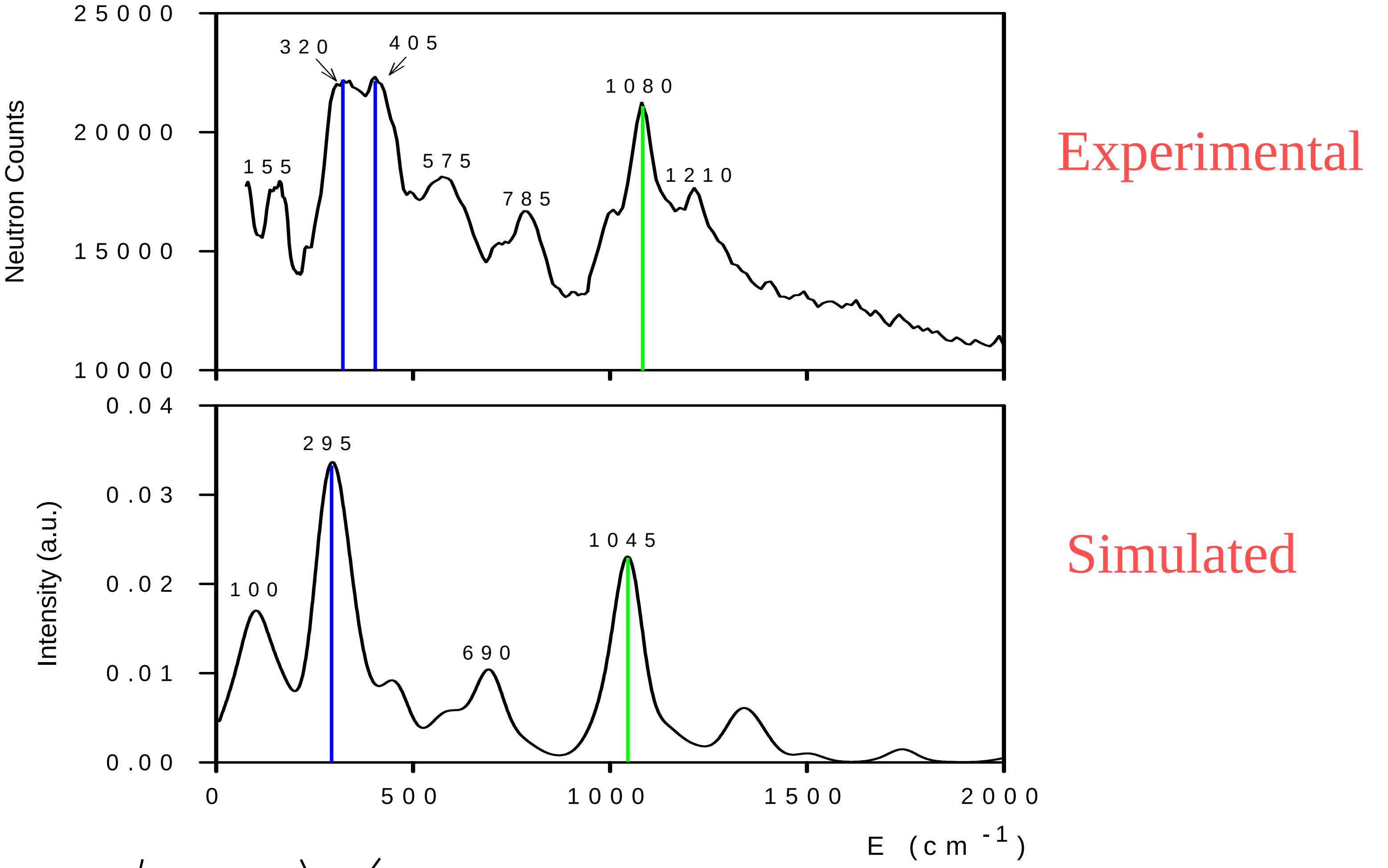


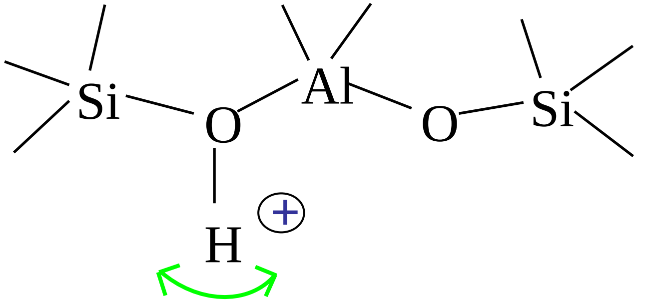


MD simulations of benzene in NaY

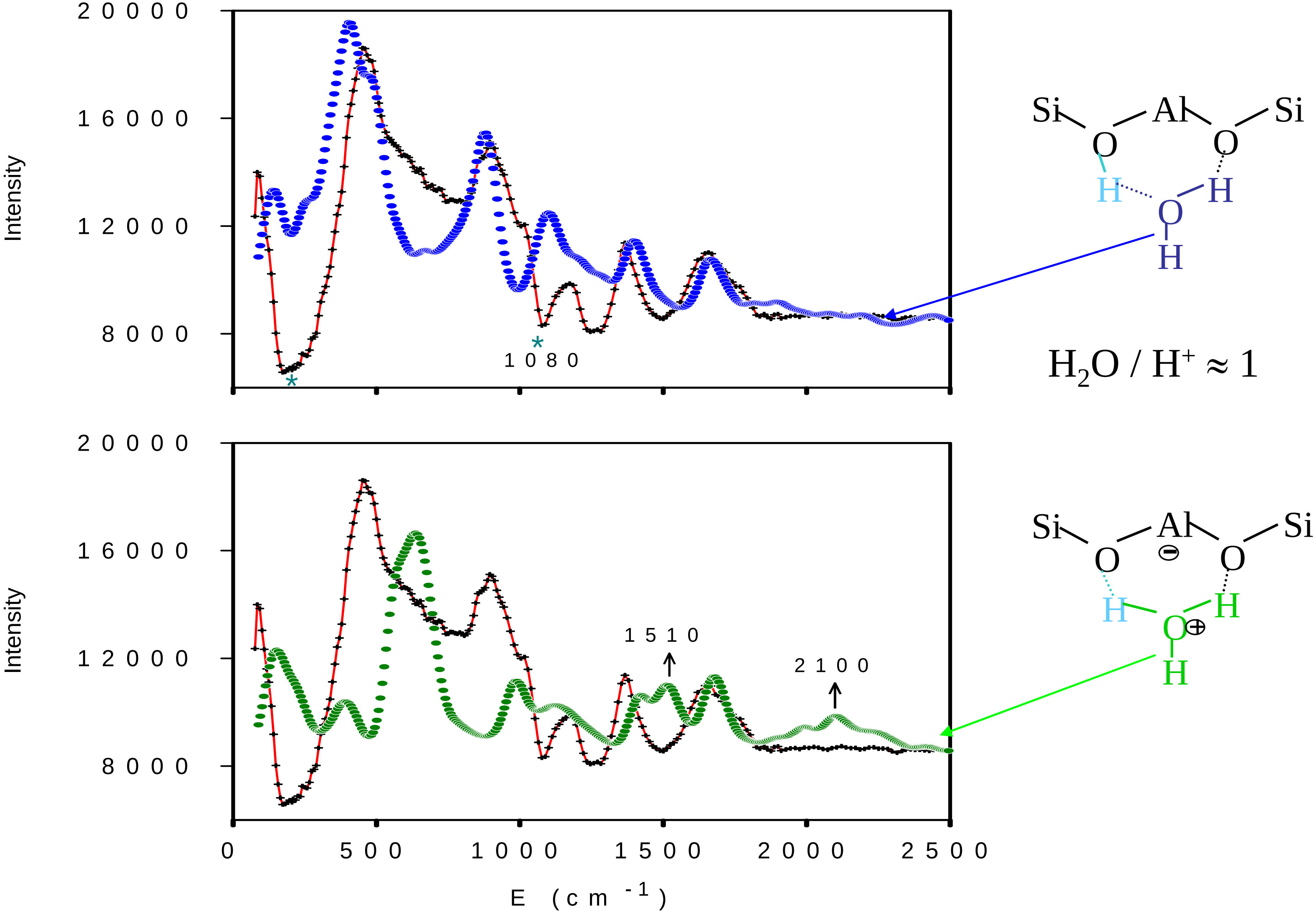


H-ZSM-5 (Si/Al = 12.5)

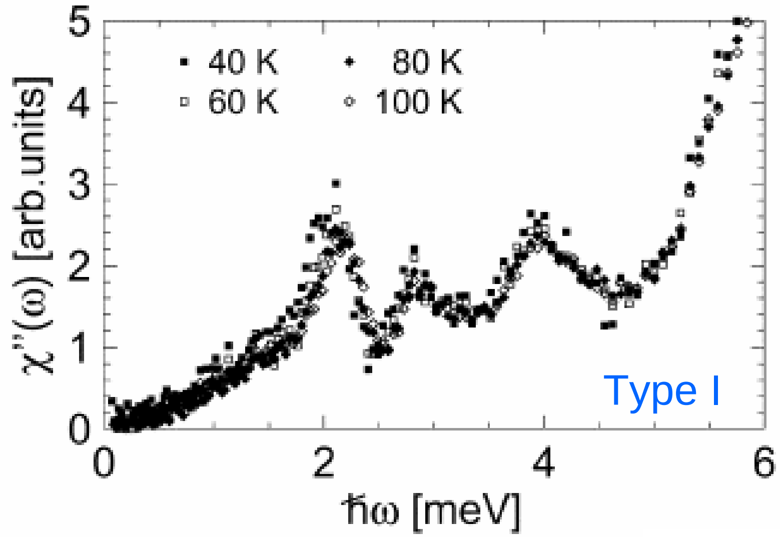




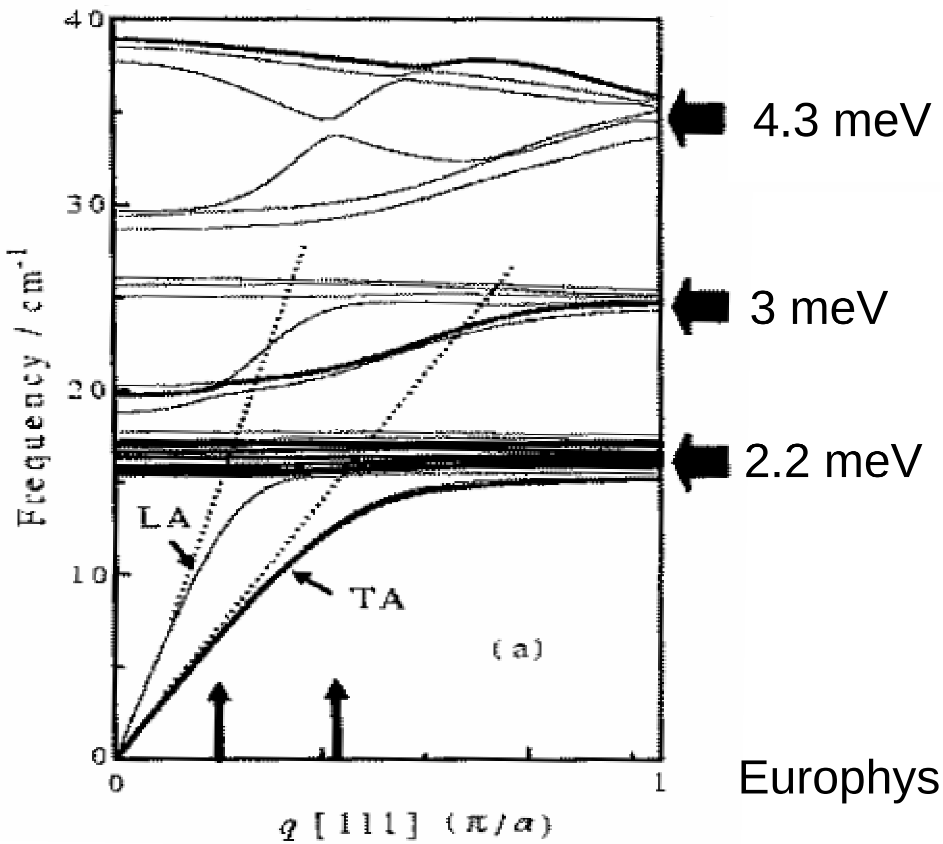
H_2O / H-ZSM-5



J. Phys. Chem. **100** (1996) 19545



Phys. Chem. Chem. Phys. 4 (2002) 4809



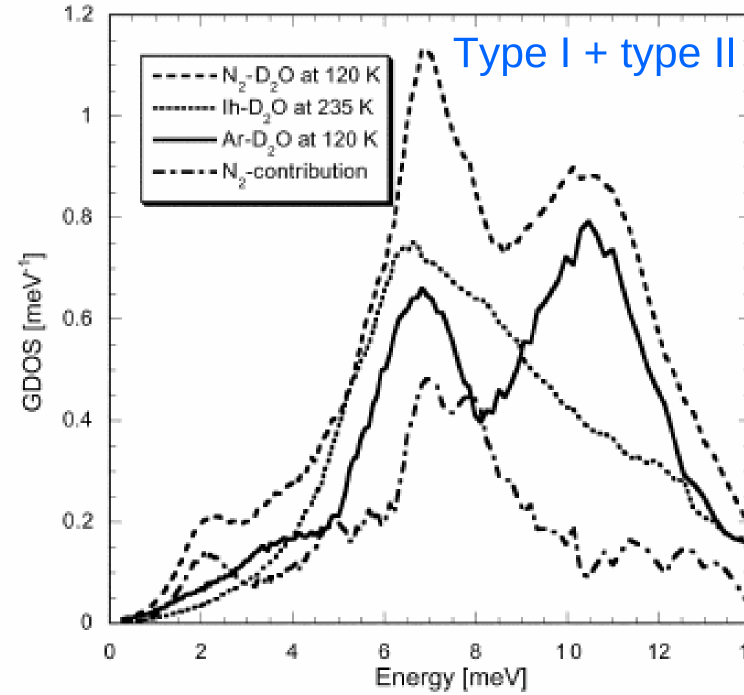
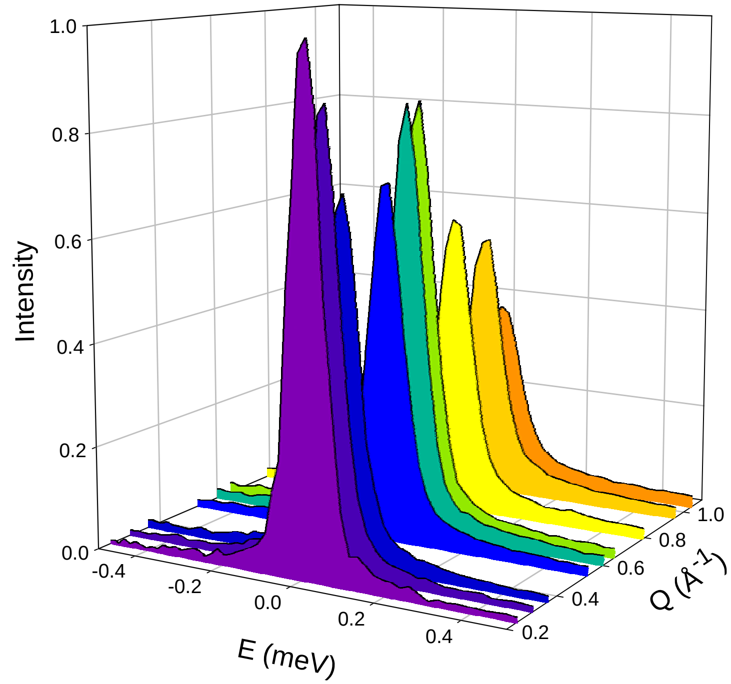
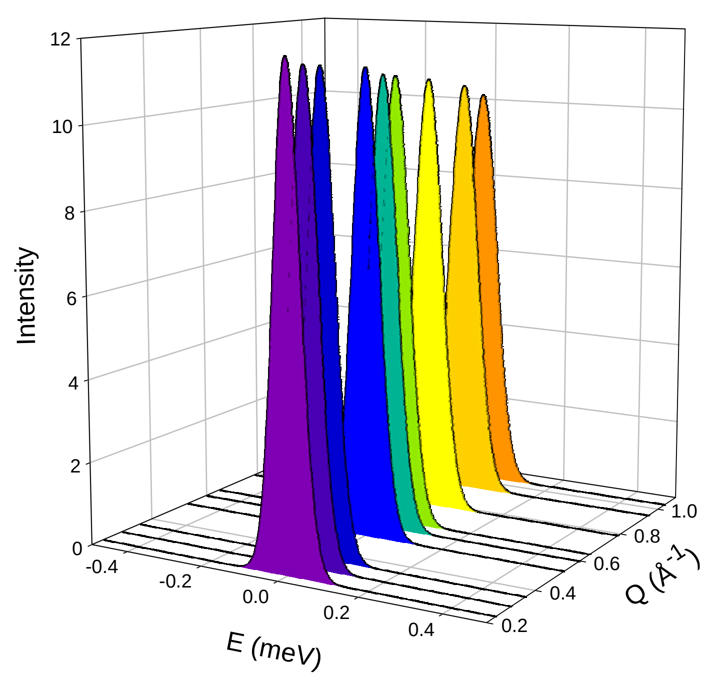


Fig. 4 GDOS of singly occupied N_2-hydrate at 120 K and comparison with Ar-hydrate and hexagonal ice Ih (The hexagonal ice contributions to the N_2-hydrate sample have been corrected for). The N_2 contribution is obtained by subtracting the Ar-hydrate from the N_2-hydrate spectrum.

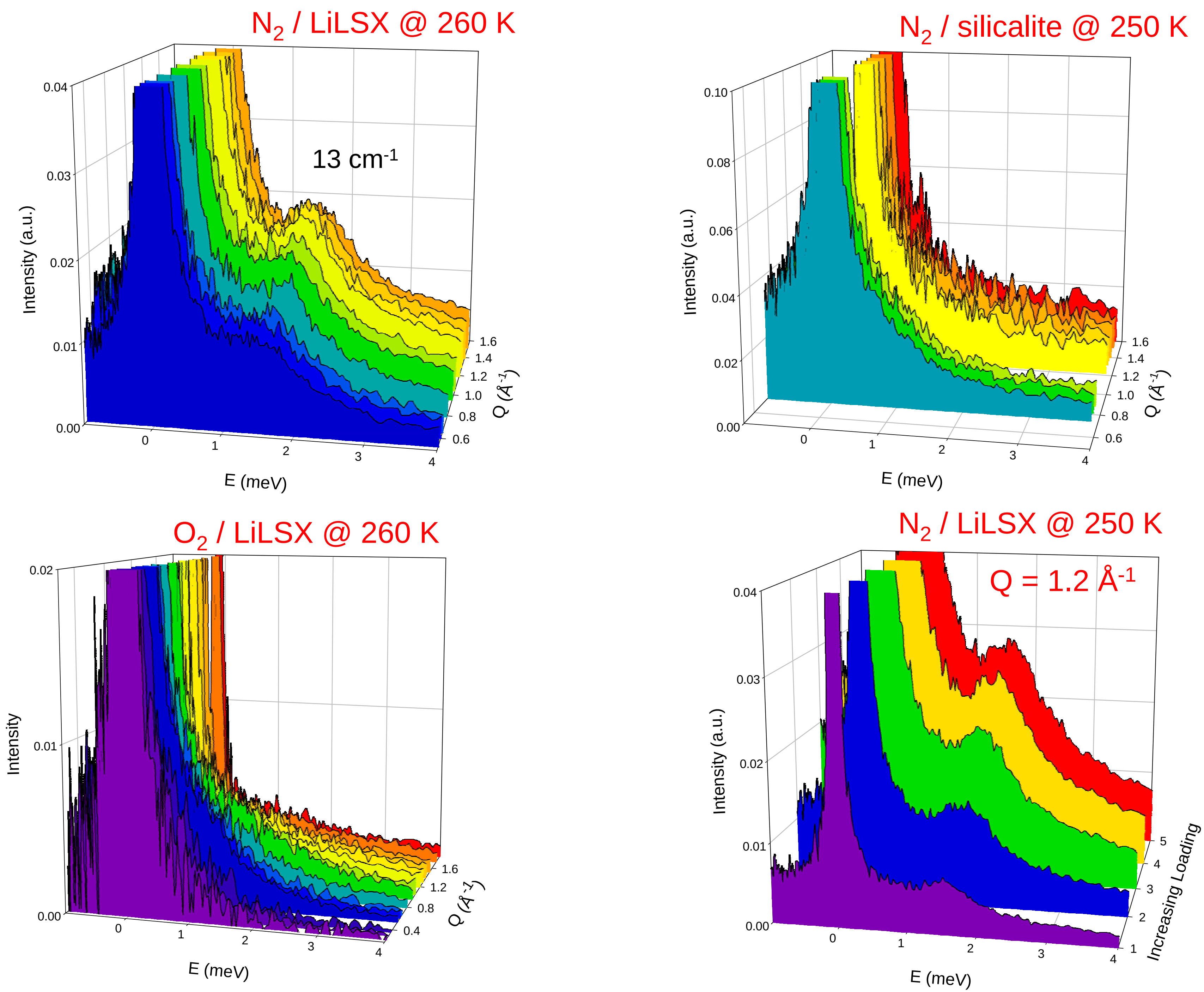
Europhys. Lett. 54 (2001) 354



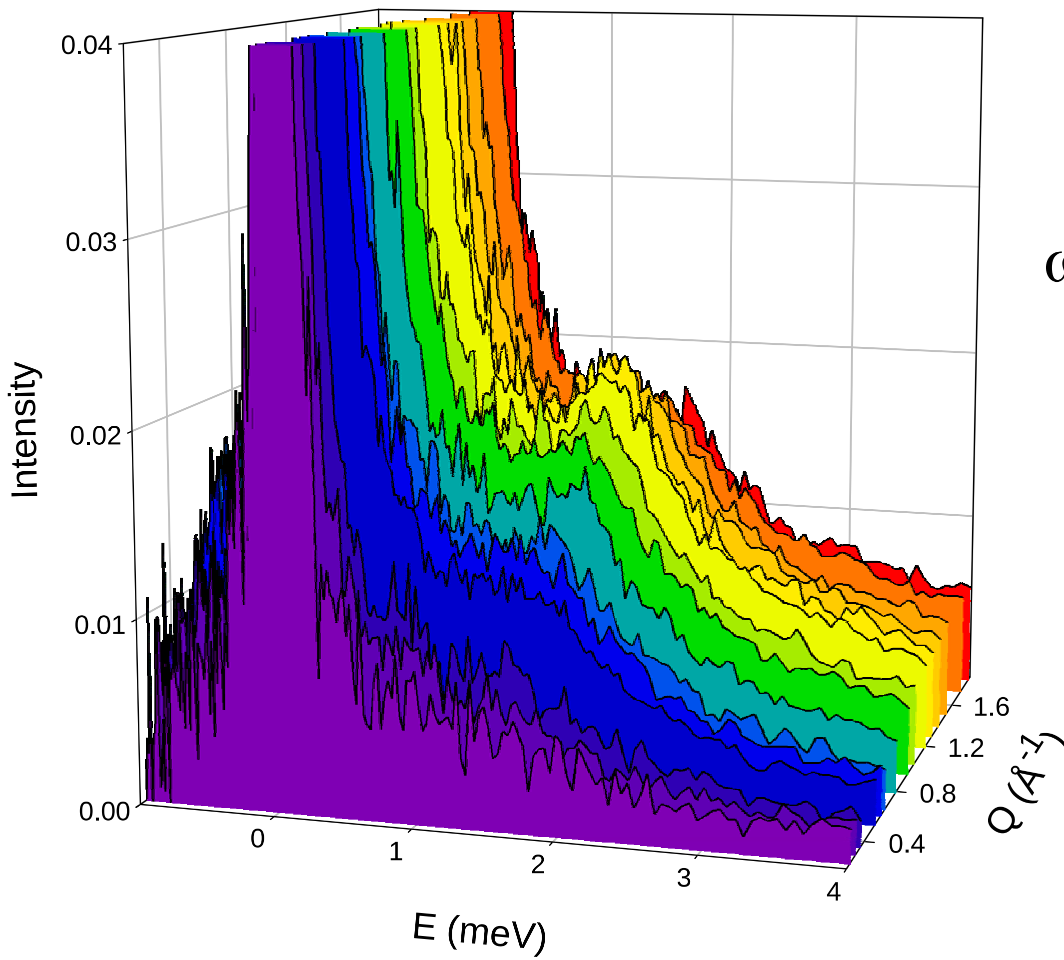
N_2 / LiLSX @ 260 K



vanadium


N2 / LiLSX @ 260 K
13 cm-1
Intensity (a.u.)
E (meV)
Q (Å-1)
N2 / silicalite @ 250 K
Intensity (a.u.)
E (meV)
Q (Å-1)
O2 / LiLSX @ 260 K
Intensity
E (meV)
Q (Å-1)
N2 / LiLSX @ 250 K
Q = 1.2 Å-1
Intensity (a.u.)
E (meV)
Increasing Loading

N2 [3] @ 260K

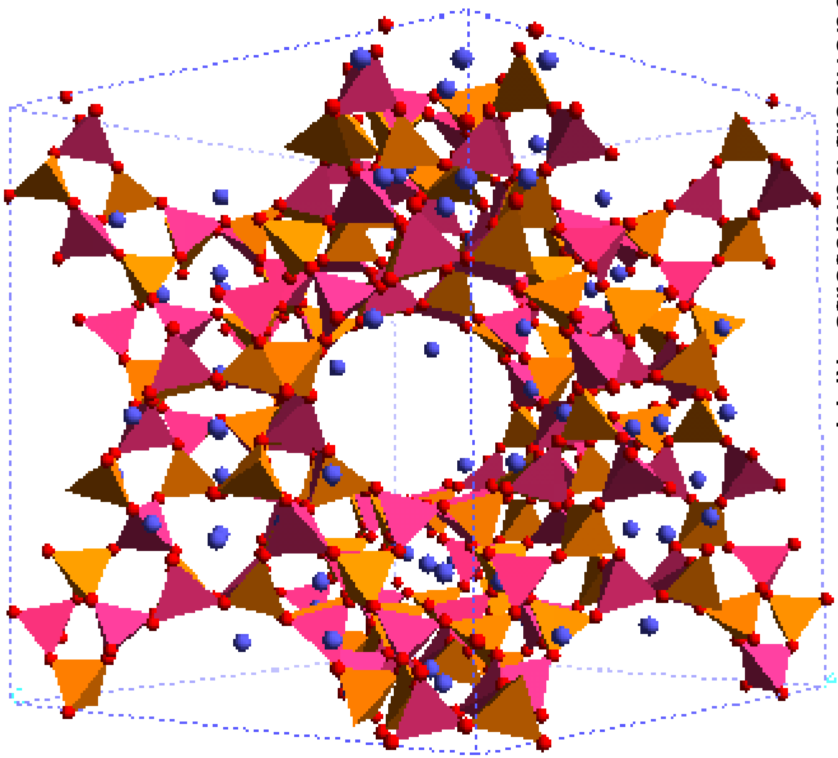


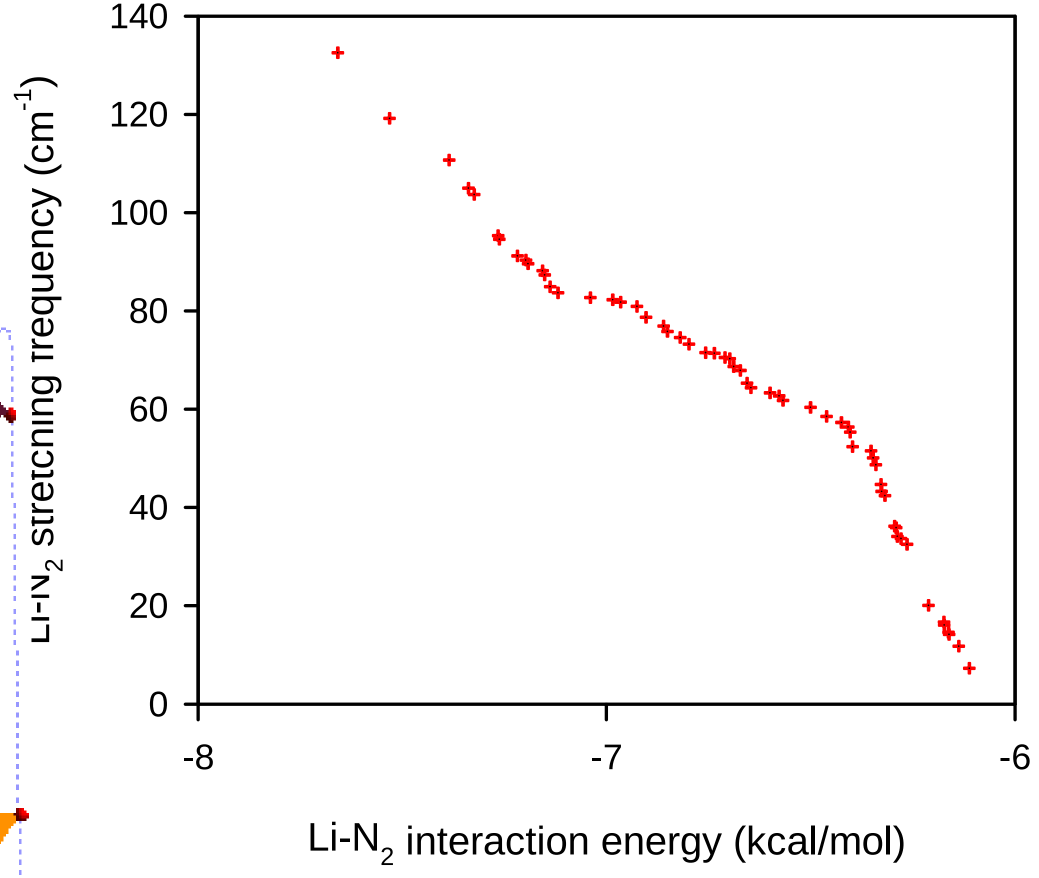
Li↔N—N

ω_λ = 1.6 meV = 13 cm^{-1}

$$S_d(\mathbf{Q},\omega) = \exp(-\mathbf{Q}^2 < \mathbf{u}_d^2 >) \frac{\hbar\left|\mathbf{Q}.\mathbf{C}_d^\lambda\right|^2}{2\omega_\lambda} \delta(\omega-\omega_\lambda)$$

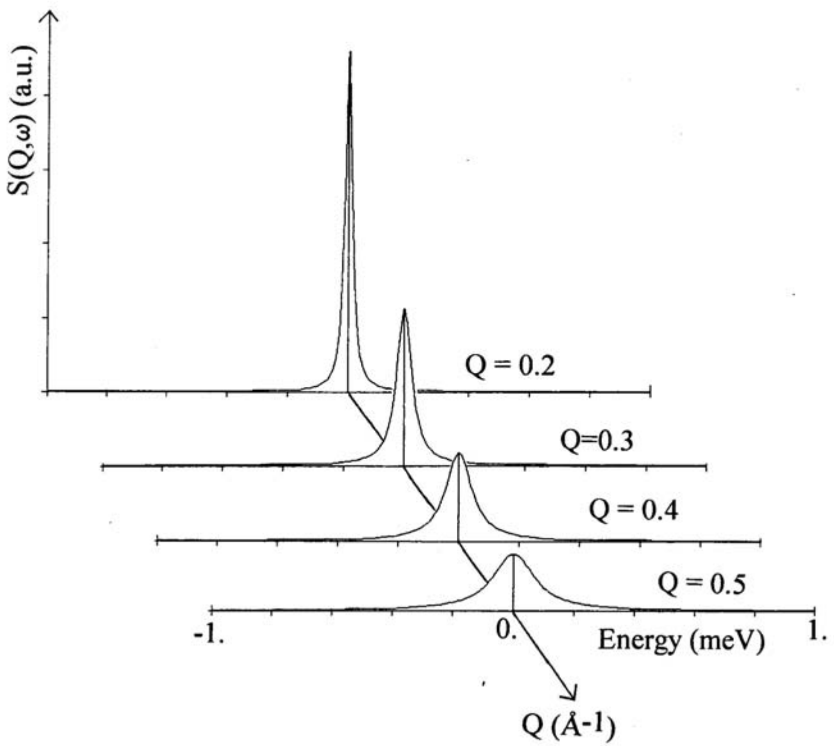
Calculated Li-N_2 vibrational frequencies in LiLSX (QM / MM)





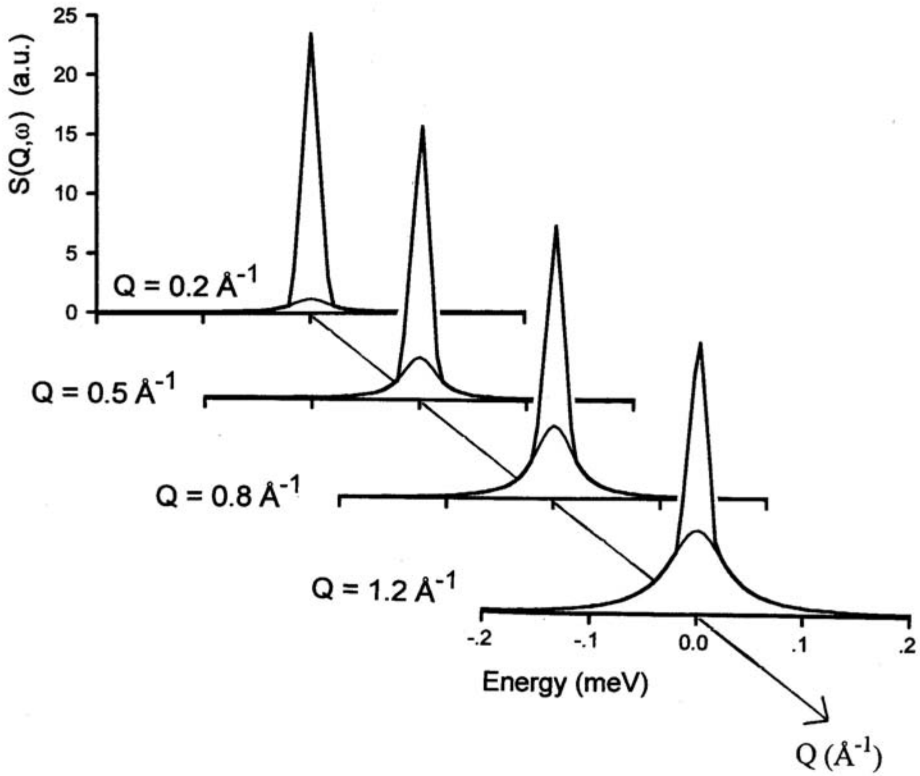
Adsorption 11 (2005) 449

Translation



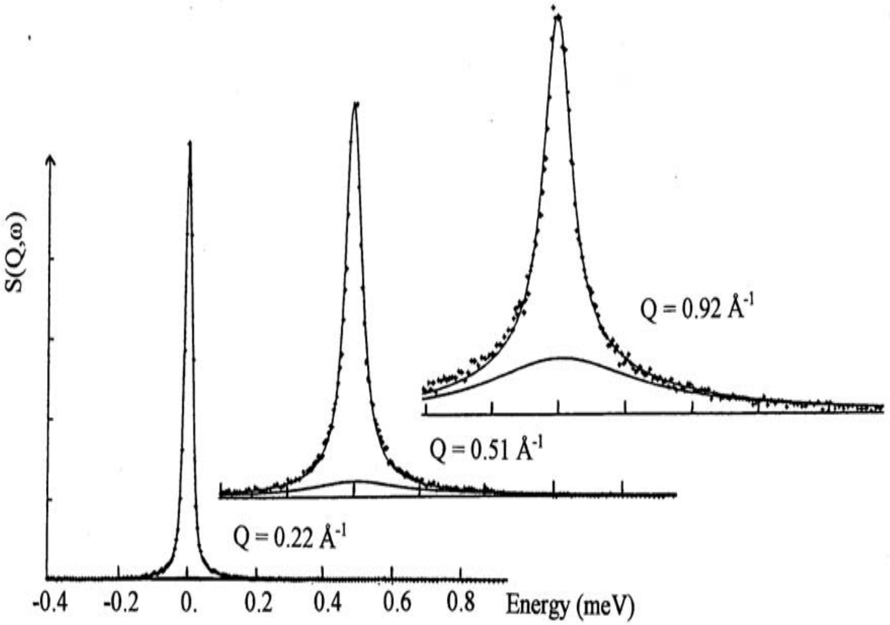
$$S_{inc}^{trans}(\mathbf{Q},\omega) = \frac{1}{\pi}\frac{D_S\, Q^2}{\omega^2 + \left(D_S\, Q^2\right)^2}$$

Rotation



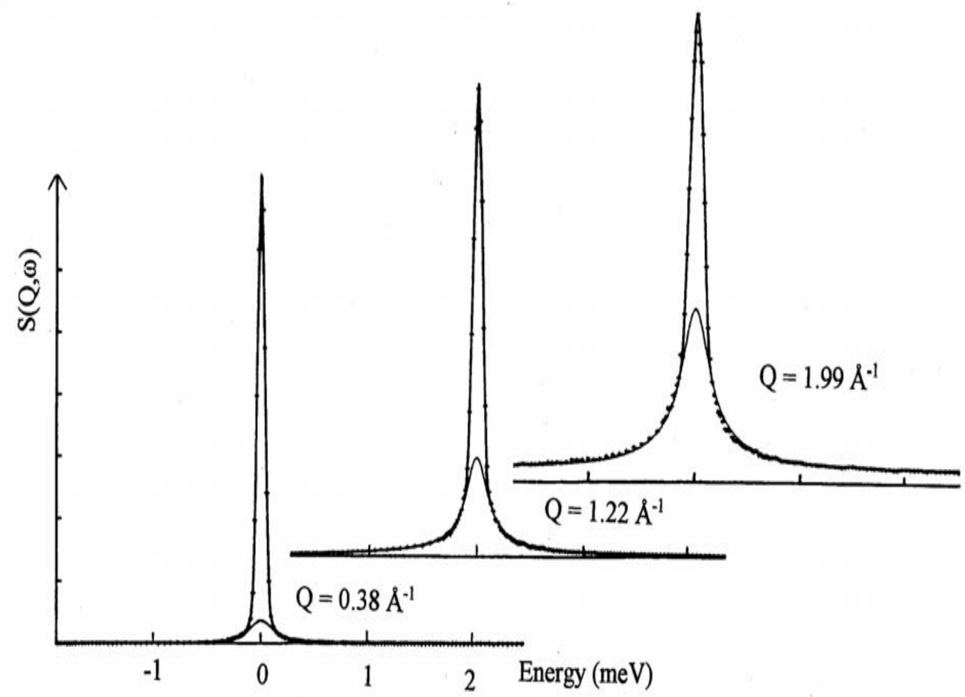
$$S_{inc}^{rot}(\mathbf{Q},\omega) = A_0(\mathbf{Q})\delta(\omega) + \sum_{\ell} A_\ell(\mathbf{Q}) L(\omega,\Gamma_\ell)$$

Translation



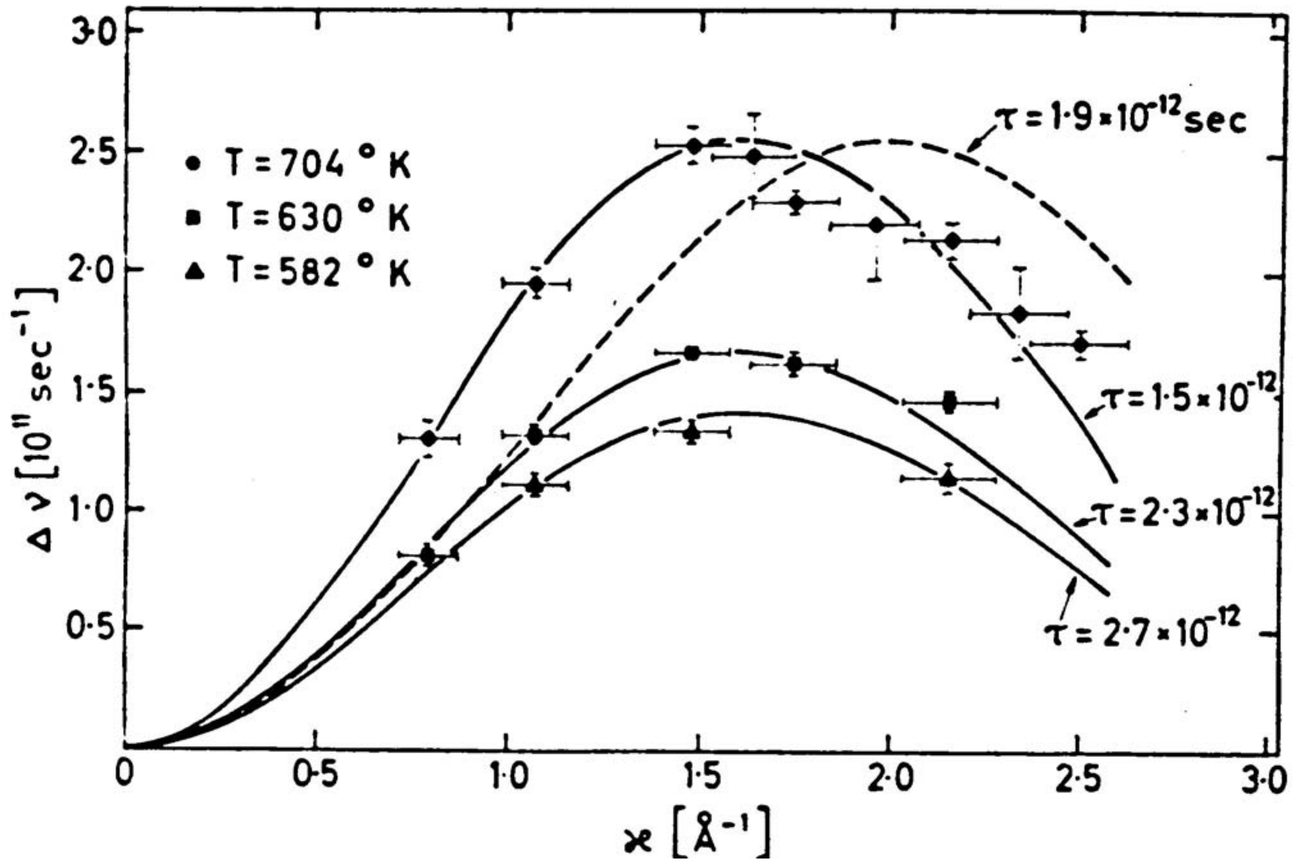
Ethane / NaX

Rotation



Benzene / ZSM-5

Diffusion of H in α-PdH

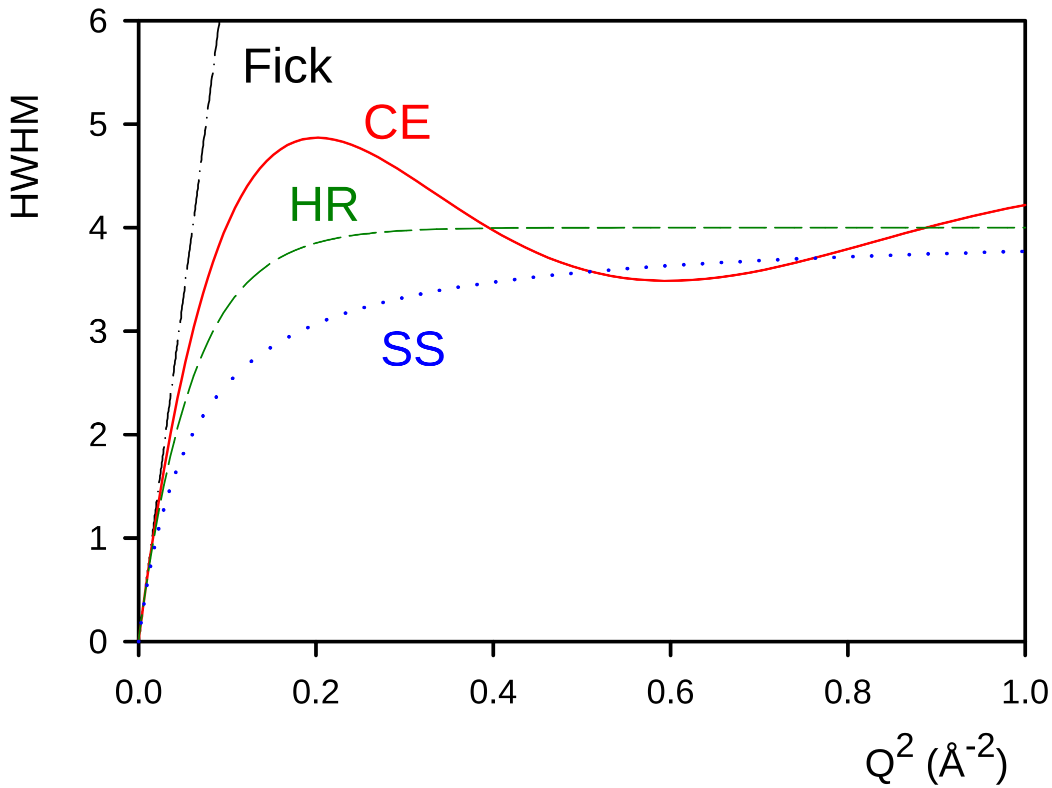


———————— : octahedral sites

- - - - - - - - : tetrahedral sites

JPCS 28 (1967) 2369

Fick: DQ^2



$<r^2>^{1/2} = 10$ Å
$\tau \equiv$
} same *D*

Chudley-Elliott (CE):

$$\frac{1}{\tau}\left(1-\frac{\sin(Qd)}{Qd}\right)$$

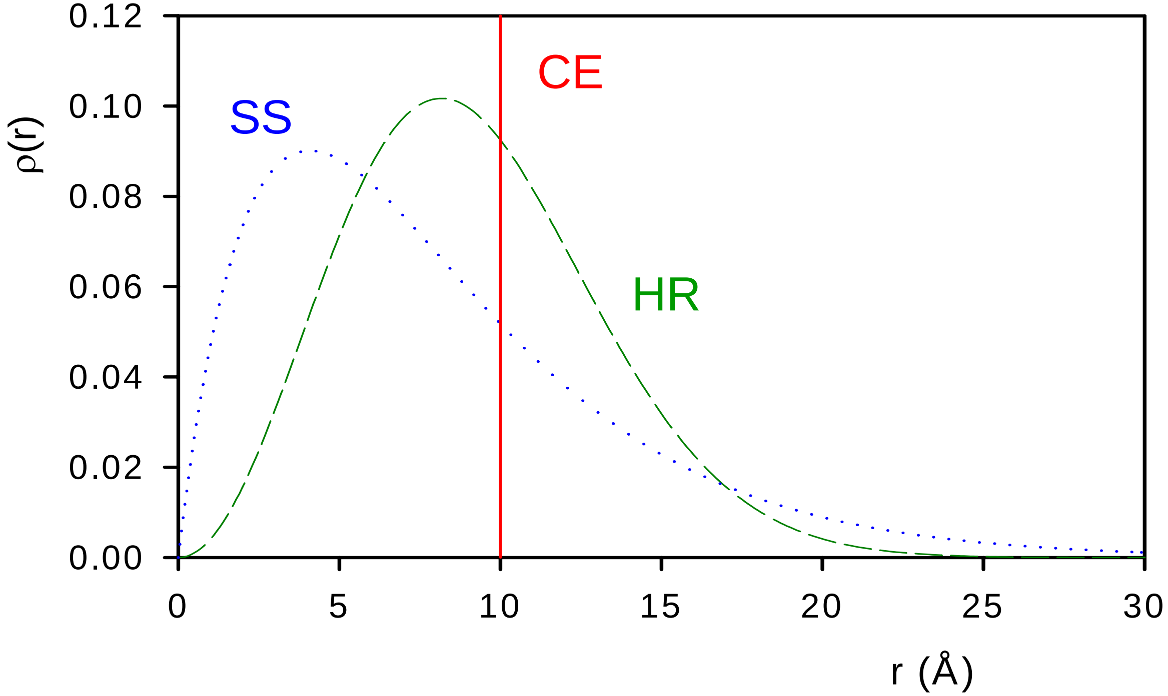
Singwi-Sjölander (SS):

$$\frac{1}{6\tau}\frac{Q^2<r^2>}{1+Q^2<r^2>/6}$$

Hall-Ross (HR):

$$\frac{1}{\tau}\left(1-\exp\left(-\frac{Q^2<r^2>}{6}\right)\right)$$

Jump length distributions



$<r>^2 = 100$ Å^2

Chudley-Elliott (CE):

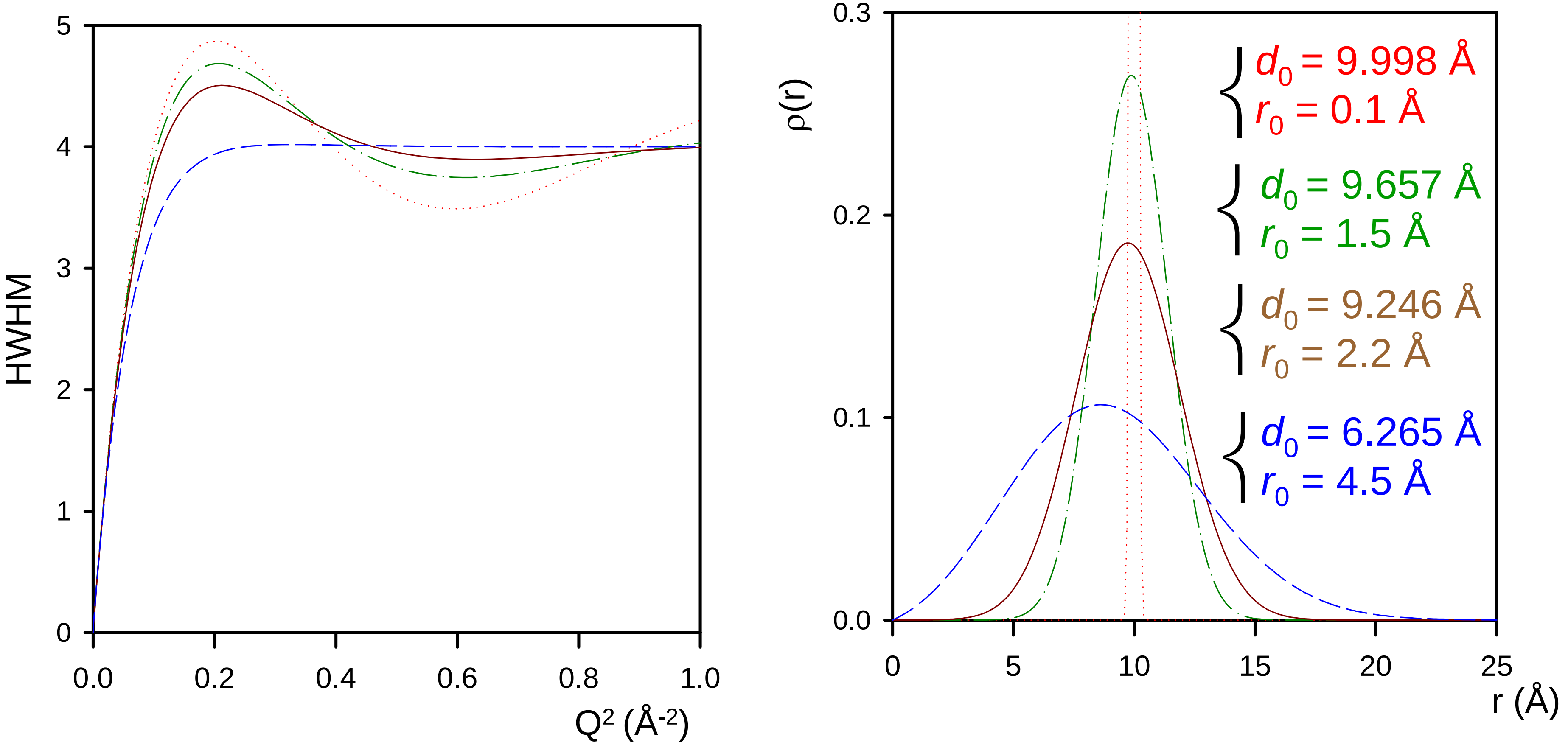
$$\rho(r) = \delta(r-d)$$

Singwi-Sjölander (SS):

$$\rho(r) = \frac{r}{r_0^2}\exp\left(-\frac{r}{r_0}\right)$$

Hall-Ross (HR):

$$\rho(r) = \frac{2r^2}{r_0^3(2\pi)^{1/2}}\exp\left(-\frac{r^2}{2r_0^2}\right)$$



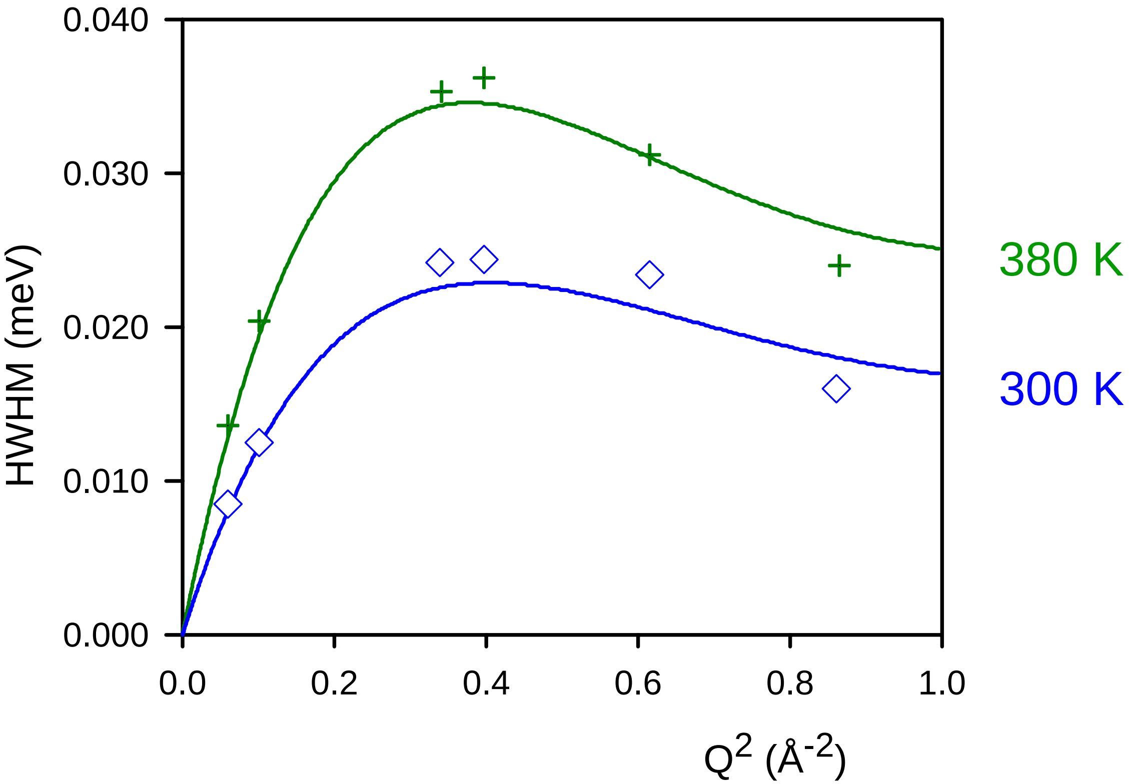
$<r>^2 = 100$ Å^2

$$HWHM = \frac{1}{\tau}\left[1 - \frac{\sin(Qd_0)}{Qd_0}\exp\left(-\frac{Q^2\ r_0^2}{2}\right)\right]$$

$$\rho(r) = \frac{r}{d_0 r_0\,(2\pi)^{1/2}}\exp\left(-\frac{(r-d_0)^2}{2r_0^2}\right)$$

n-pentane / NaX

1 molecule / supercage

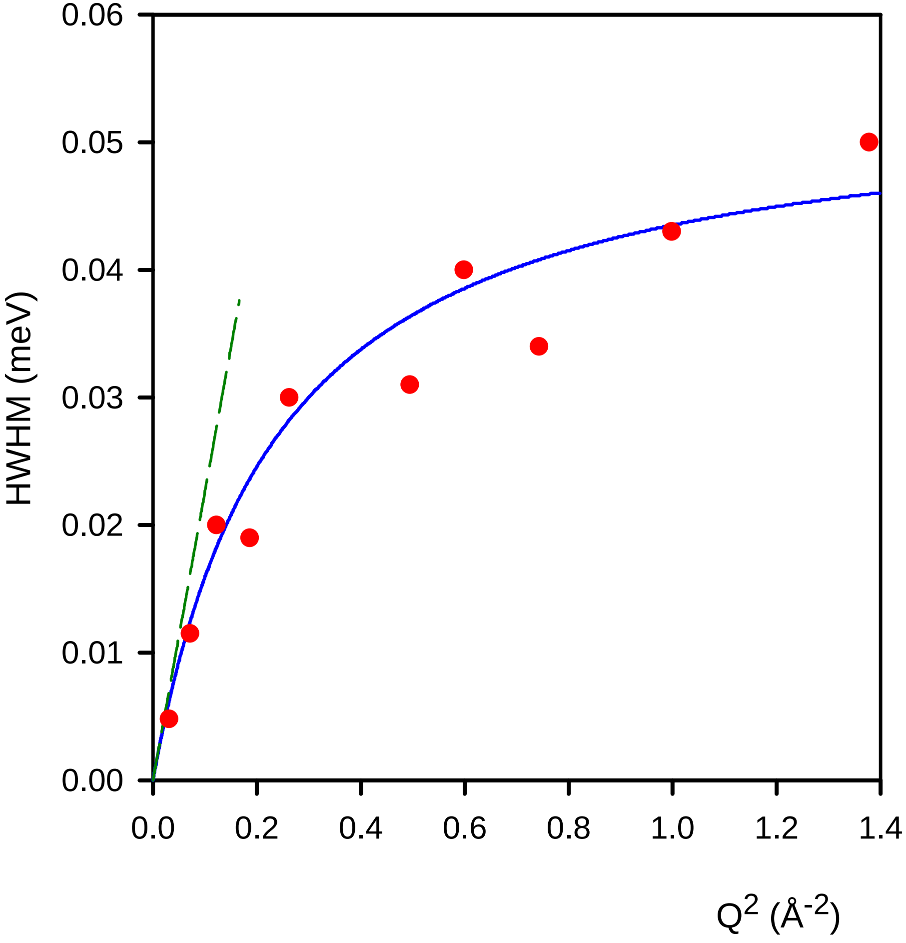


	D (m^2/s)	τ (s)	d (Å)
300 K	2.4×10^{-9}	3.5×10^{-11}	7
380 K	3.9×10^{-9}	2.28×10^{-11}	″

Phys. Chem. Chem. Phys. 1 (1999) 525

NH_3 / silicalite

4.3 molecules / u.c. T = 360 K



$<d>^{1/2}$ = 5 Å

τ = 12 ps

Microp. Mesop. Mater. 26 (1998) 67

J. Kärger and D. M. Ruthven: Diffusion in Zeolites (1992)

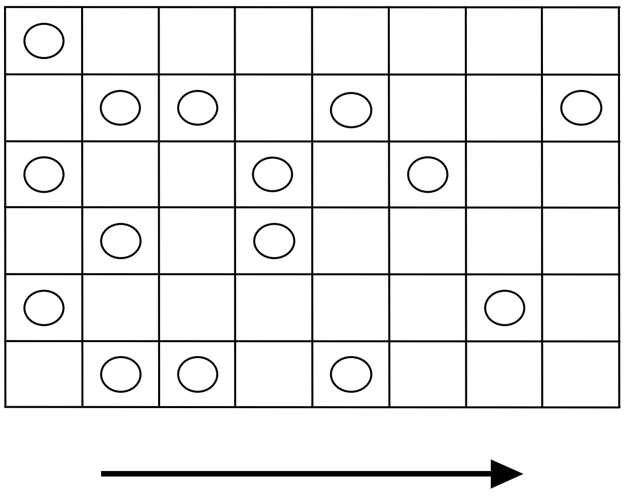
$\mathcal{D}$	self-diffusivity (defined by Eq. 1.11 or 1.12)
$\mathcal{D}_\infty$	pre-exponential factor in Arrhenius expression for temperature dependence of $\mathcal{D}$ (Eq. 4.70)
$\mathcal{D}_{\text{inter}}$	self-diffusivity in inter-crystalline space
$\mathcal{D}_{\text{intra}}$	intracrystalline self-diffusivity
$\mathcal{D}_{\text{l.r.}}$	long range self-diffusivity (through a bed of microporous crystals)
D	transport diffusivity (defined by Eq. 1.1)
D_0	corrected transport diffusivity (defined by Eq. 1.29)
D_c	intracrystalline diffusivity
D_e	effective diffusivity
D_K	Knudsen diffusivity
D_L	axial dispersion coefficient
D_m	molecular diffusivity
D_p	pore diffusivity
D_p'	micropore diffusivity (Eq. 11.3)
D_s	surface diffusivity
D_{AB}	molecular diffusivity in binary A-B mixture
D_{des}	diffusivity calculated from desorption rate
D_{micro}	diffusivity in micropores
D_{macro}	diffusivity in macropores
$D_{\text{Poiseuille}}$	equivalent diffusivity for Poiseuille flow
$\tilde{D}$	integral diffusivity (derived from uptake rate measurement over a large concentration step)
$\bar{D}$	average diffusivity (over a defined concentration range)

Techniques for measuring diffusion coefficients

Out of equilibrium

- gravimetry
- chromatography
- frequency response
- infrared (FT & surface)
- permeability

...



$$J = -D_T \frac{dc}{dx}$$

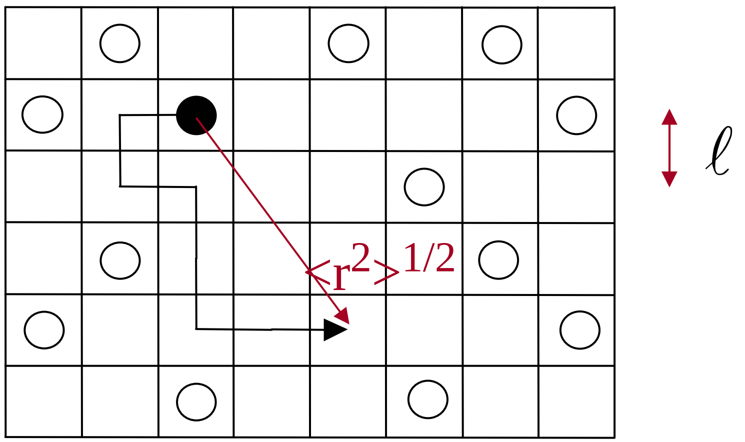
At equilibrium

- PFG NMR , QENS (inc. scattering)

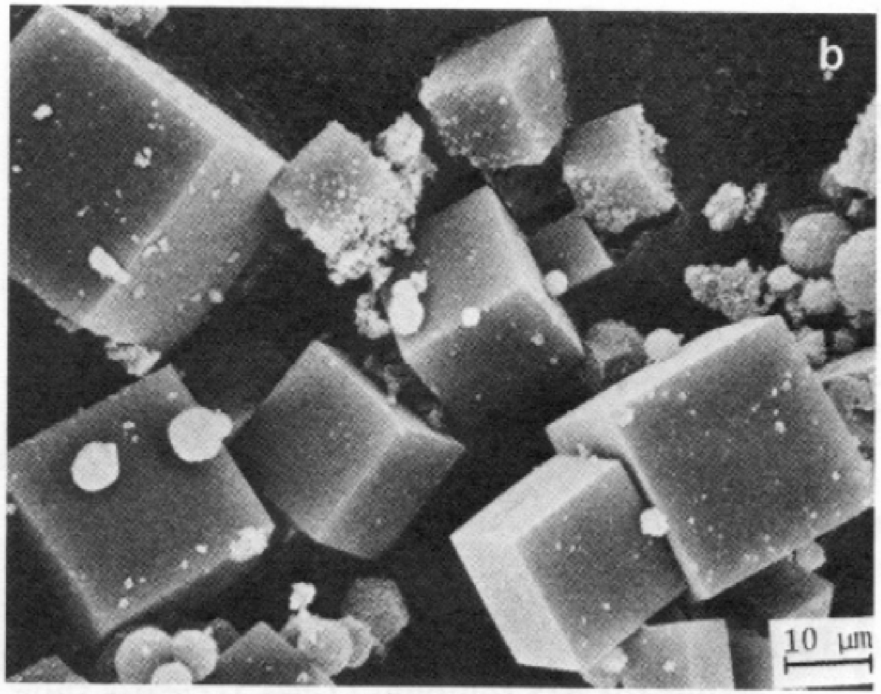
$$D_S = \frac{1}{6} \frac{< r^2(t) >}{t} = \frac{\ell^2}{6\tau}$$

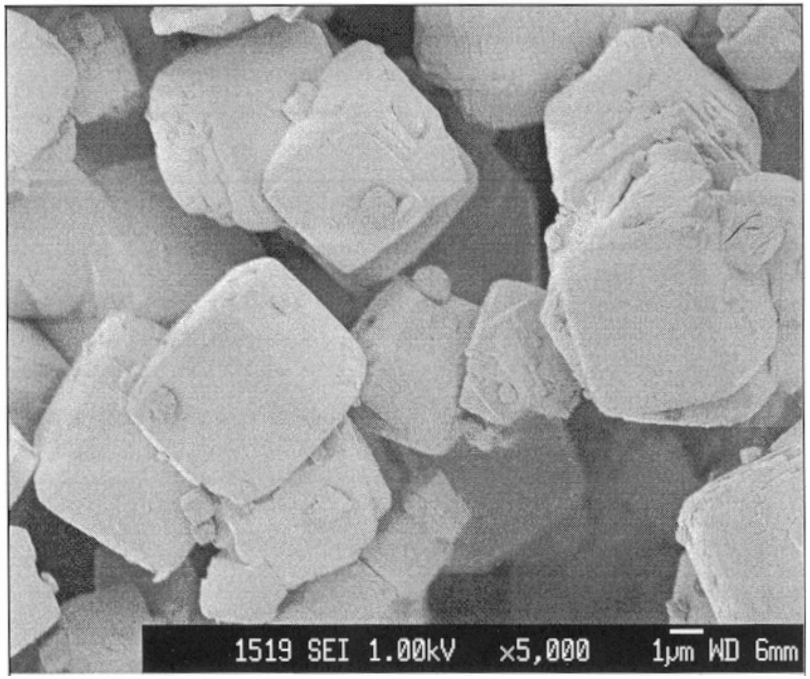
- QENS, NSE (coh. scattering):

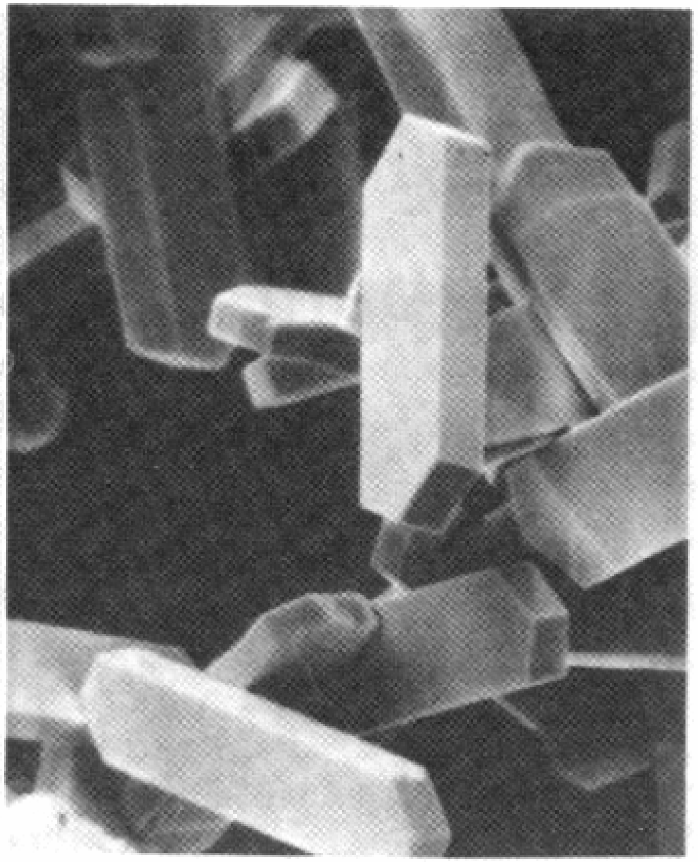
$$D_T$$

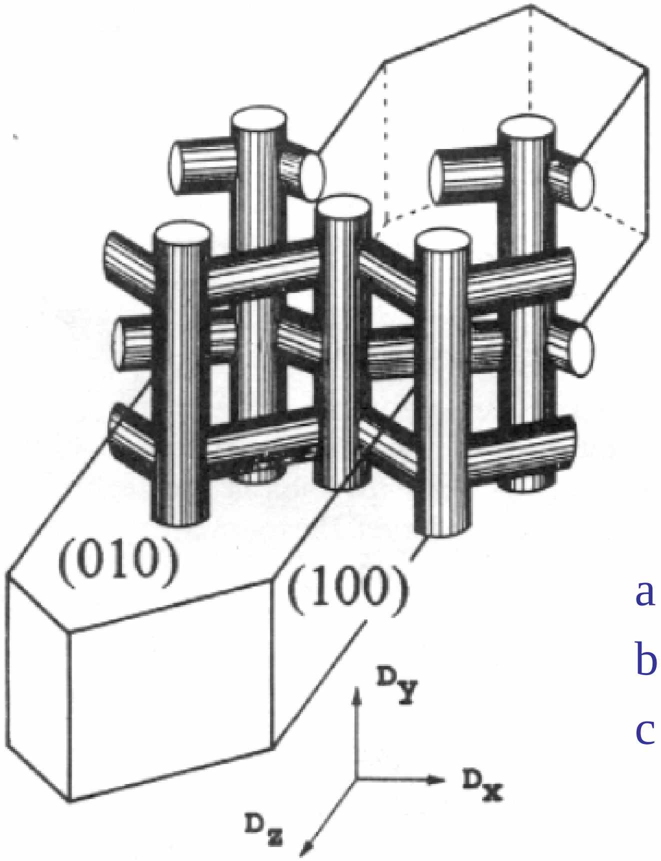


A-type zeolite crystals





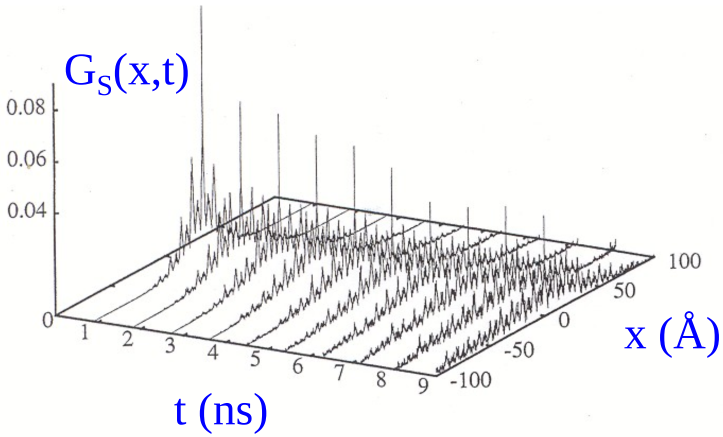


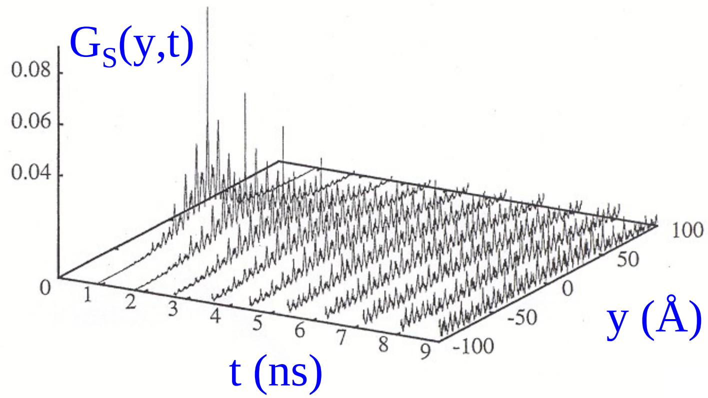


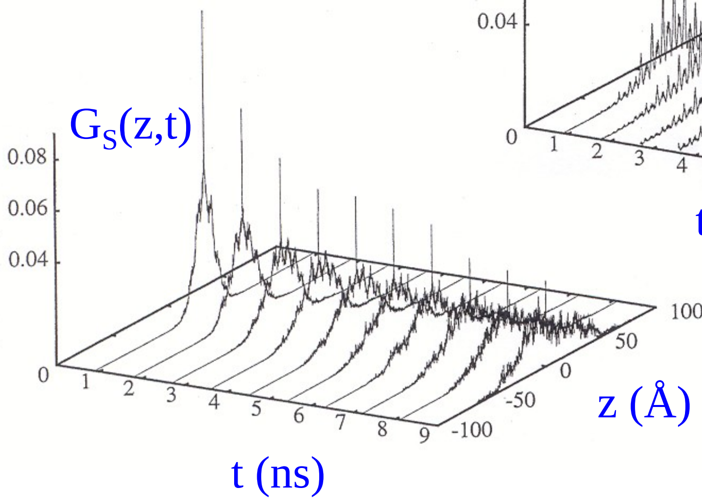
a = 20.07 Å
b = 19.92 Å
c = 13.42 Å

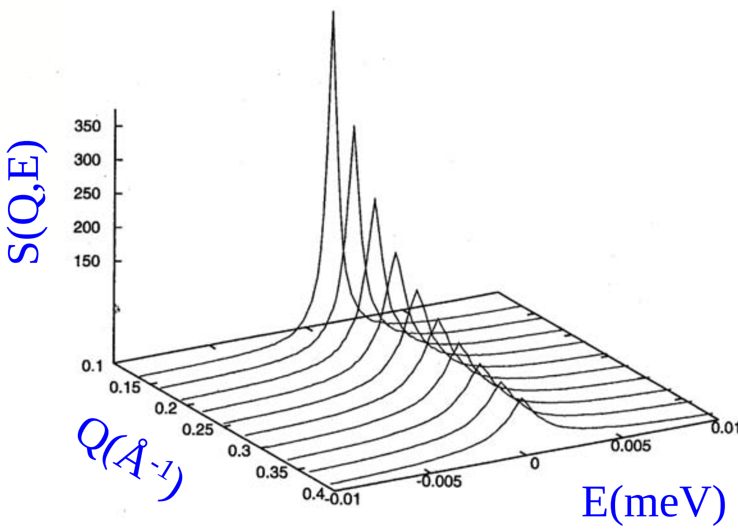
MFI structure (silicalite, ZSM-5)

CH_4 / silicalite (200 K)

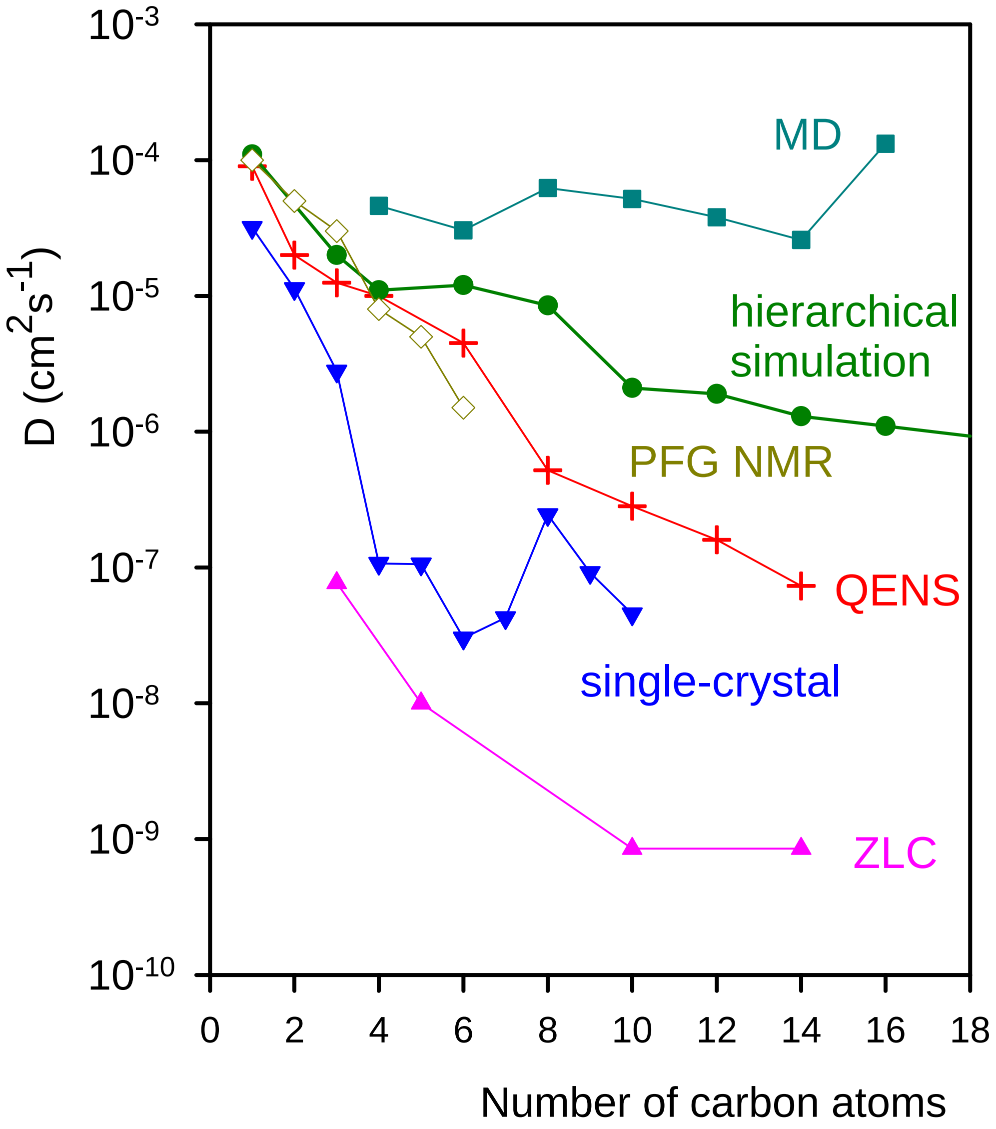




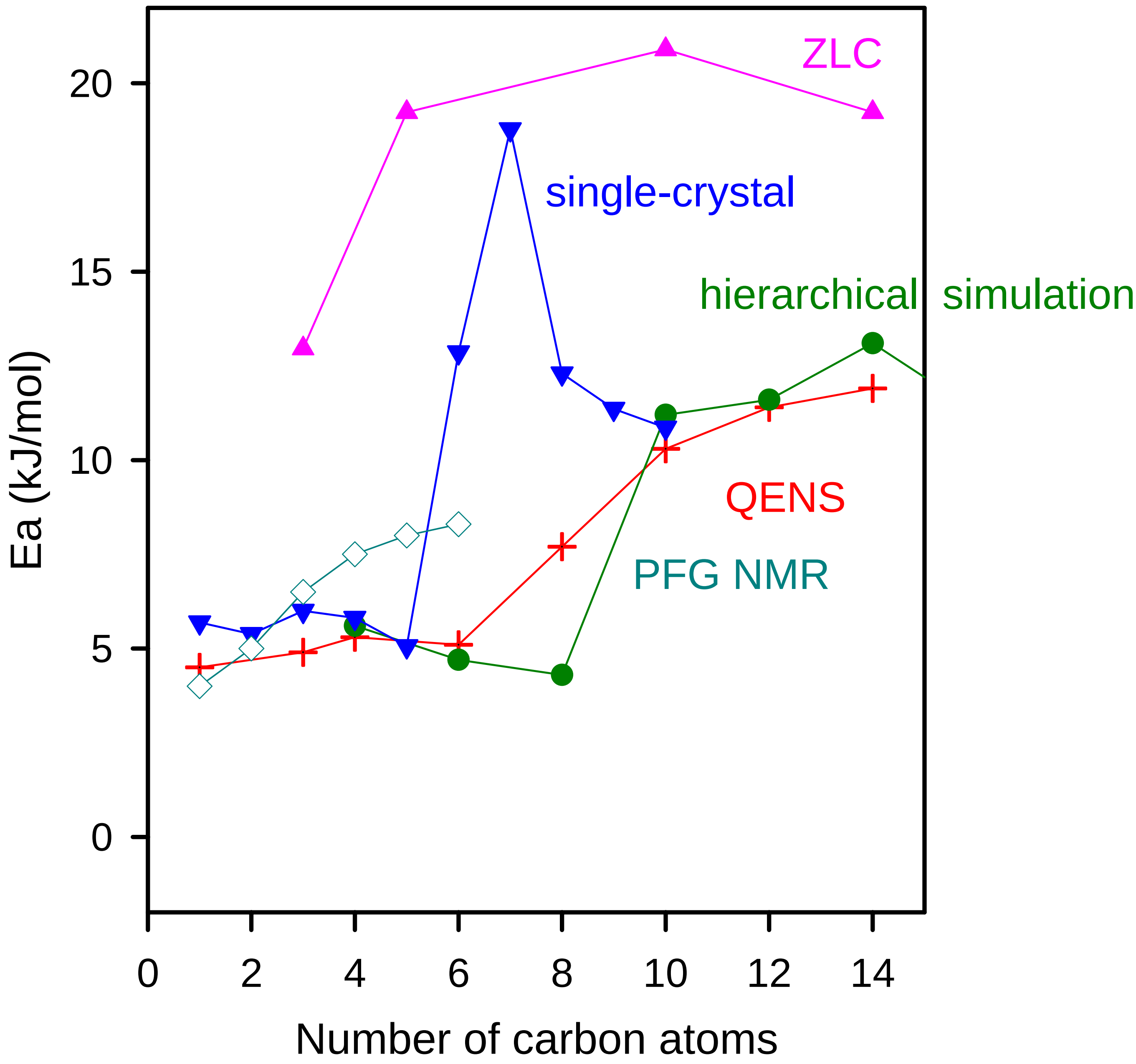


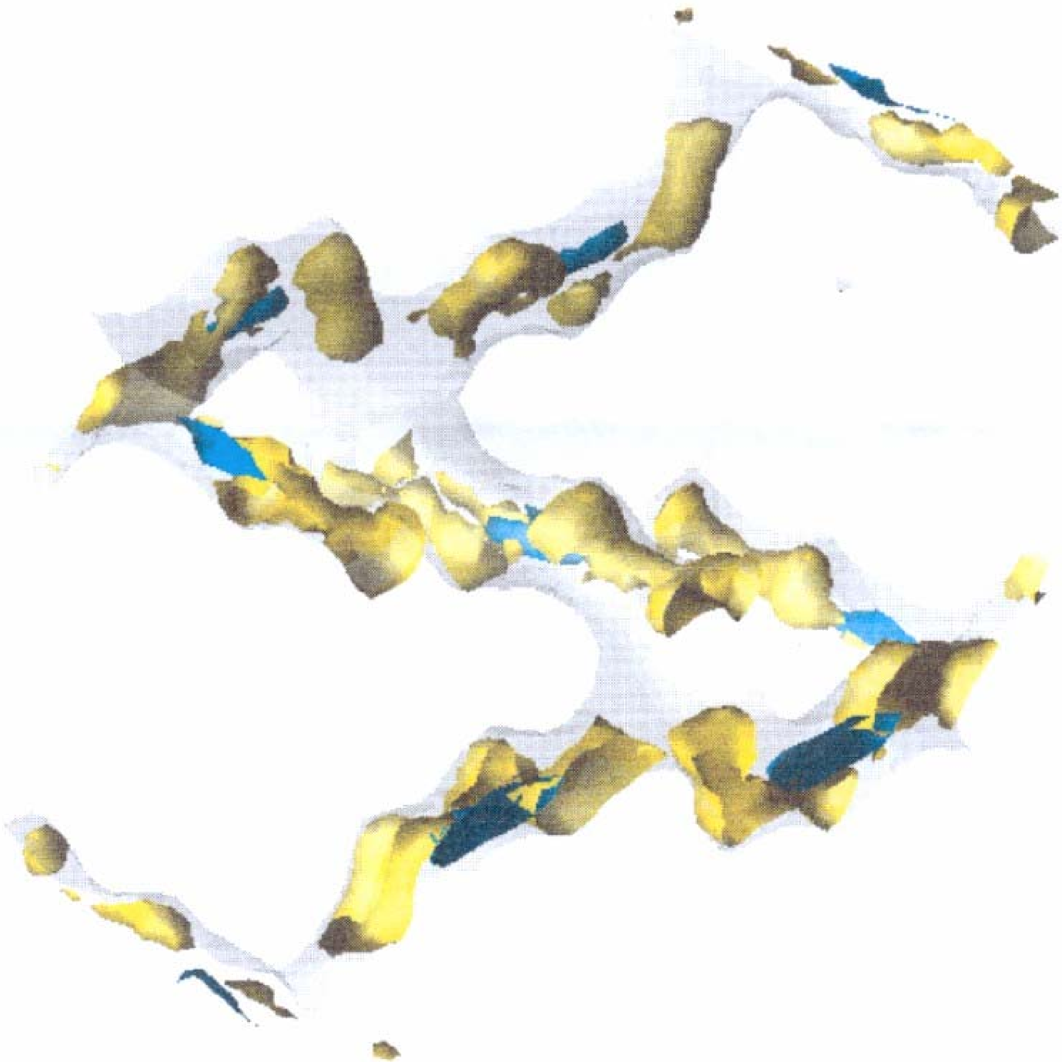


linear alkanes / MFI
(T = 300 K)



J. Mol. Catal. A 158 (2000) 135


ZLC
single-crystal
hierarchical simulation
QENS
PFG NMR
Ea (kJ/mol)
Number of carbon atoms
0
5
10
15
20
0
2
4
6
8
10
12
14

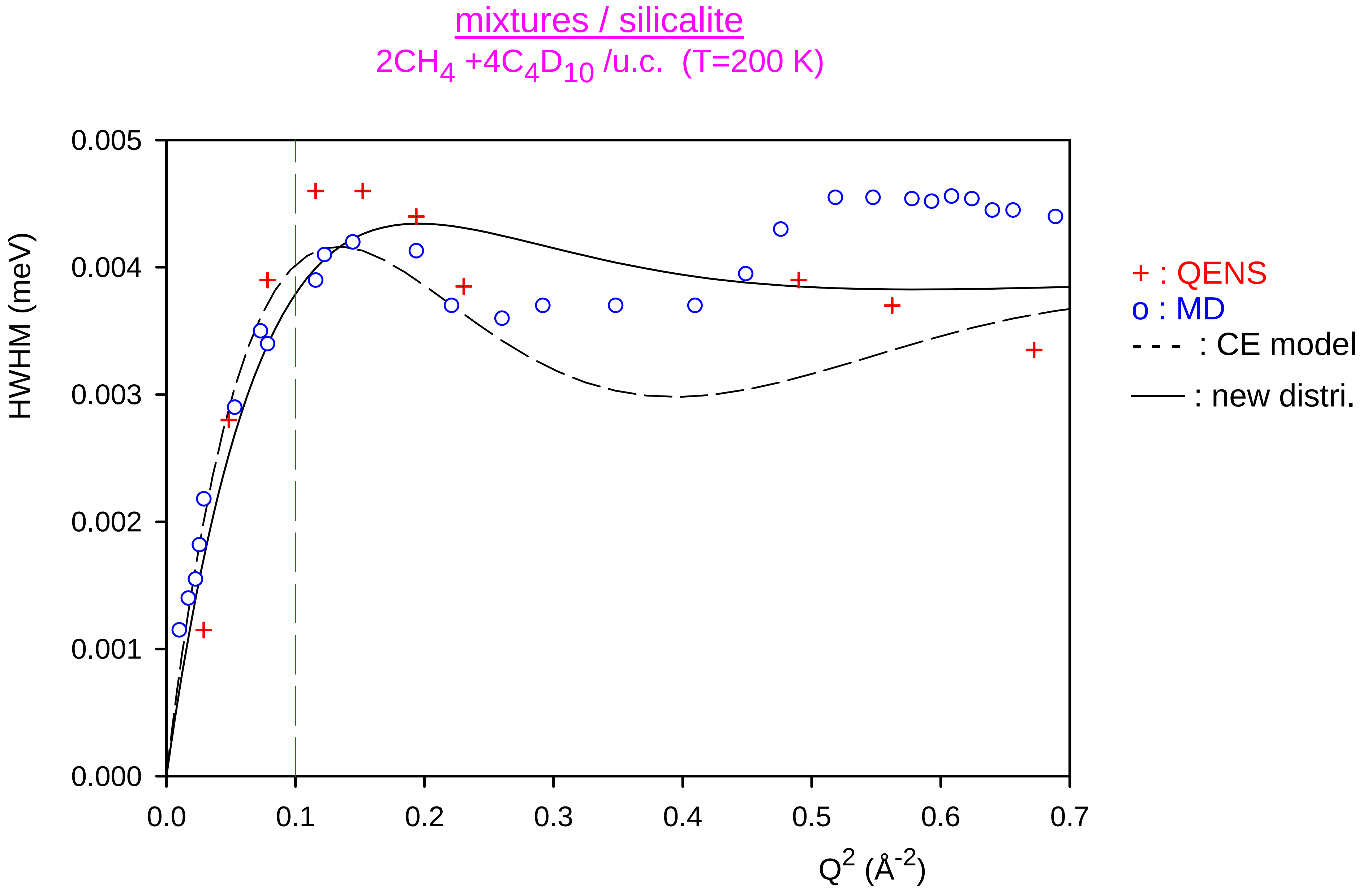


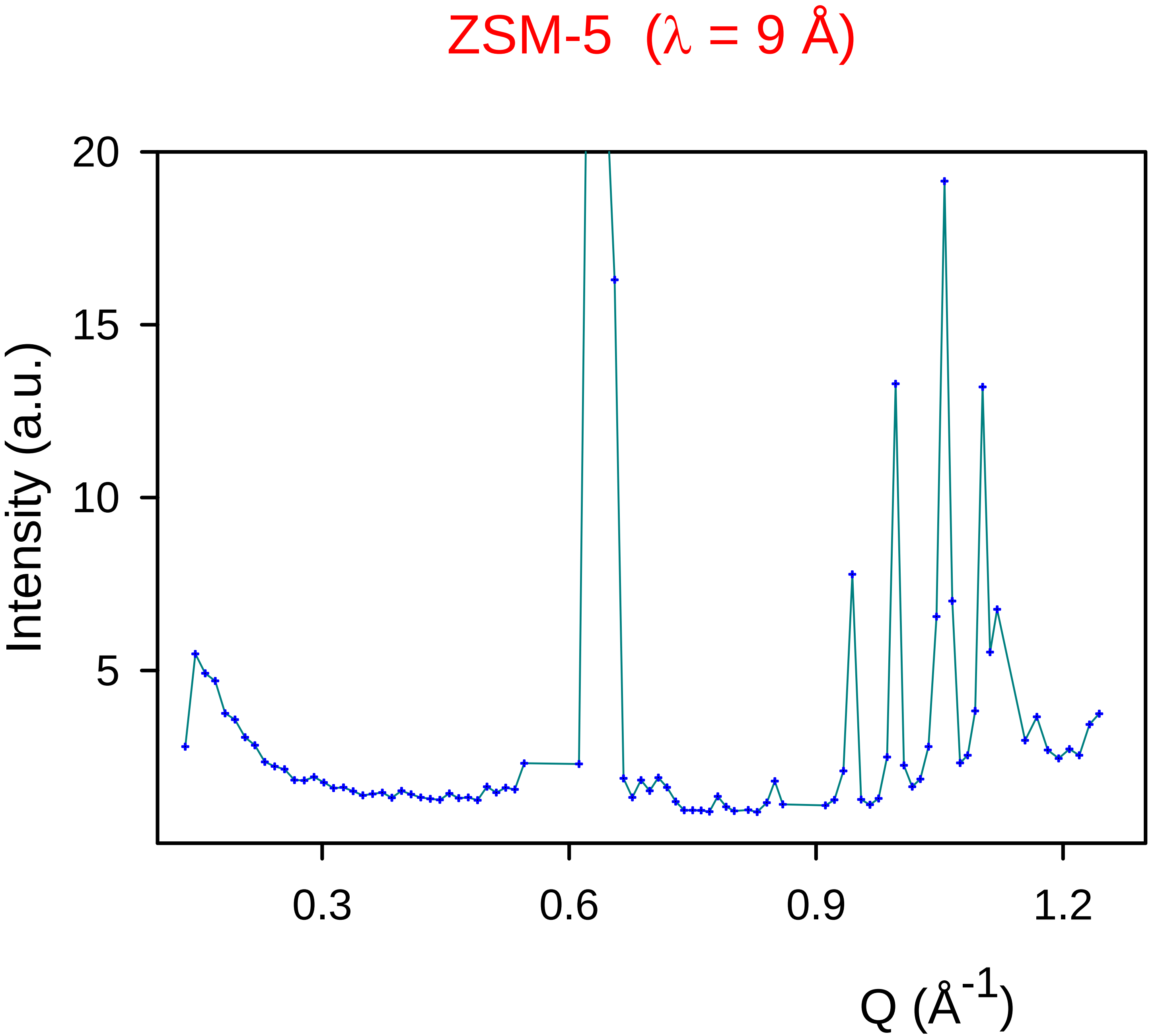
5 CH_4

4 *n*-C_4H_{10}

(300 K)

J. Phys. Chem.B **103** (1999) 3380

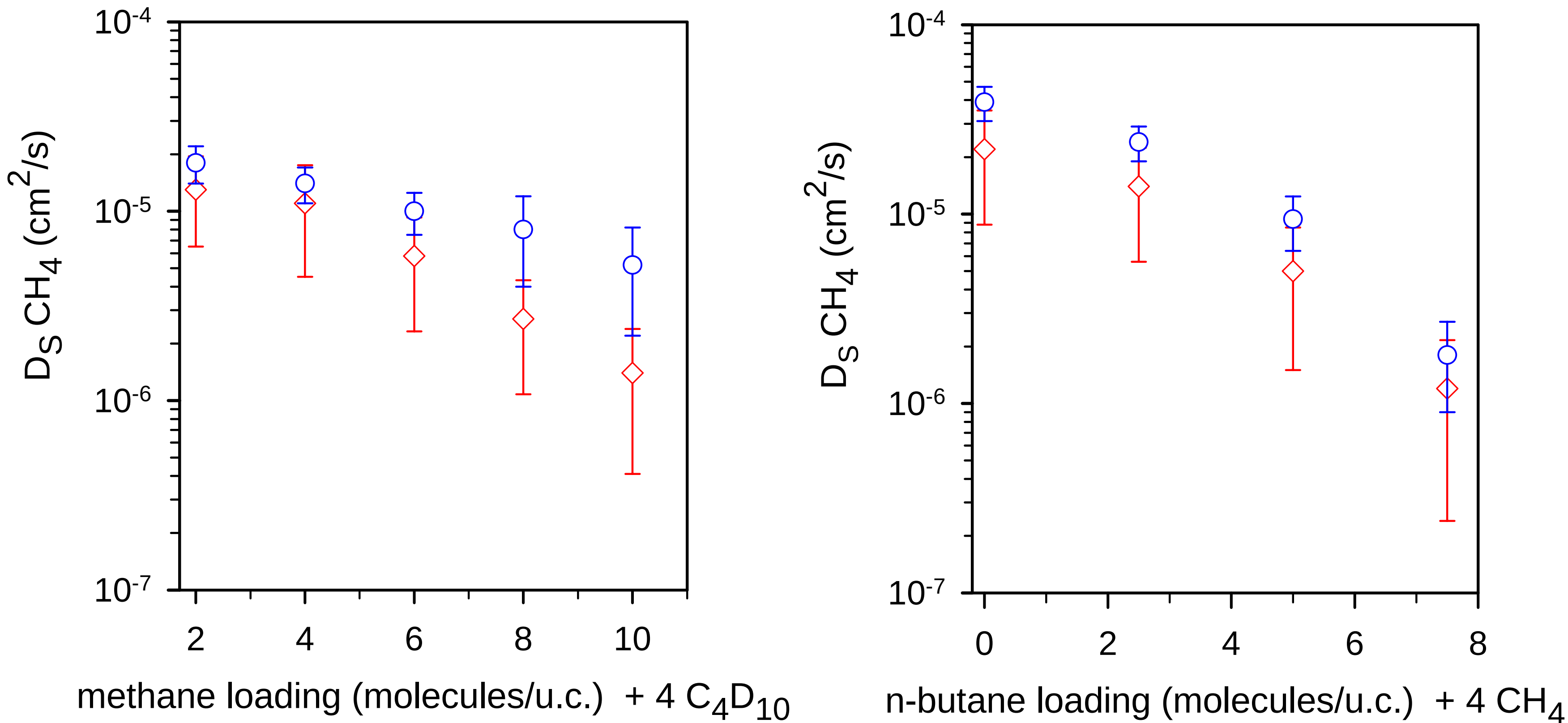

mixtures / silicalite
2CH4 +4C4D10 /u.c. (T=200 K)
HWHM (meV)
0.000
0.001
0.002
0.003
0.004
0.005
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Q2 (Å-2)
+ : QENS
o : MD
- - - : CE model
: new distri.



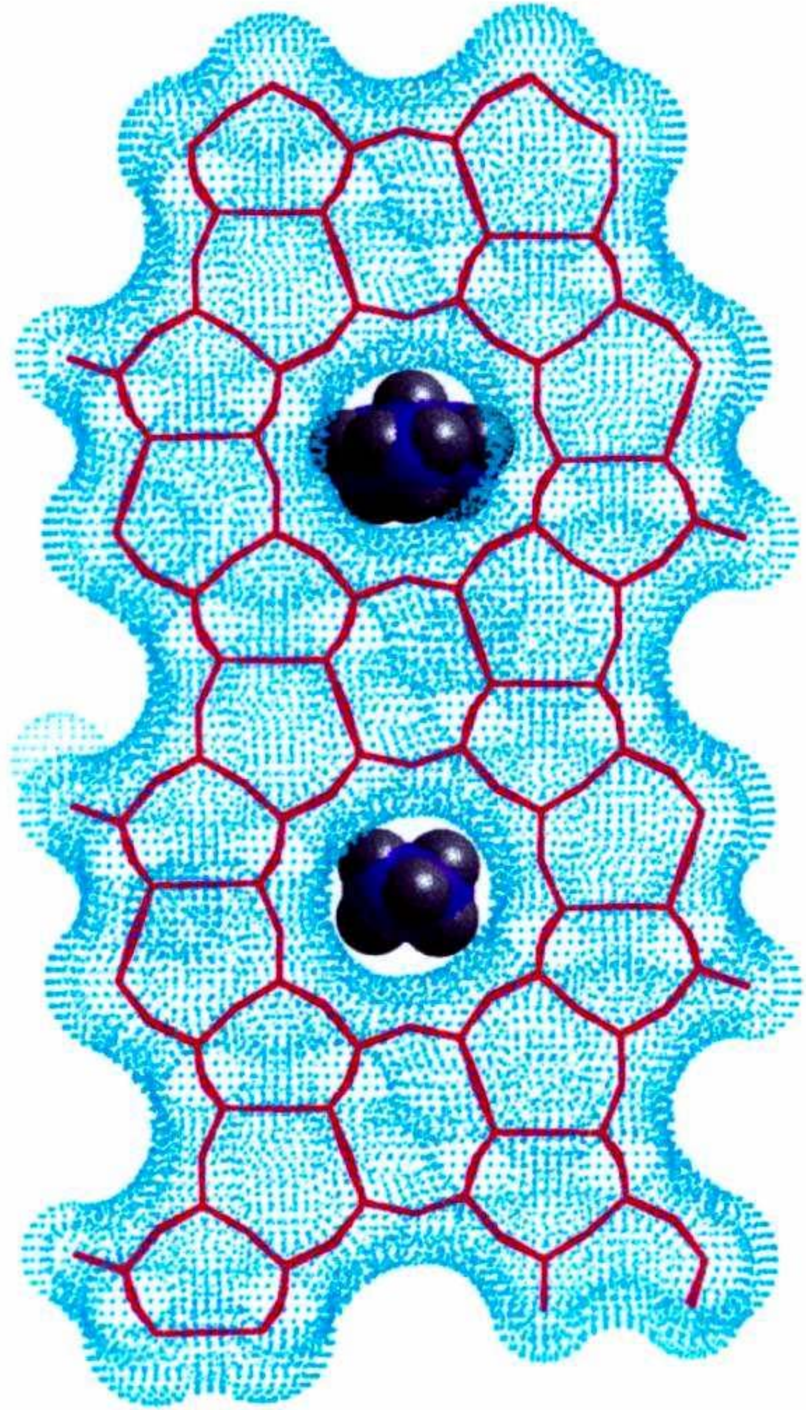
ZSM-5 (λ = 9 Å)
Intensity (a.u.)
20
15
10
5
0.3
0.6
0.9
1.2
Q (Å^{-1})

n-butane – methane mixtures (200 K)

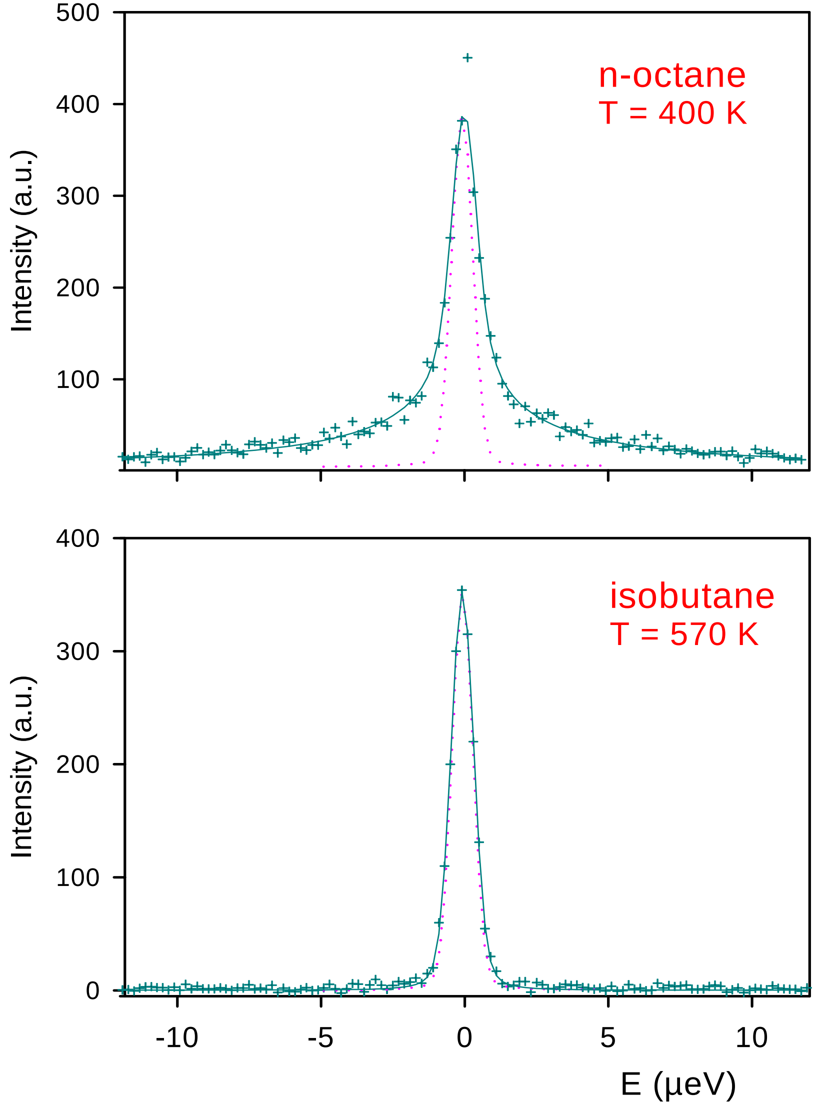
◊ : QENS
o : MD



J. Phys. Chem. B 104 (2000) 5541

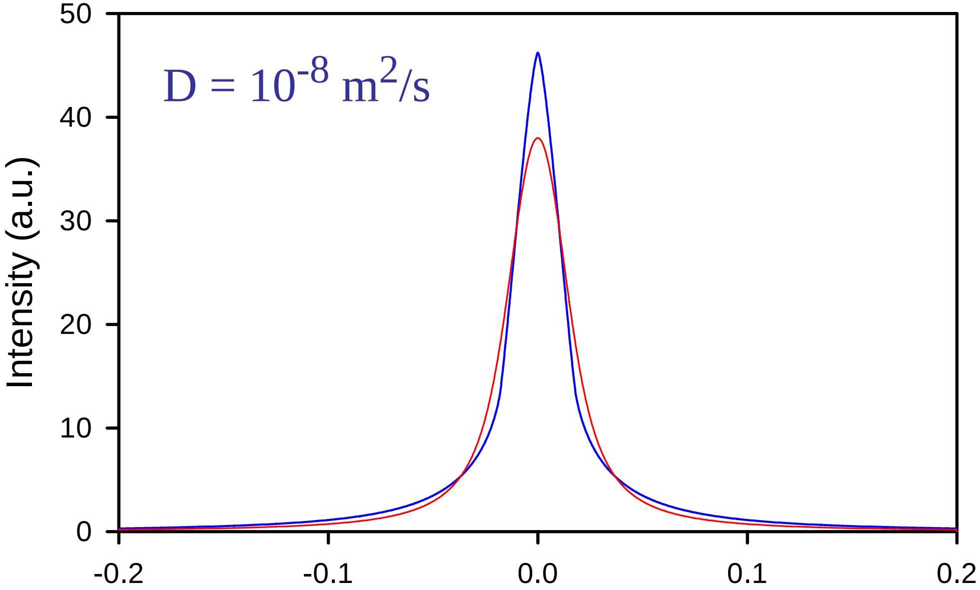


Q = 0.87 Å^{-1}



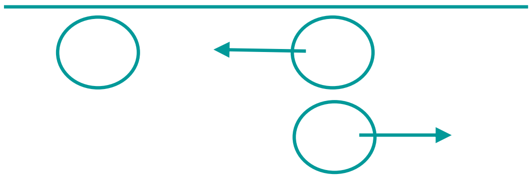
J. Phys. Chem. B 103 (1999) 1096

Diffusion in 1D channel systems

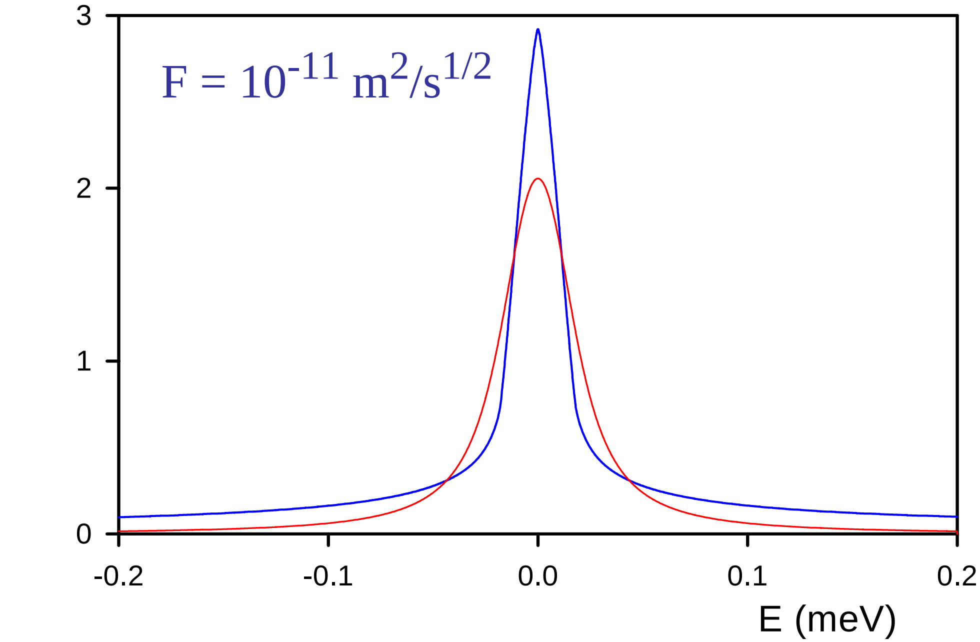


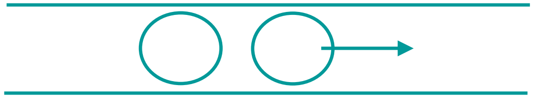
Resolution: FWHM: 18 μeV

Q = 0.3 Å^{-1}



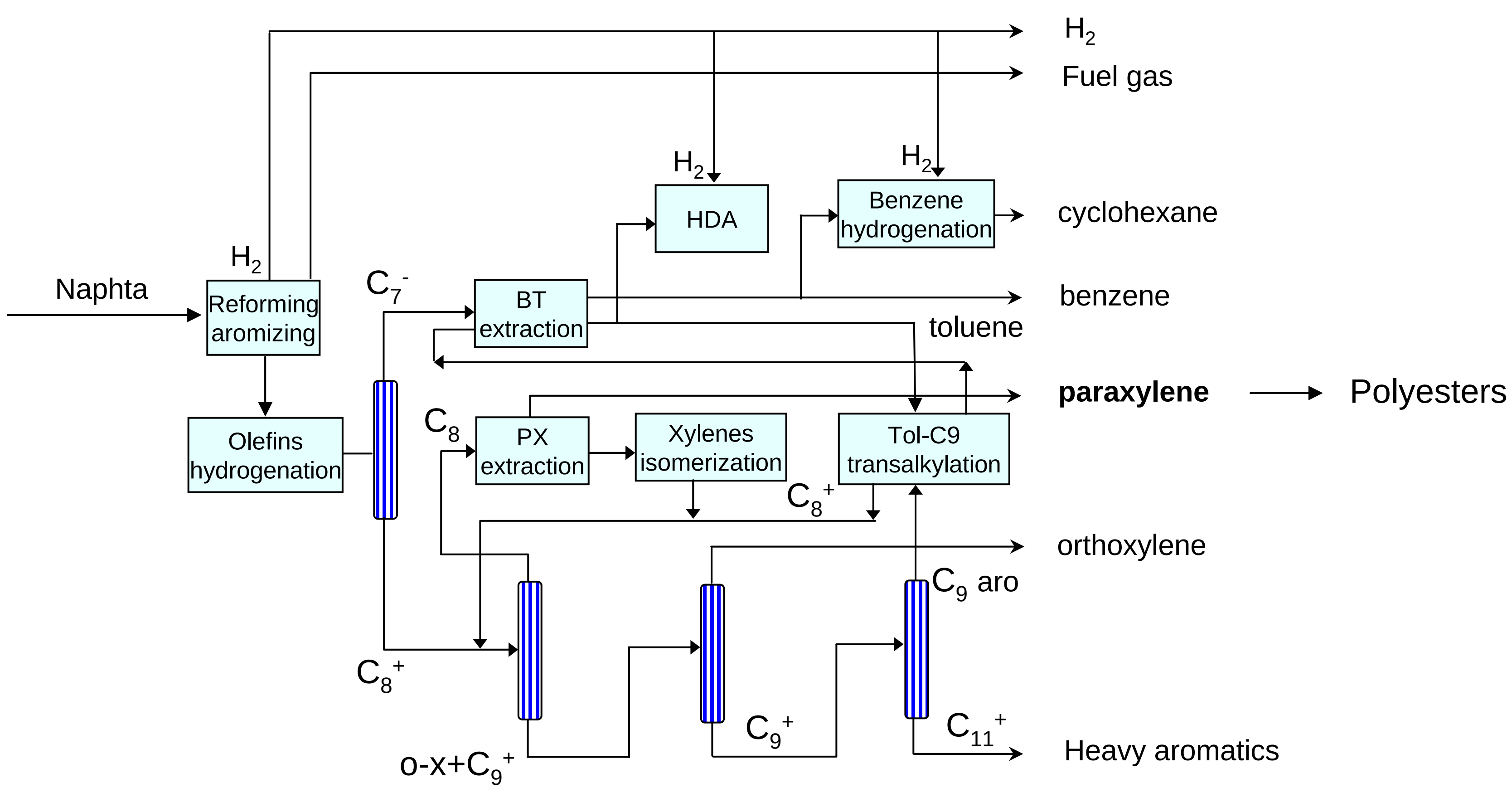
CH_4 / $AlPO_4$-5



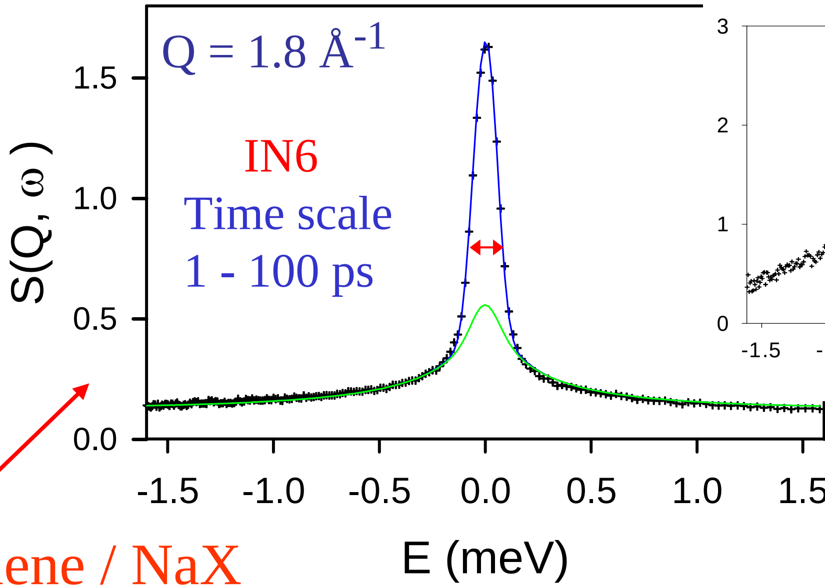


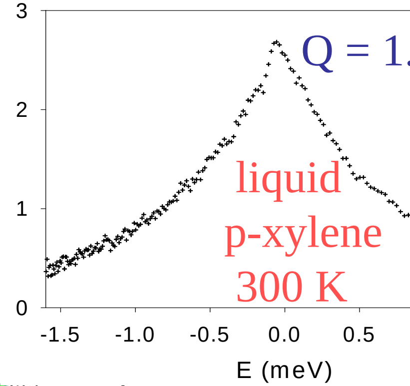
CH_4 / ZSM-48

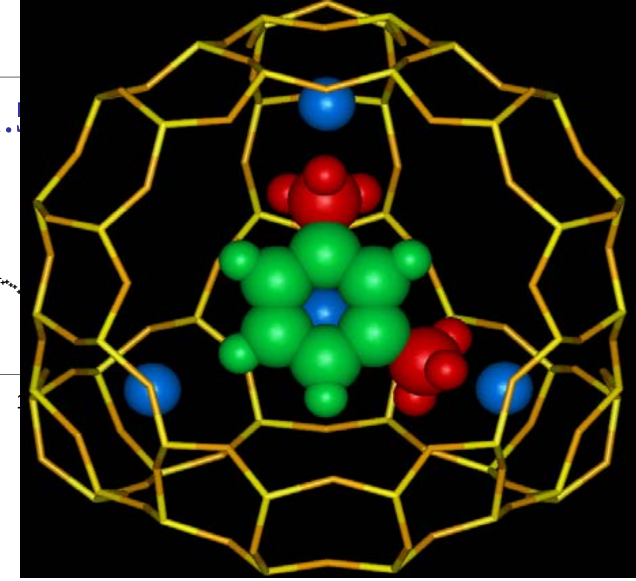
Aromatics



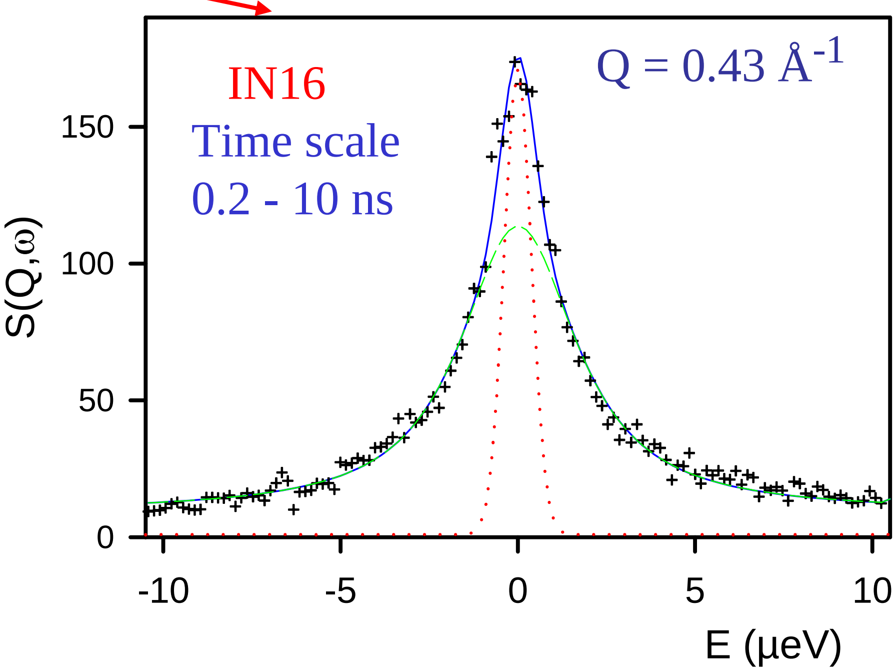
H2
Fuel gas
H2
H2
HDA
Benzene hydrogenation
cyclohexane
H2
Naphta
Reforming aromizing
C7-
BT extraction
benzene
toluene
paraxylene
Polyesters
Olefins hydrogenation
C8
PX extraction
Xylenes isomerization
Tol-C9 transalkylation
C8+
orthoxylene
C9 aro
C8+
C9+
C11+
Heavy aromatics
o-x+C9+

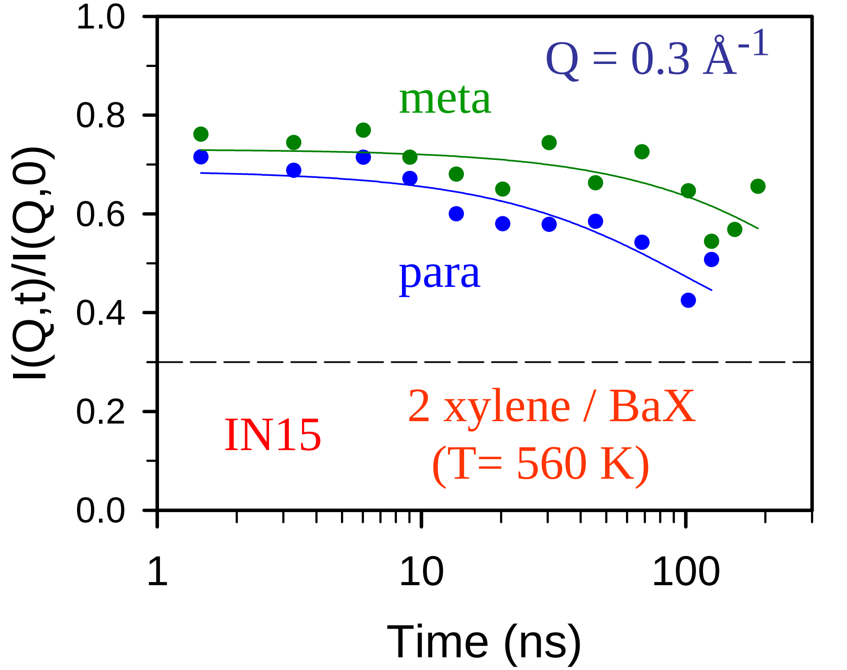




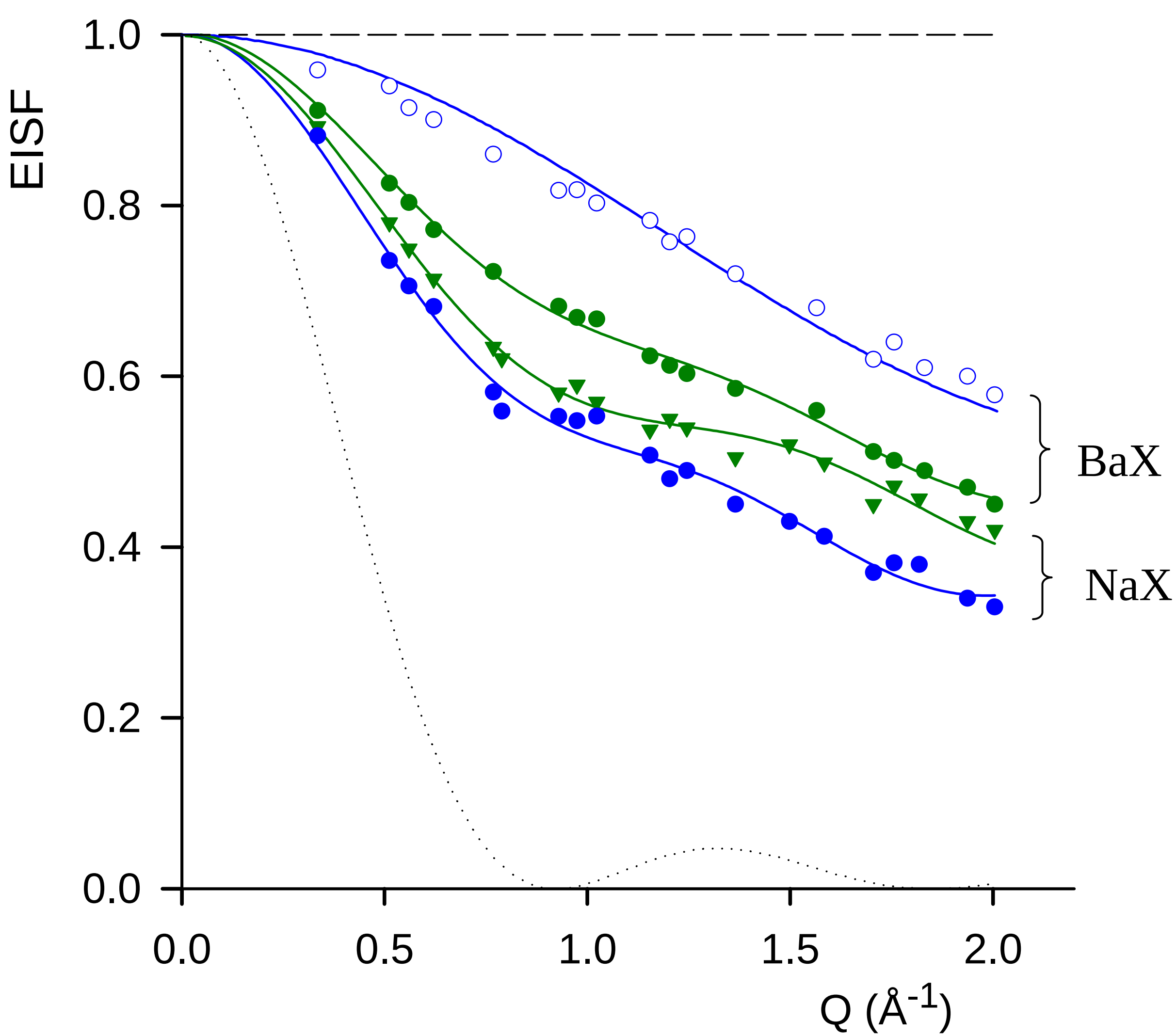


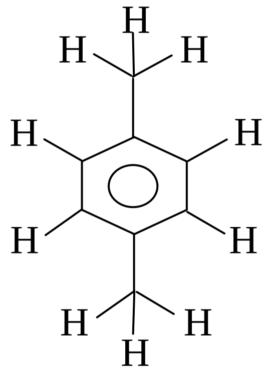
3 p-xylene / NaX
(T = 460 K)



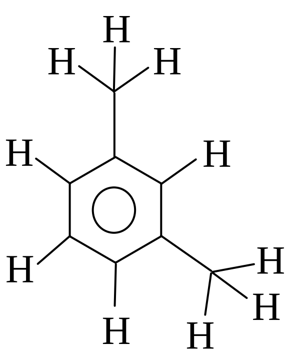


3 molecules / supercage (460 K)

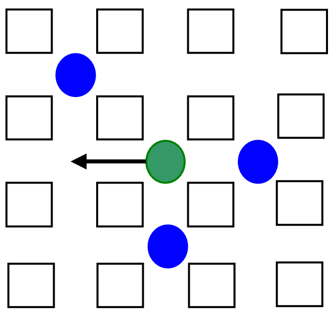


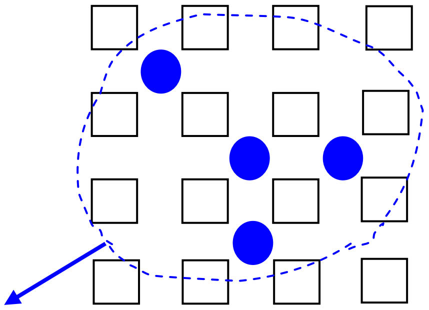


para-xylene



meta-xylene





$$\frac{\partial G_S(\mathbf{r},t)}{\partial t} = D_S \nabla^2 G_S(\mathbf{r},t)$$

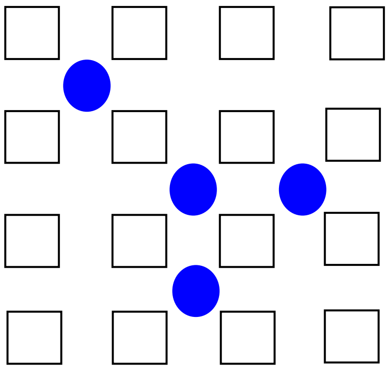
$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = D_t \nabla^2 \rho(\mathbf{r},t)$$

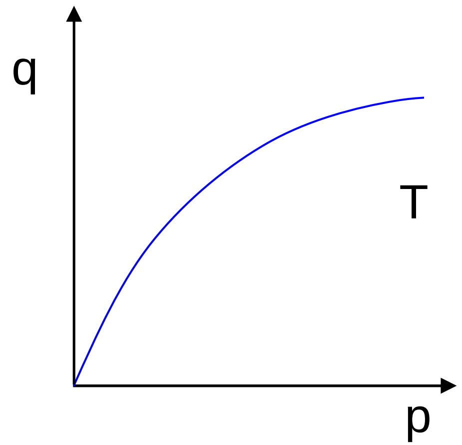
$$\mathbf{J} = -D_t \frac{\partial q}{\partial x} = -Bq \frac{\partial \mu}{\partial x}$$

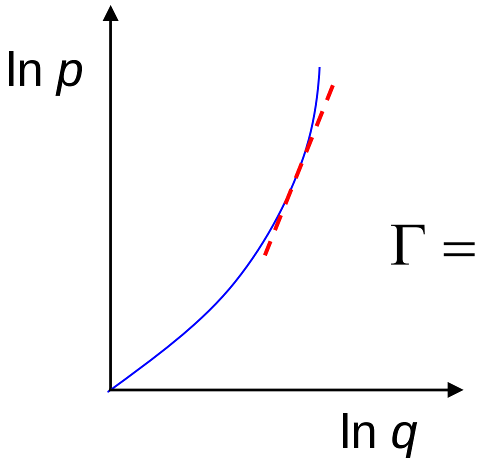
$$\mu = \mu^0 + RT \ln p$$

$$D_t = BRT \frac{d \ln p}{d \ln q} = D_0 \frac{d \ln p}{d \ln q}$$

Thermodynamic factor





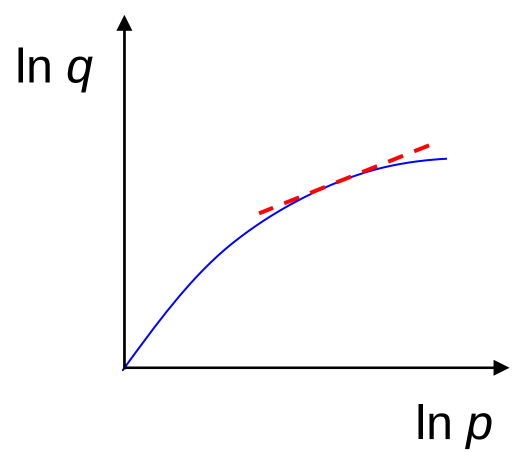


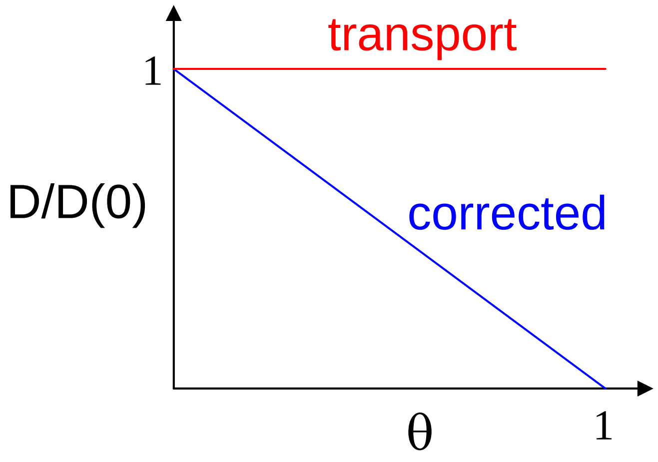
$$\Gamma = \frac{d \ln p}{d \ln q}$$

$$S(Q)_{Q \to 0} = \frac{\overline{\left(N - \overline{N}\right)^2}}{\overline{N}} = \rho k_B T \kappa_T$$

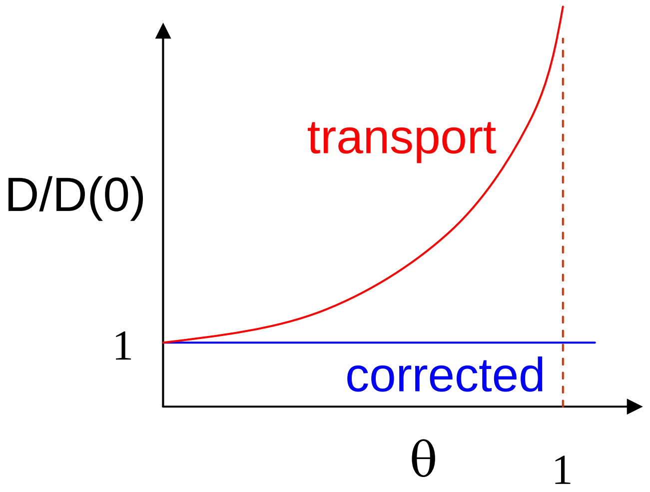
$$\kappa_T = \frac{1}{\rho k_B T} \left(\frac{d \ln q}{d \ln p} \right)$$

$$S(Q)_{Q \to 0} = \frac{d \ln q}{d \ln p} = \frac{1}{\Gamma}$$





Lattice gas model



Darken approximation

at low q : $D_0 = D_t = D_S$

Simulations

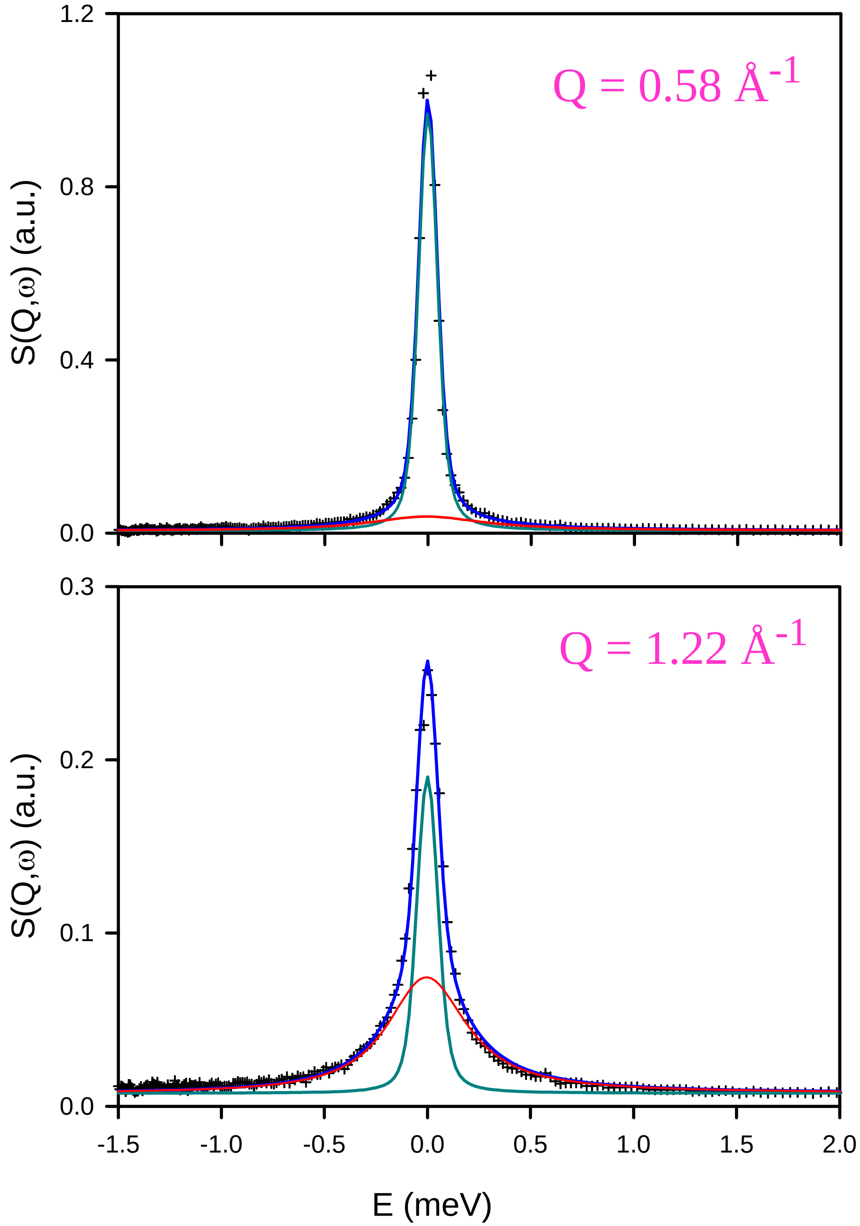
$$D_S = \frac{1}{3}\int_0^{\infty} dt \left\langle \frac{1}{N}\sum_{i=1}^{N} \mathbf{v}_i(t).\mathbf{v}_i(0) \right\rangle = \lim_{t\to\infty} \frac{d}{dt}\frac{1}{6}\left\langle \frac{1}{N}\sum_{i=1}^{N}\left[\mathbf{r}_i(t)-\mathbf{r}_i(0)\right]^2 \right\rangle$$

$$D_0 = \frac{1}{3N}\int_0^{\infty} dt \sum_{i=1}^{N}\sum_{j=1}^{N} < \mathbf{v}_i(t).\mathbf{v}_j(0) > = D_S + \frac{1}{3N}\int_0^{\infty} dt \sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N} < \mathbf{v}_i(t).\mathbf{v}_j(0) >$$

D_2 / NaX

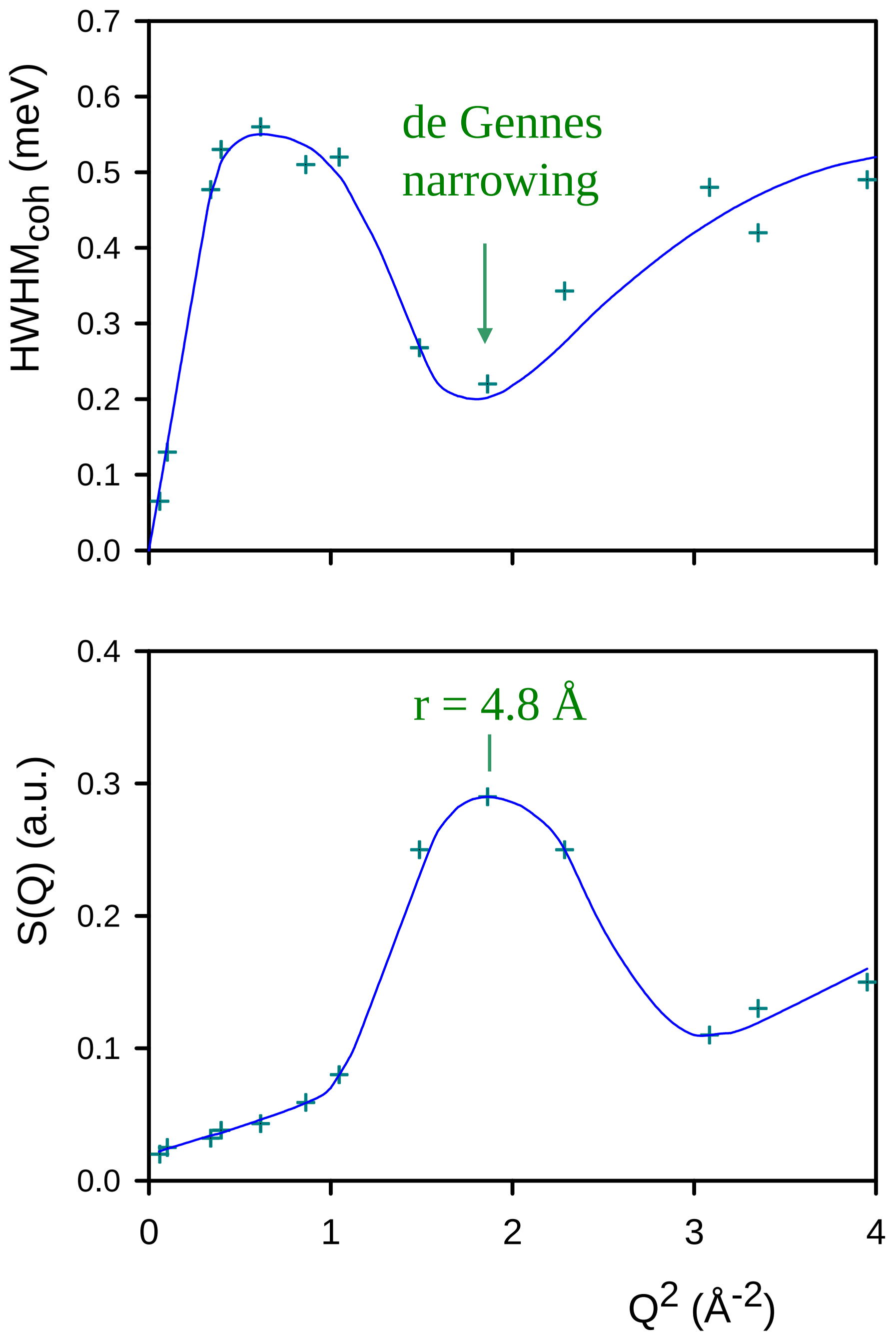
4 molecules / supercage

(100 K)



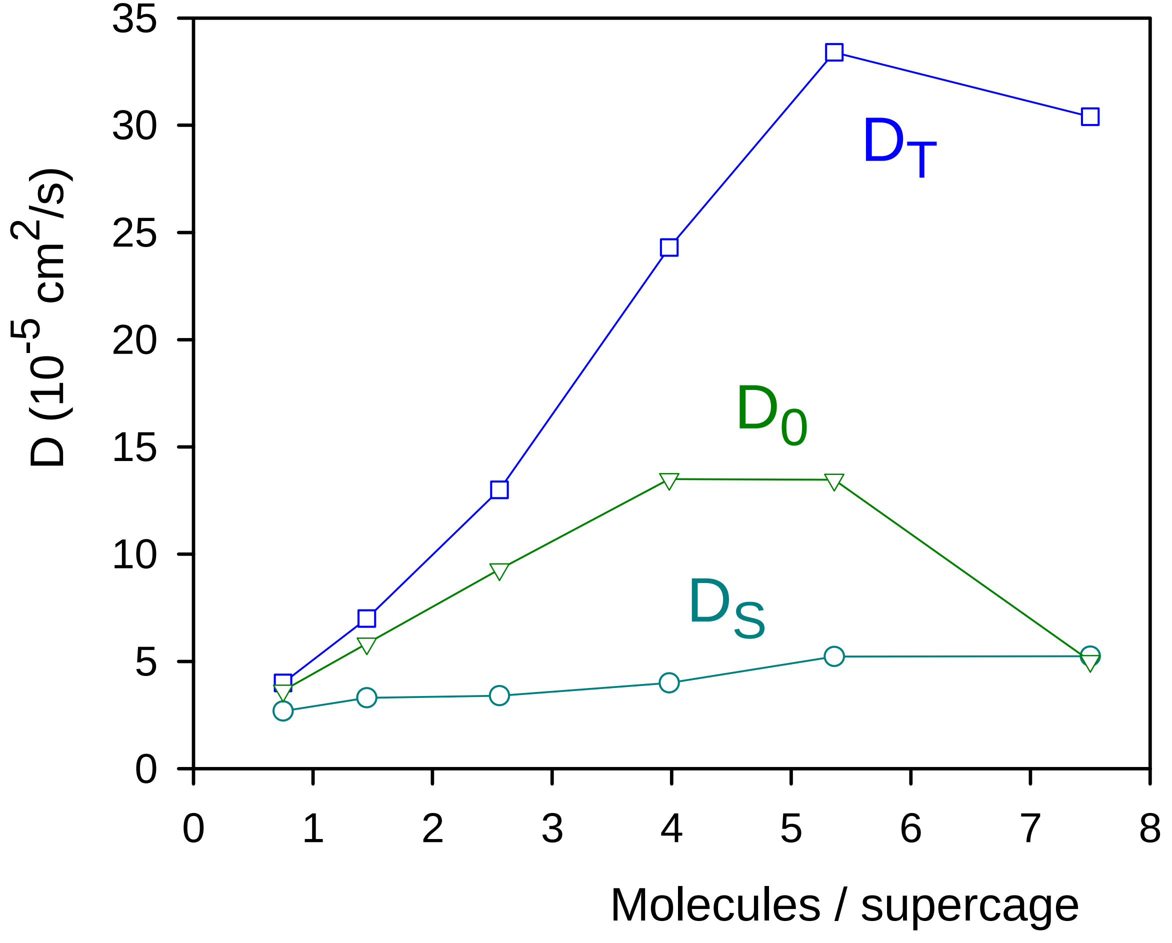
$$\frac{d^2\sigma}{d\Omega\, dE} \;\alpha\; \sigma_{inc}\, \mathcal{L}_{inc} + \sigma_{coh}\, S(Q)\, \mathcal{L}_{coh}$$

D_2 / NaX



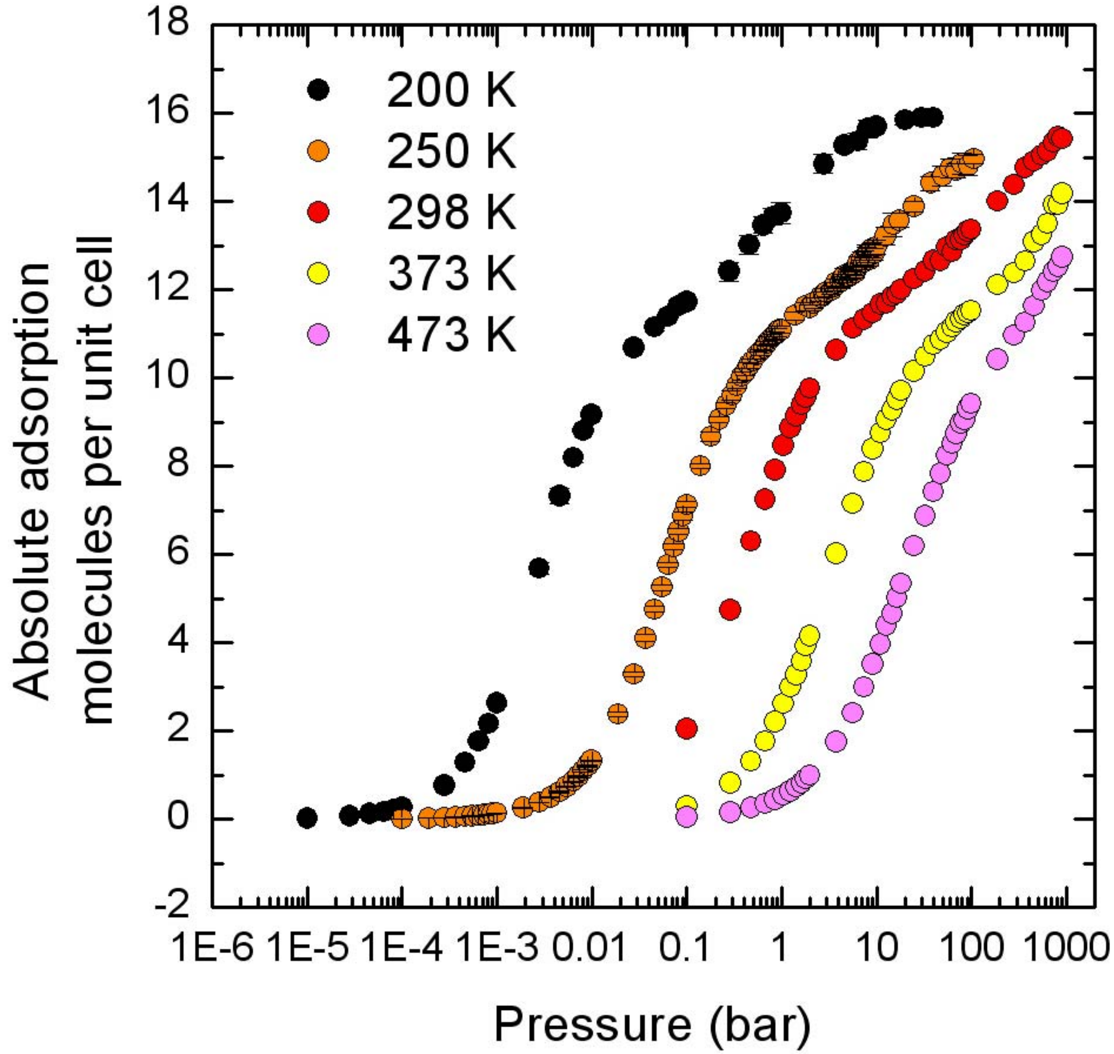
HWHM$_{coh}$ (meV)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
de Gennes
narrowing
S(Q) (a.u.)
0.4
0.3
0.2
0.1
0.0
r = 4.8 Å
0
1
2
3
4
Q^2 ($Å^{-2}$)

D_2 / NaX (100 K)



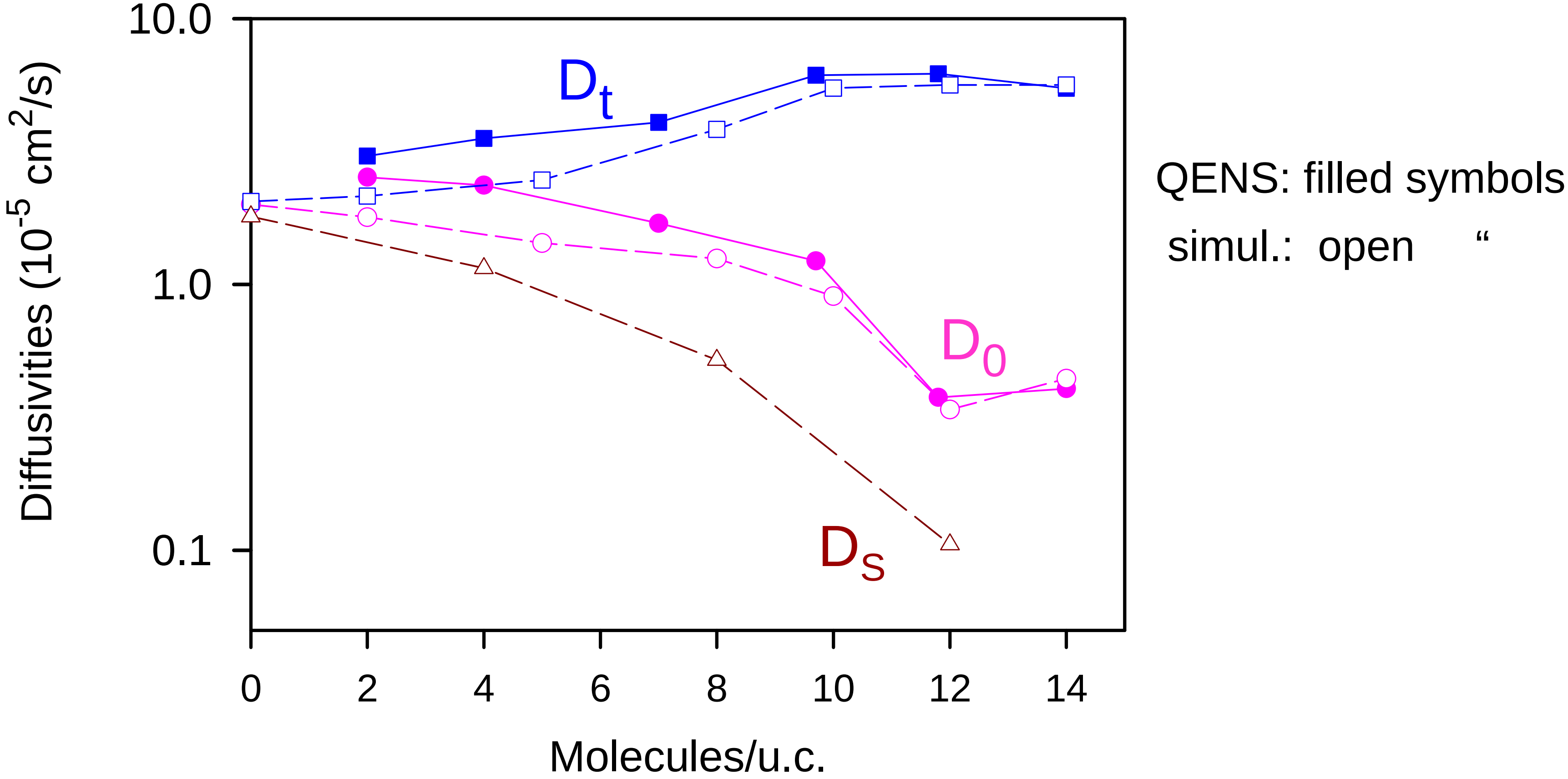
PRL **82** (1999) 4260

CF_4 / silicalite



J. Phys. Chem. B 108 (2004) 10613

CF_4 / silicalite @ 200 K



J. Phys. Chem. B 108 (2004) 10613

Sears, *Can. J. Phys.* *45* (1967) 237

$$\left|\sum_{m=1}^{n} b_{coh}^{m}\; j_0(Qr_m)\right|^2 S(Q)\Lambda_t$$

$$+\sum_{m=1}^{n} {b_{inc}^{m}}^{2}\; {j_0}^{2}(Qr_m)\,\Lambda_s$$

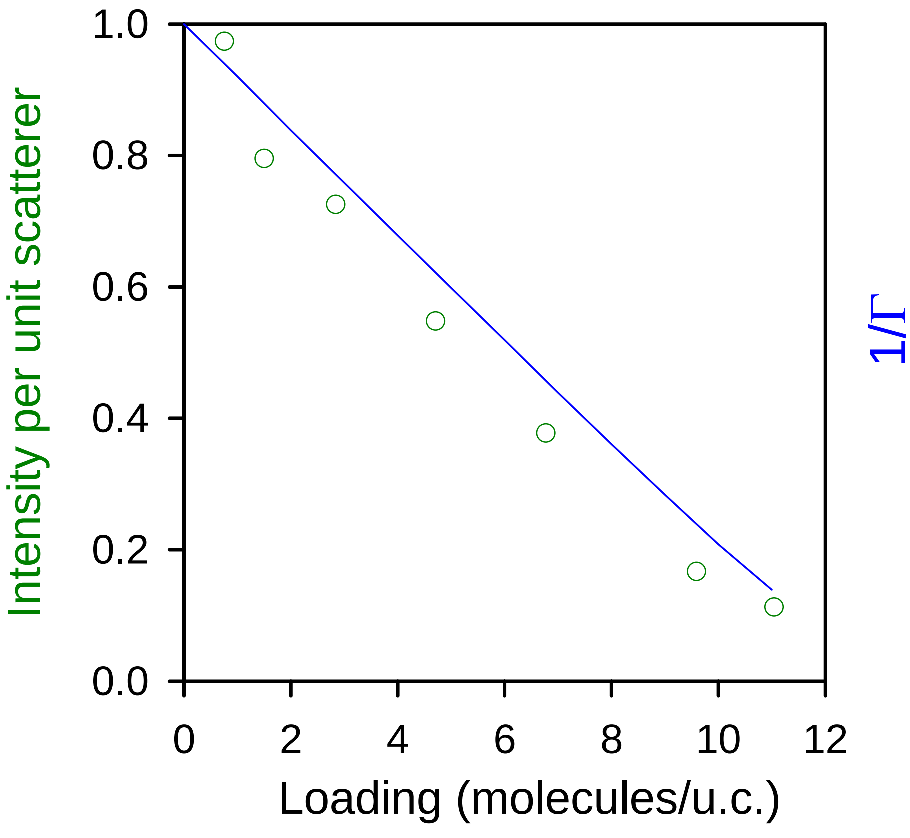
$$+\sum_{\ell=1}^{\infty}(2\ell+1)\sum_{m,m'=1}^{n}\left\{b_{coh}^{m}\; b_{coh}^{m'}+{b_{inc}^{m}}^{2}\;\delta_{mm'}\right\} j_\ell(Q\,r_m)\; j_\ell(Q\,r_{m'})\; P_\ell(\cos\Theta_{m\,m'})\,\Lambda_s\otimes{\Lambda_\ell}^{rot}$$

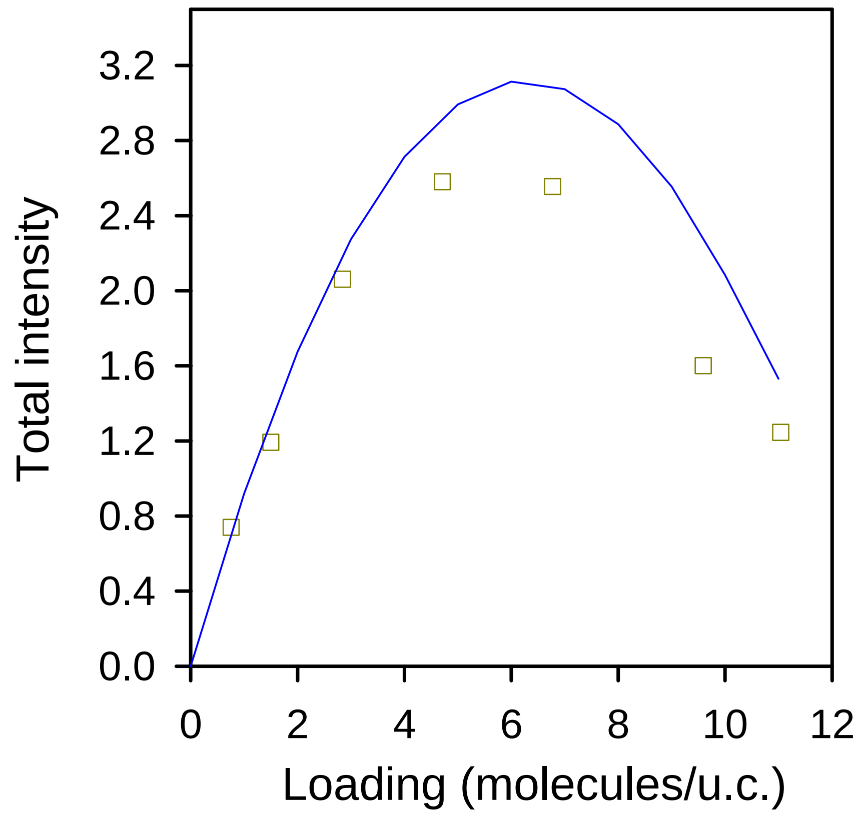
CH_4 : incoherent scattering : $4{b_{inc}^{H}}^{2}\;\Lambda_s\otimes\left[A_0(Q)\,\delta(\omega)+\sum_{\ell=1}^{\infty}A_\ell(Q)\;\Lambda_\ell^{rot}\right]$

$$A_\ell(Q)=(2\ell+1)\; j_\ell^{2}(QR)$$

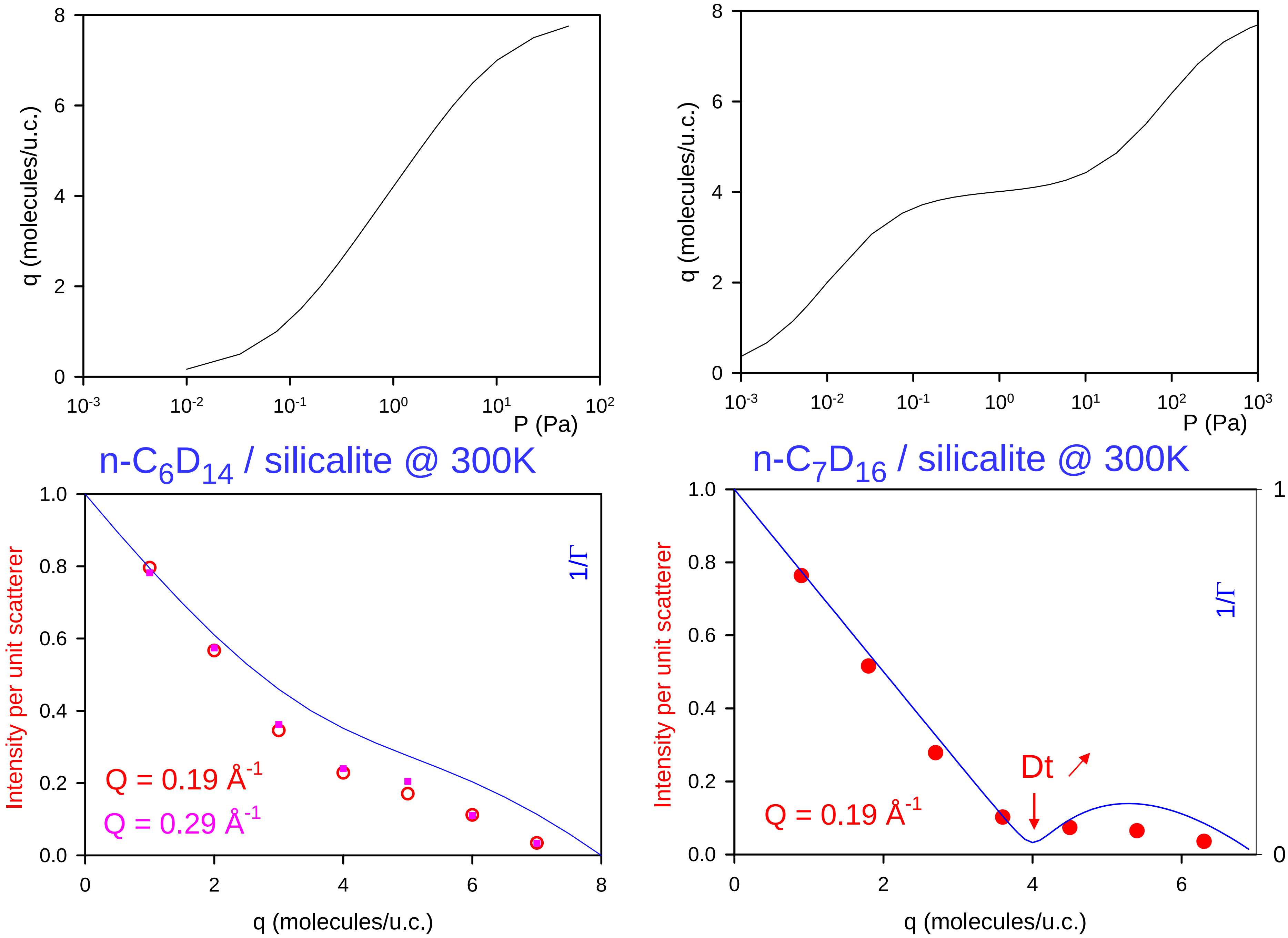
CF_4 : coherent scattering : $\left|\sum_{m=1}^{n} b_{coh}^{m}\; j_0(Qr_m)\right|^2 S(Q)\Lambda_t$

C_2D_6 in silicalite @ 300K



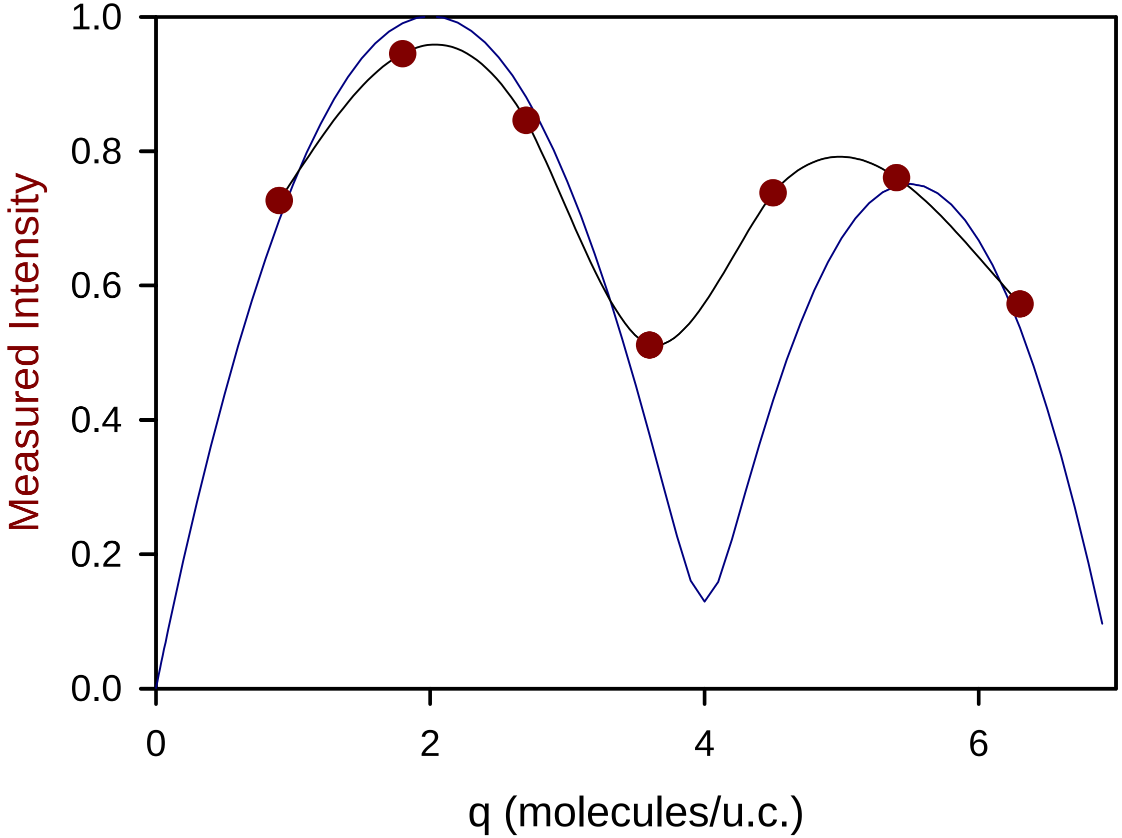


$Q = 0.2$ Å^{-1}



q (molecules/u.c.)
P (Pa)
n-C6D14 / silicalite @ 300K
n-C7D16 / silicalite @ 300K
Intensity per unit scatterer
1/Γ
Q = 0.19 Å-1
Q = 0.29 Å-1
Dt
q (molecules/u.c.)

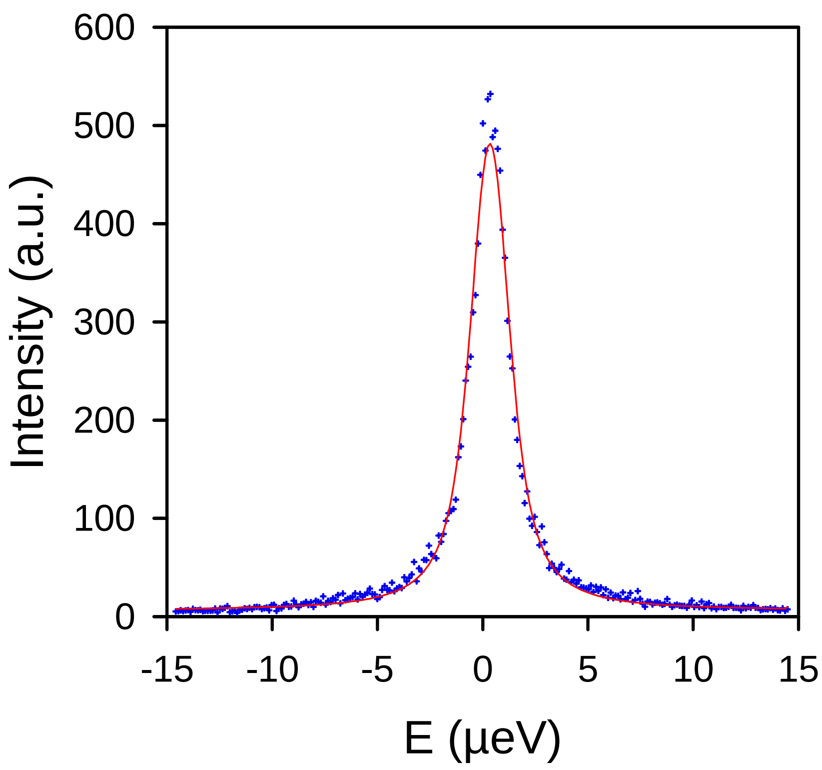
n-C_7D_{16} / silicalite @ 300K



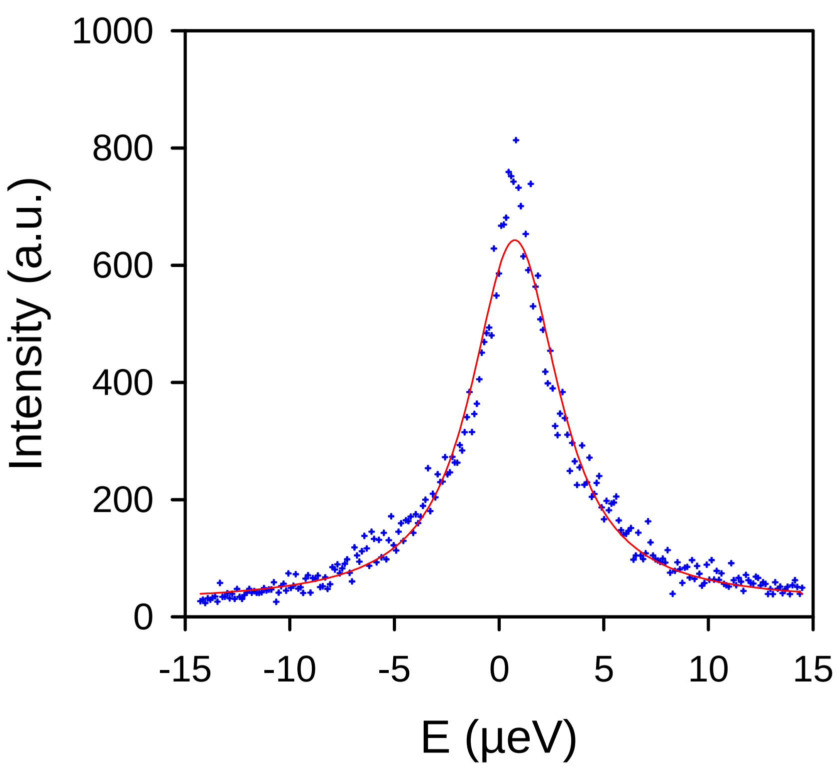
Q = 0.19 Å^{-1}

n-hexane / silicalite @ 300 K ; 4 molecules / u.c.

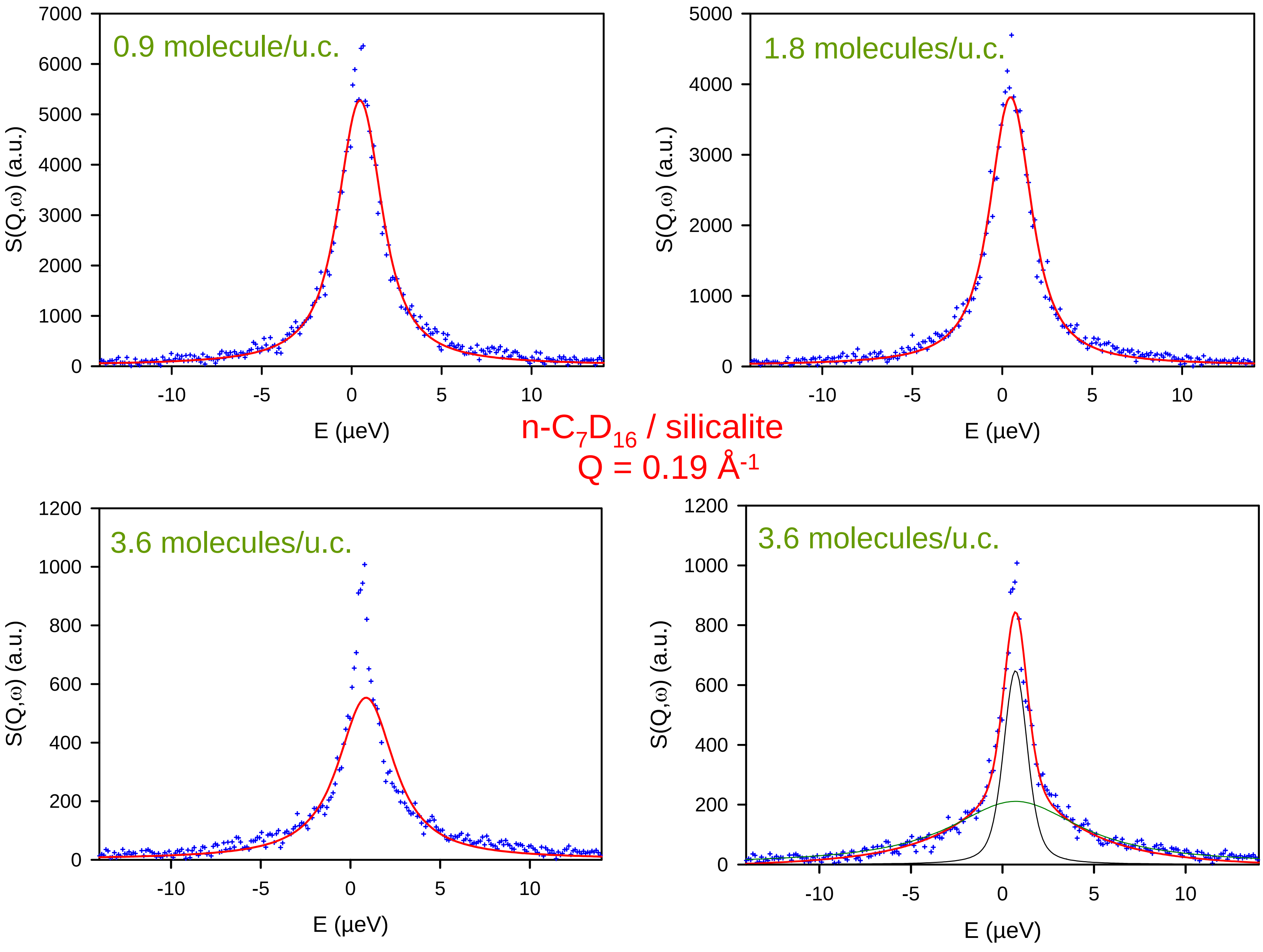
Q = 0.29 Å^{-1} (IN16)

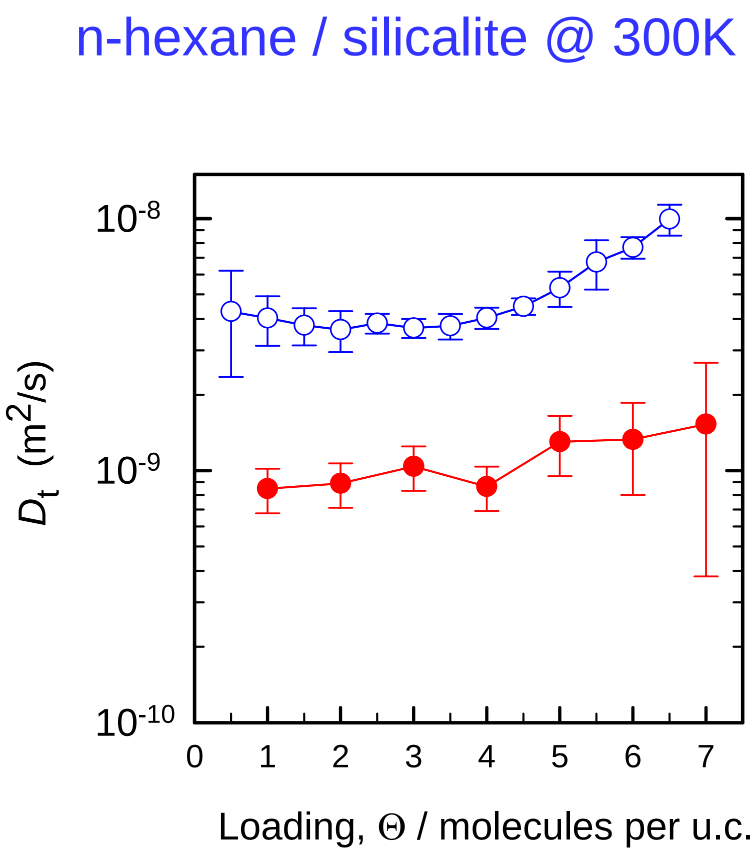


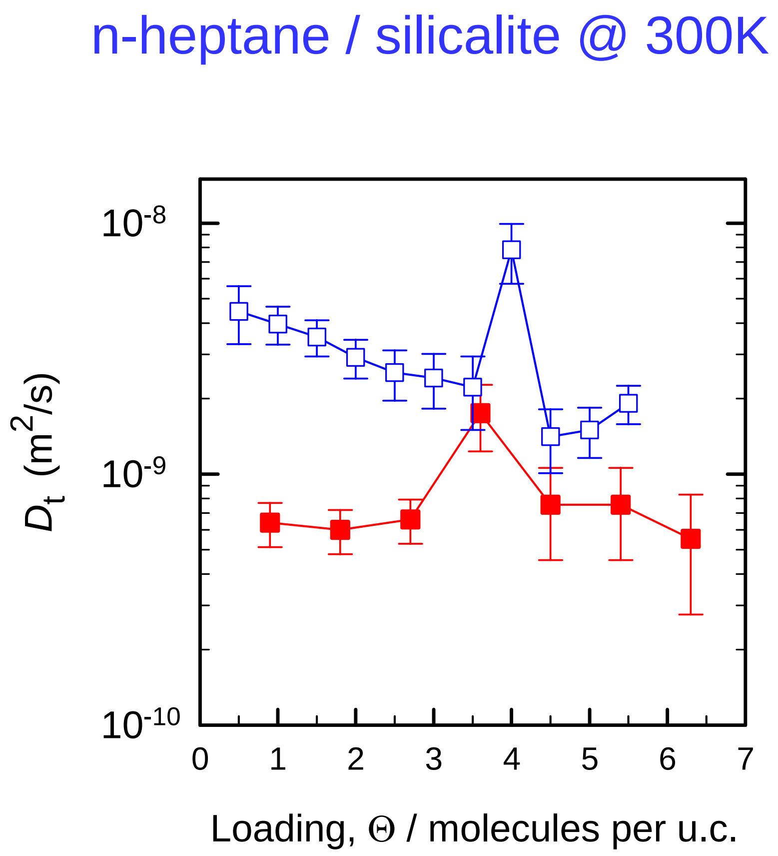
C_6H_{14}

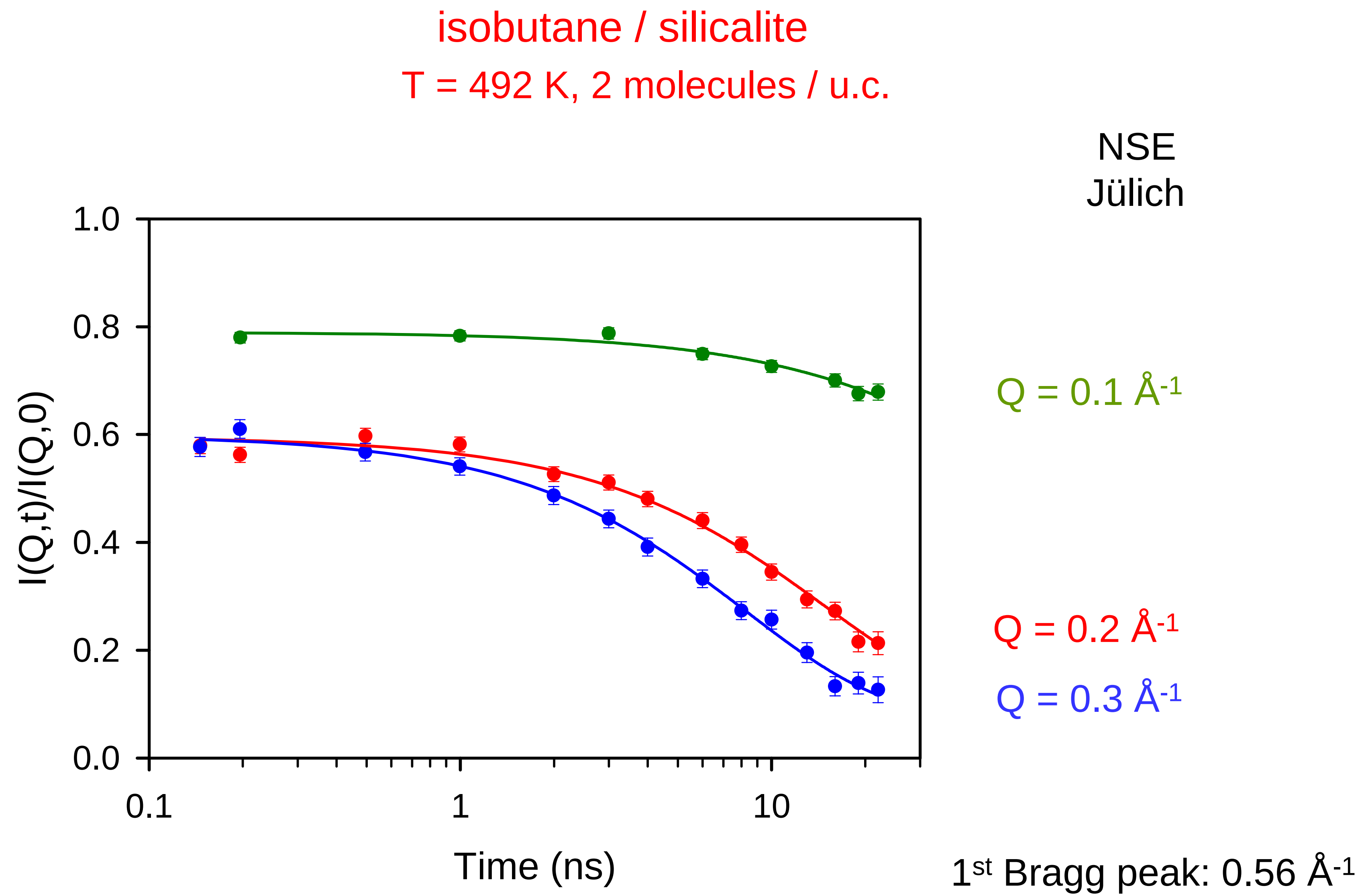


C_6D_{14}

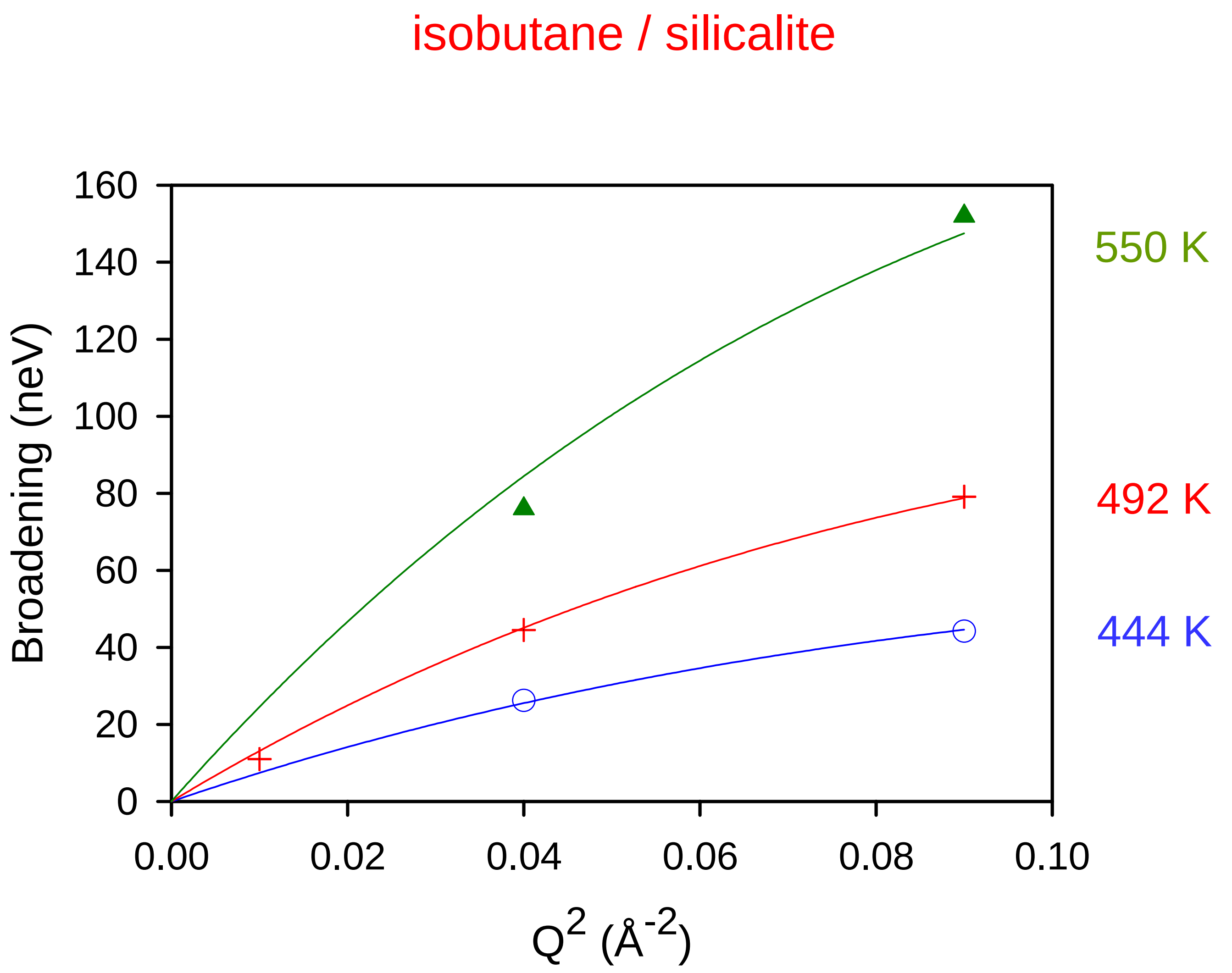

0.9 molecule/u.c.
1.8 molecules/u.c.
3.6 molecules/u.c.
3.6 molecules/u.c.
n-C7D16 / silicalite
Q = 0.19 Å-1
S(Q,ω) (a.u.)
E (μeV)
0
1000
2000
3000
4000
5000
6000
7000
200
400
600
800
1200
-10
-5
5
10


n-hexane / silicalite @ 300K
D_t (m^2/s)
10^{-8}
10^{-9}
10^{-10}
0
1
2
3
4
5
6
7
Loading, Θ / molecules per u.c.


n-heptane / silicalite @ 300K
D_t (m^2/s)
10^{-8}
10^{-9}
10^{-10}
0
1
2
3
4
5
6
7
Loading, Θ / molecules per u.c.

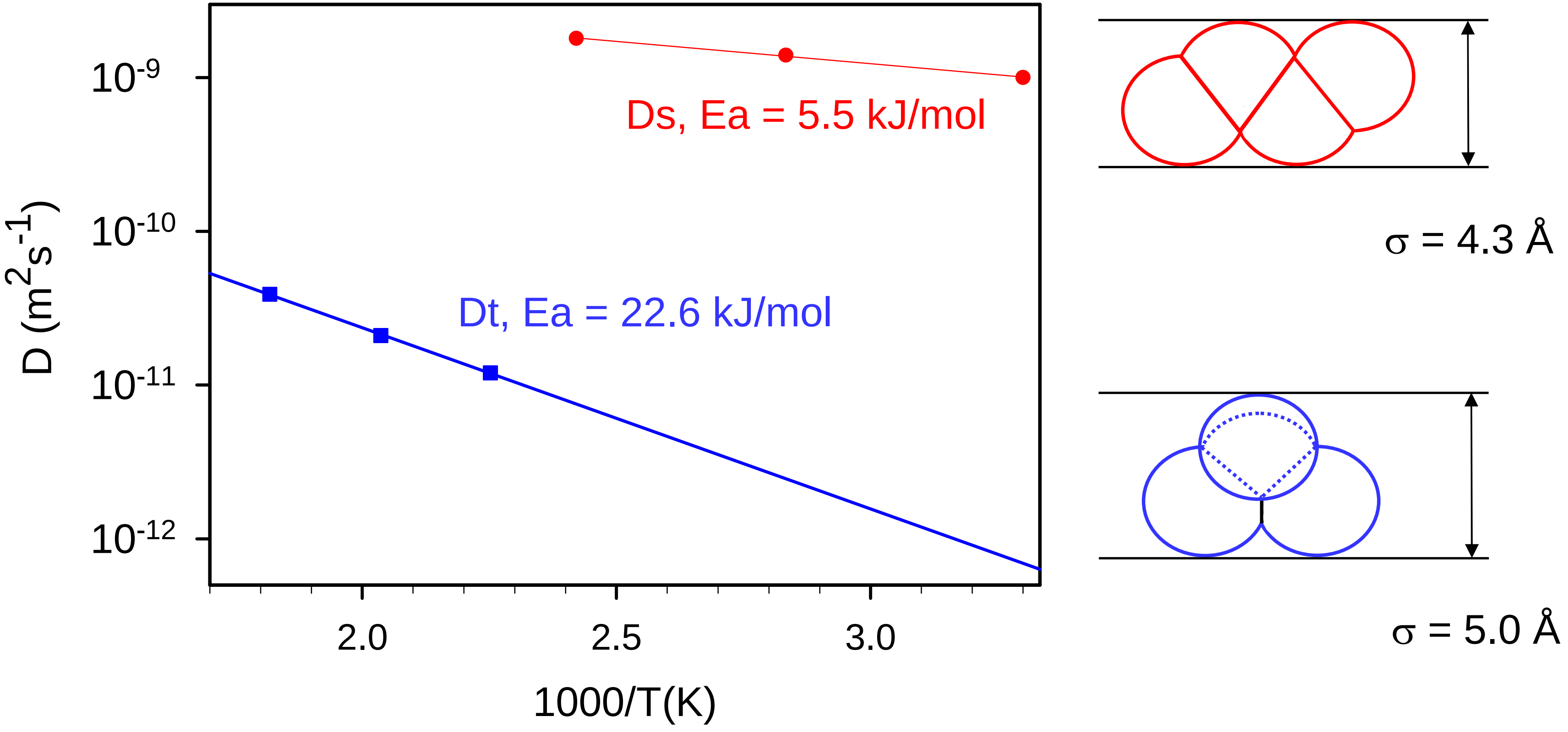


isobutane / silicalite
T = 492 K, 2 molecules / u.c.
NSE
Jülich
1.0
0.8
0.6
0.4
0.2
0.0
I(Q,t)/I(Q,0)
0.1
1
10
Time (ns)
Q = 0.1 Å-1
Q = 0.2 Å-1
Q = 0.3 Å-1
1st Bragg peak: 0.56 Å-1

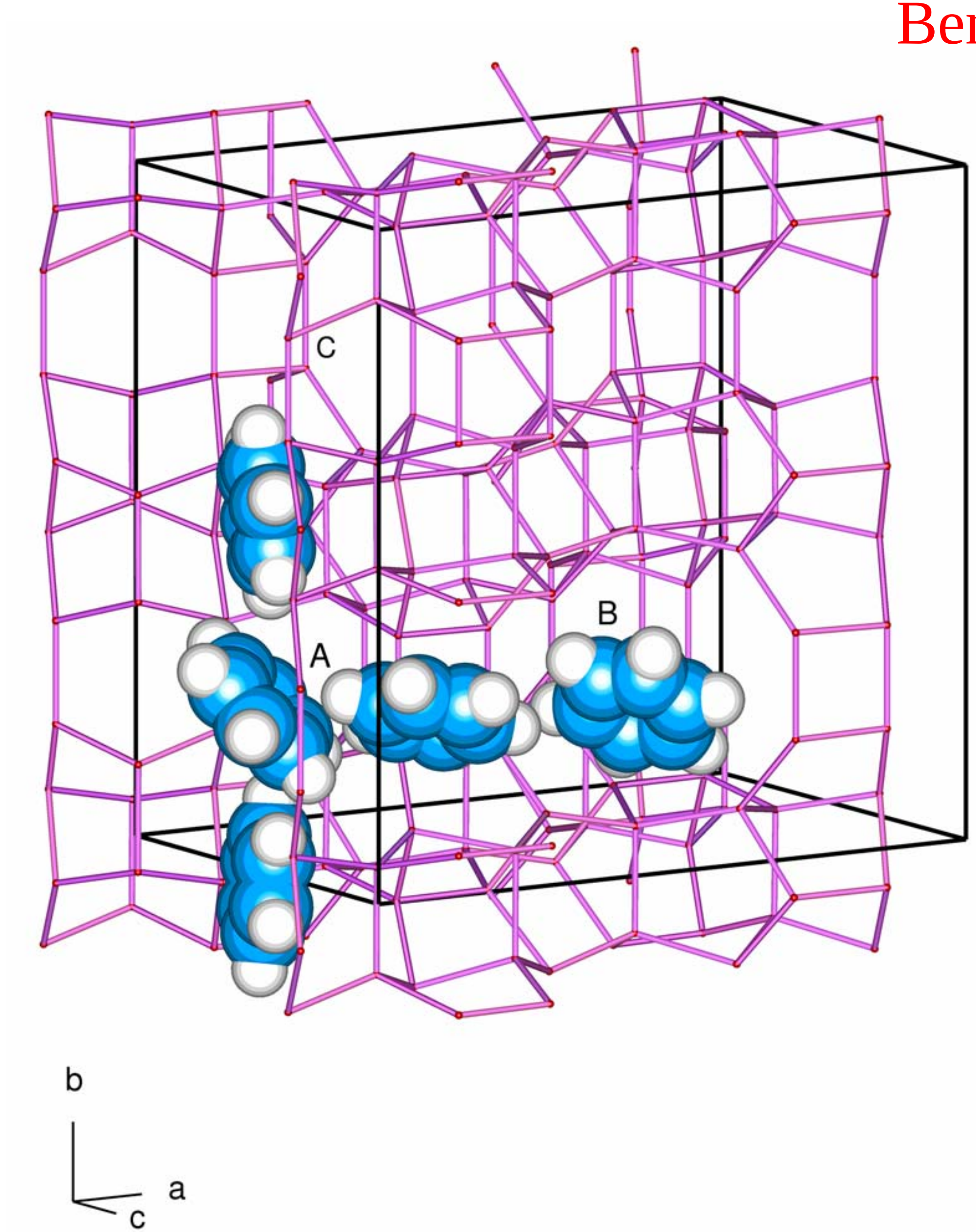


isobutane / silicalite
Broadening (neV)
160
140
120
100
80
60
40
20
0
0.00
0.02
0.04
0.06
0.08
0.10
Q2 (Å-2)
550 K
492 K
444 K

C4 / silicalite



Benzene / ZSM-5 (300 K)



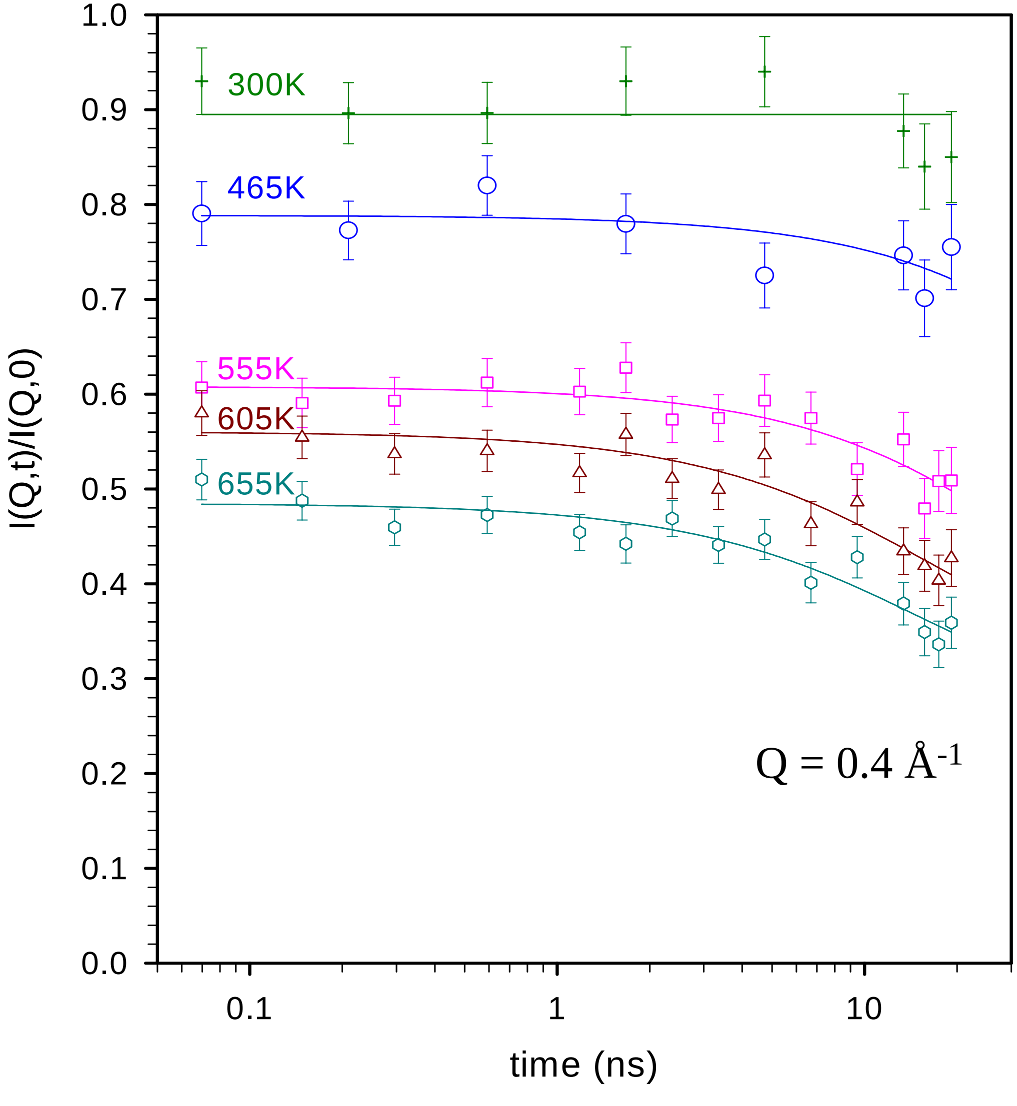
I: 3.77

Z: 2.6

S: 1.18

7.55 molecules/u.c.

J. Phys. Chem. B **104** (2000) 2878

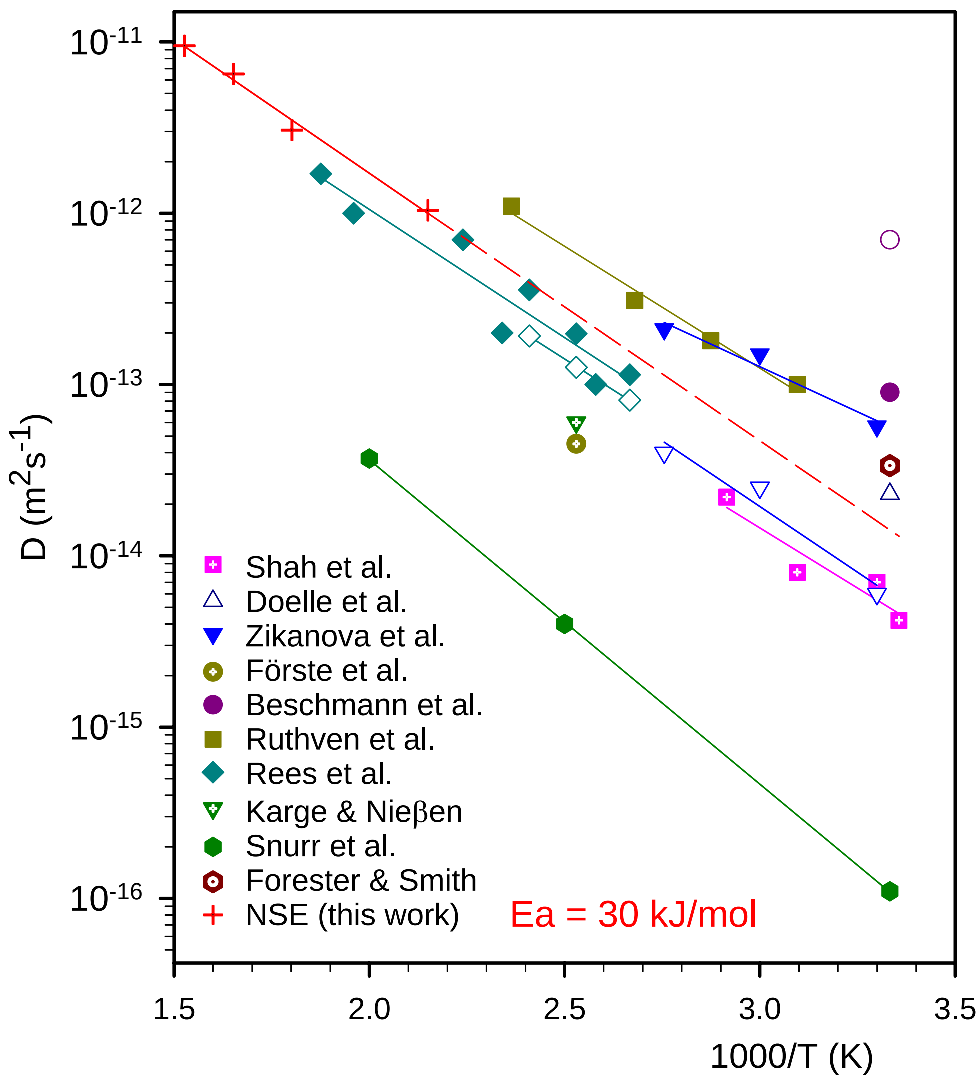


C_6D_6 / ZSM-5

(3 molecules/u.c.)

IN11
ILL

Benzene / MFI

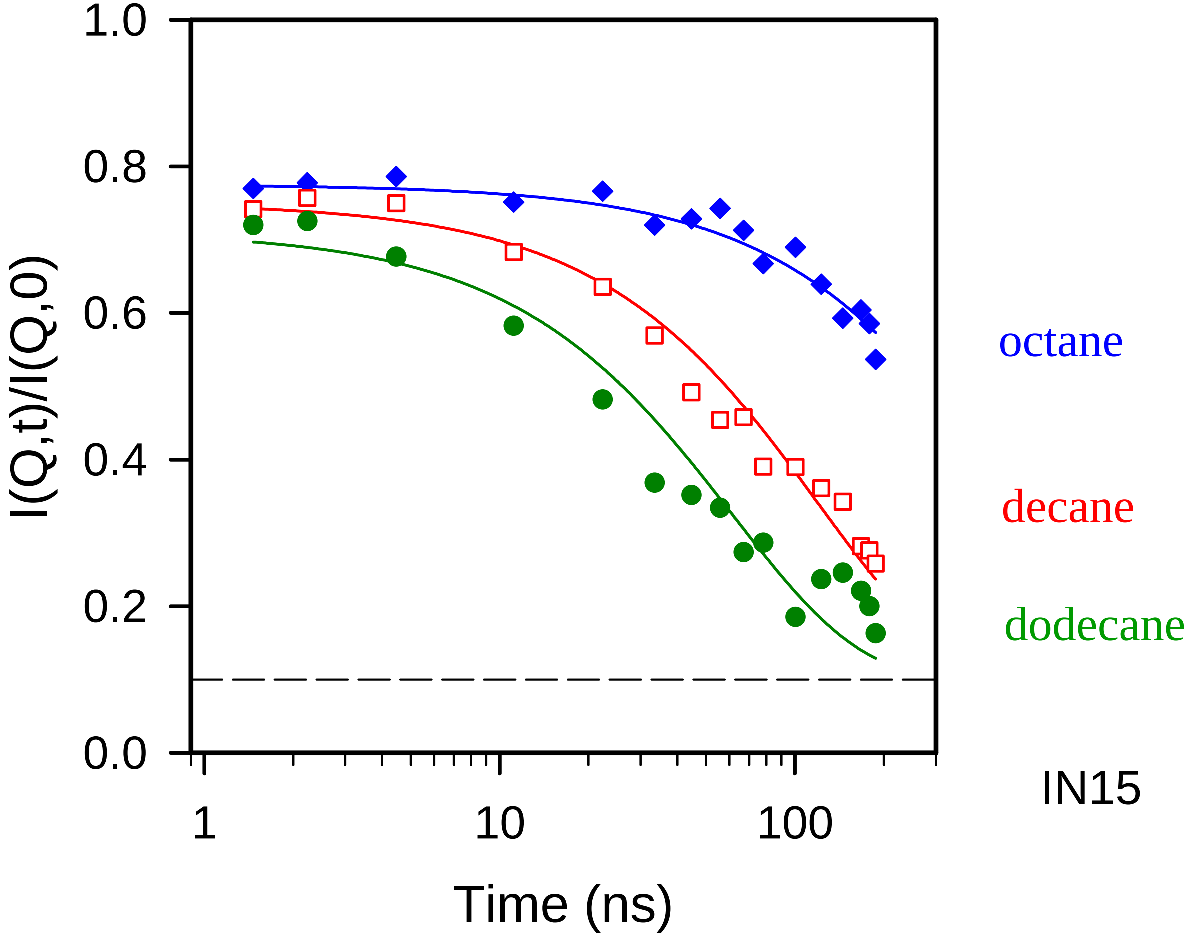


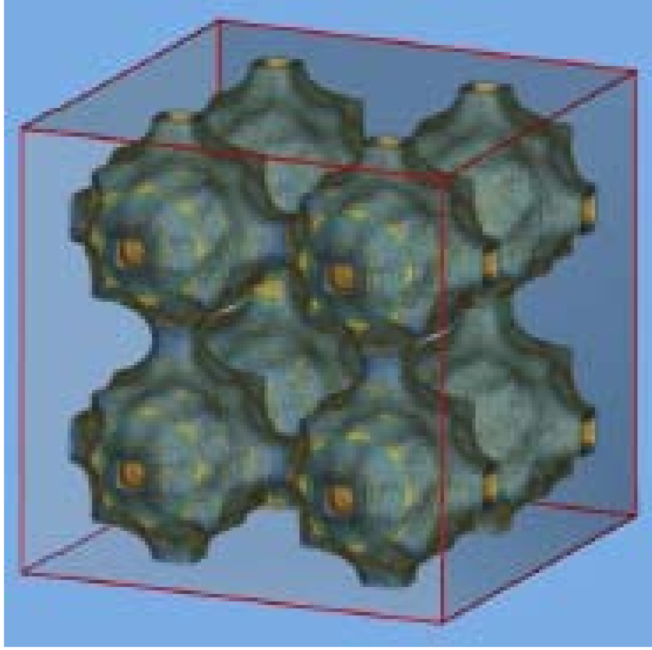
silicalite (●, ◆, ▼)
ZSM-5 (○, ◇, ▽)

J. Phys. Chem. B 104 (2000) 7130

n-alkanes in NaCaA (5A)

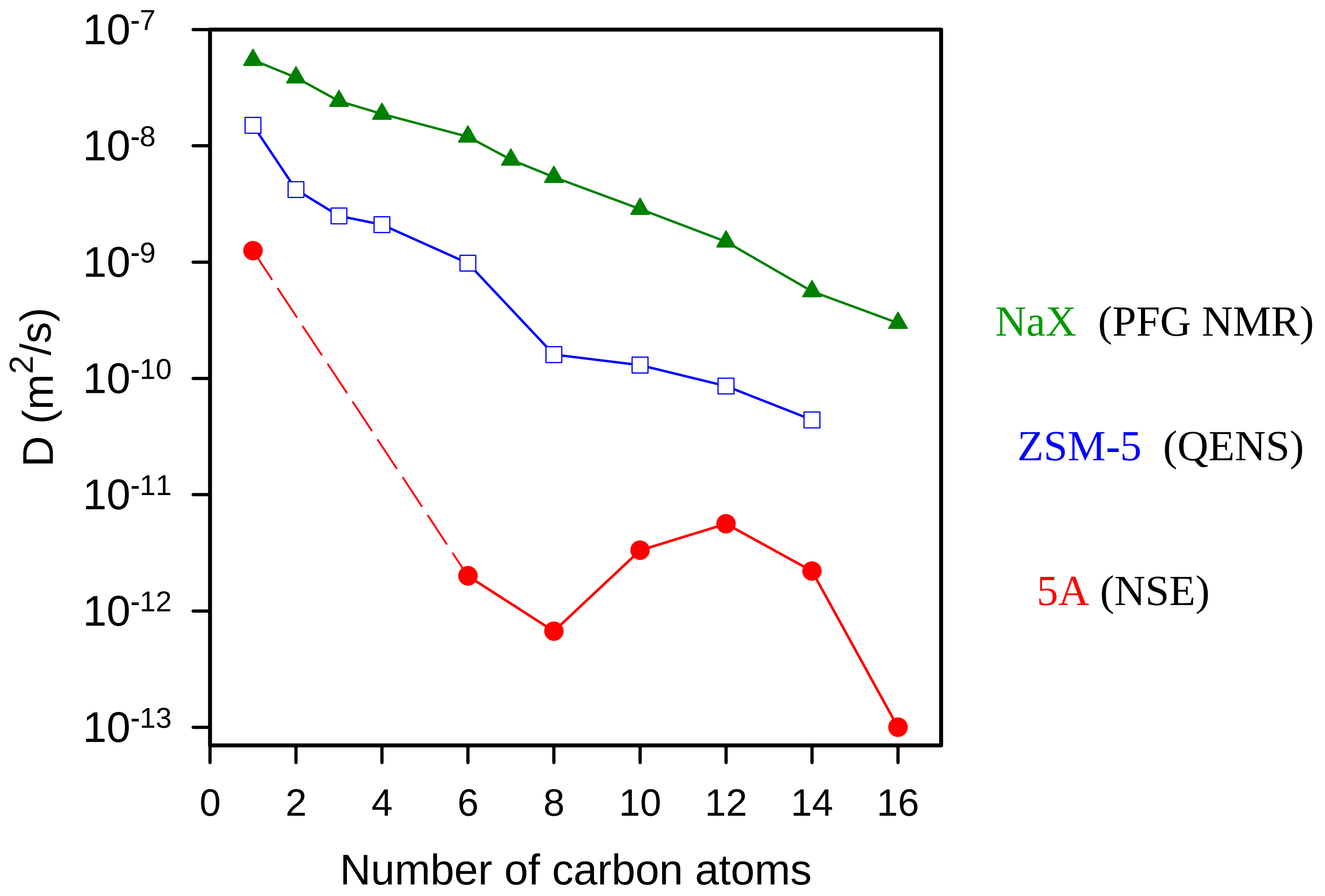
(T = 475 K, Q = 0.2 Å^{-1})

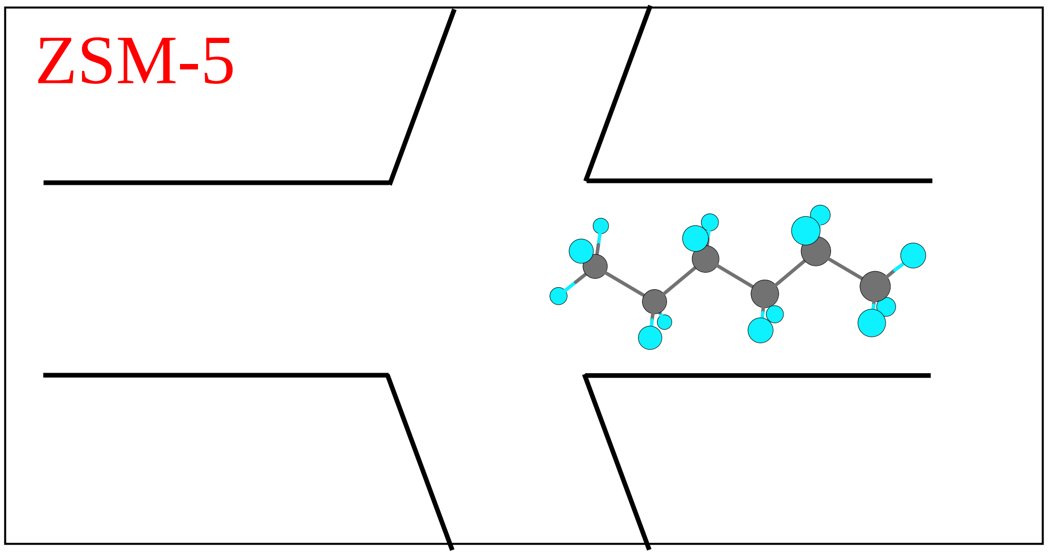


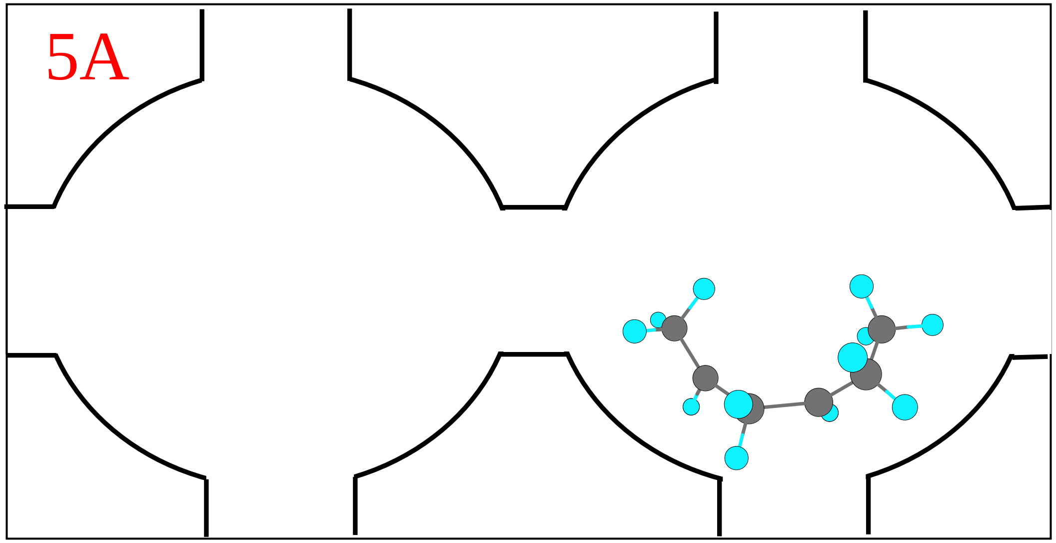


12 C / cage

n-alkanes in various zeolites (T = 475 K)





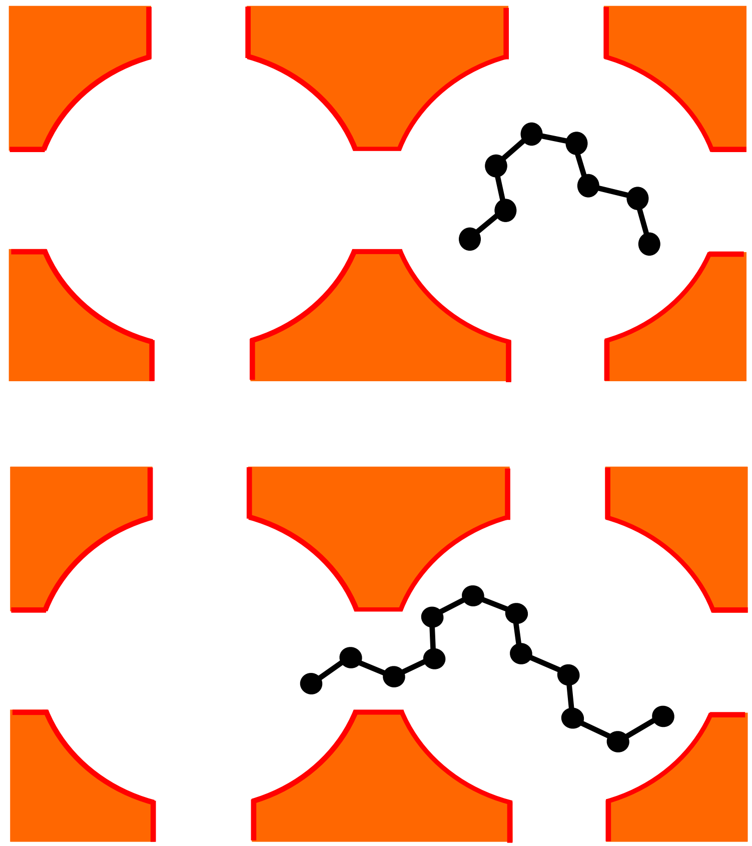


Molecule residence time at 300 K :

in a channel segment:
2×10^{-10} s

in a cage:
2×10^{-5} s

‘Window effect’



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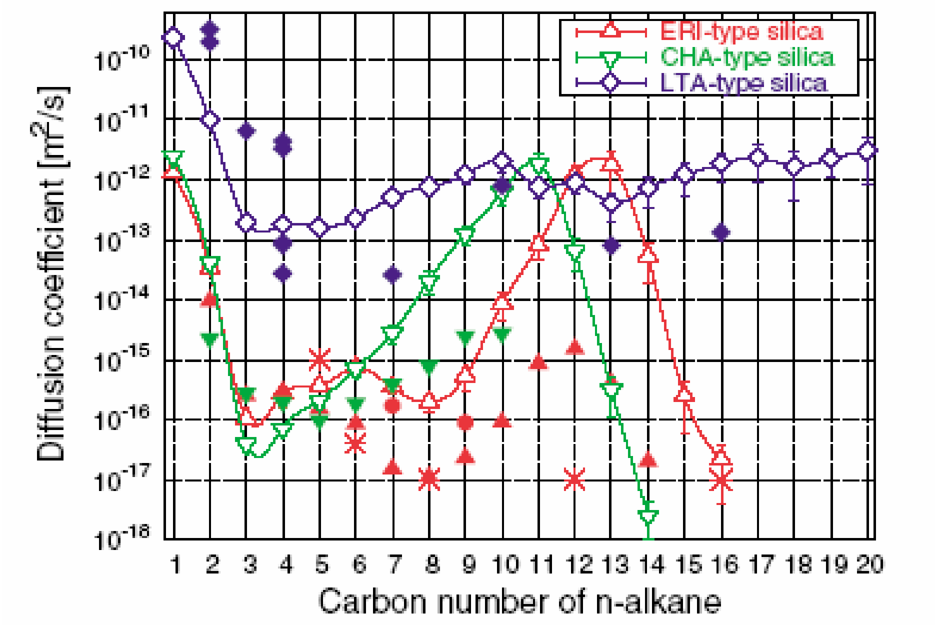
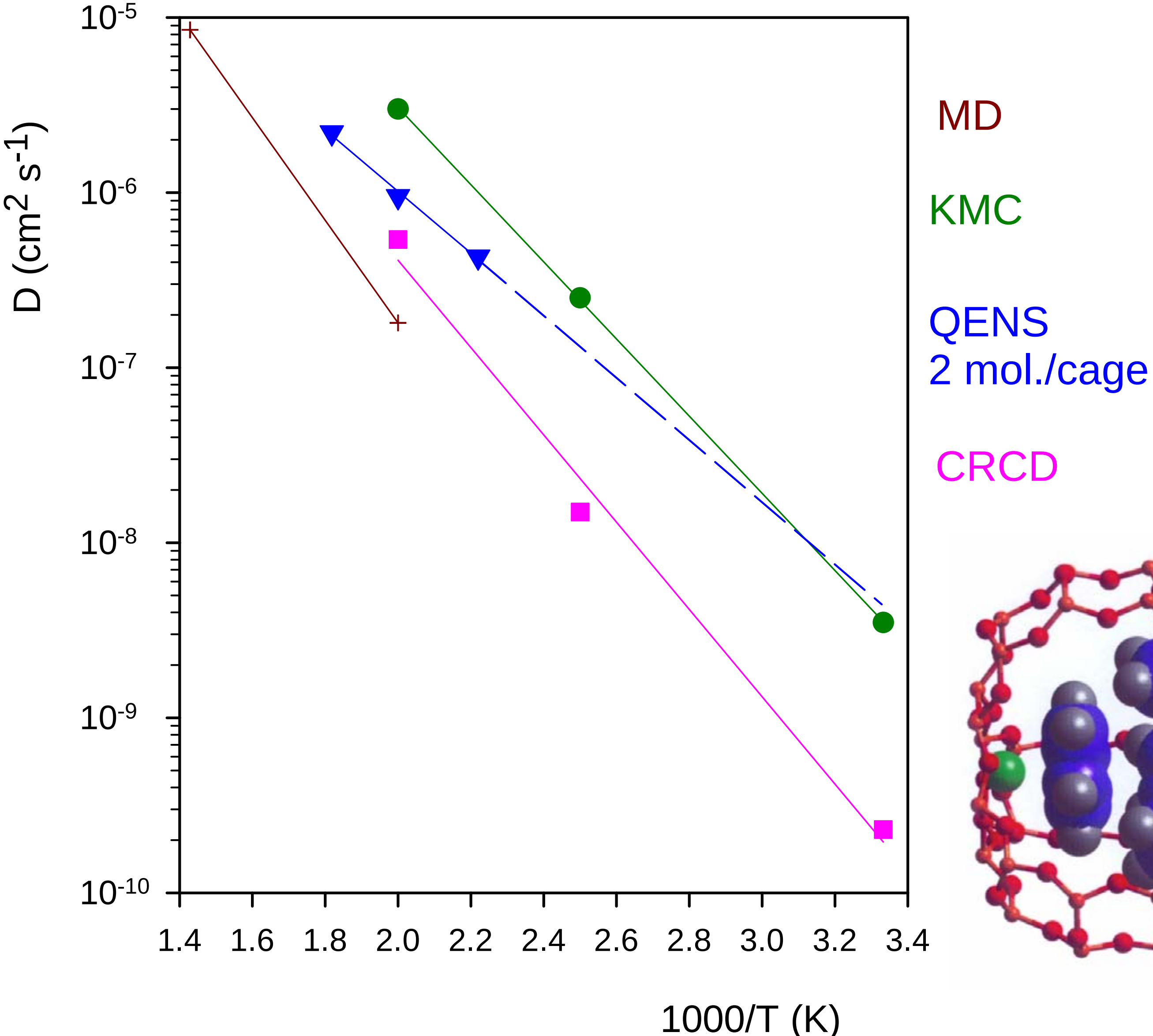
‘Incommensurate diffusion’

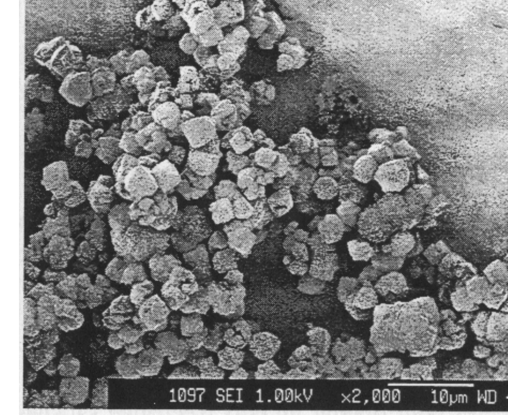


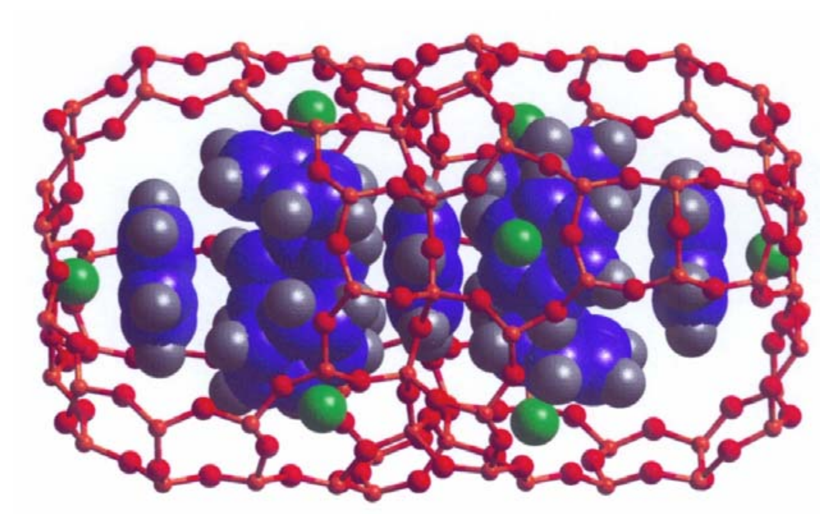
600 K

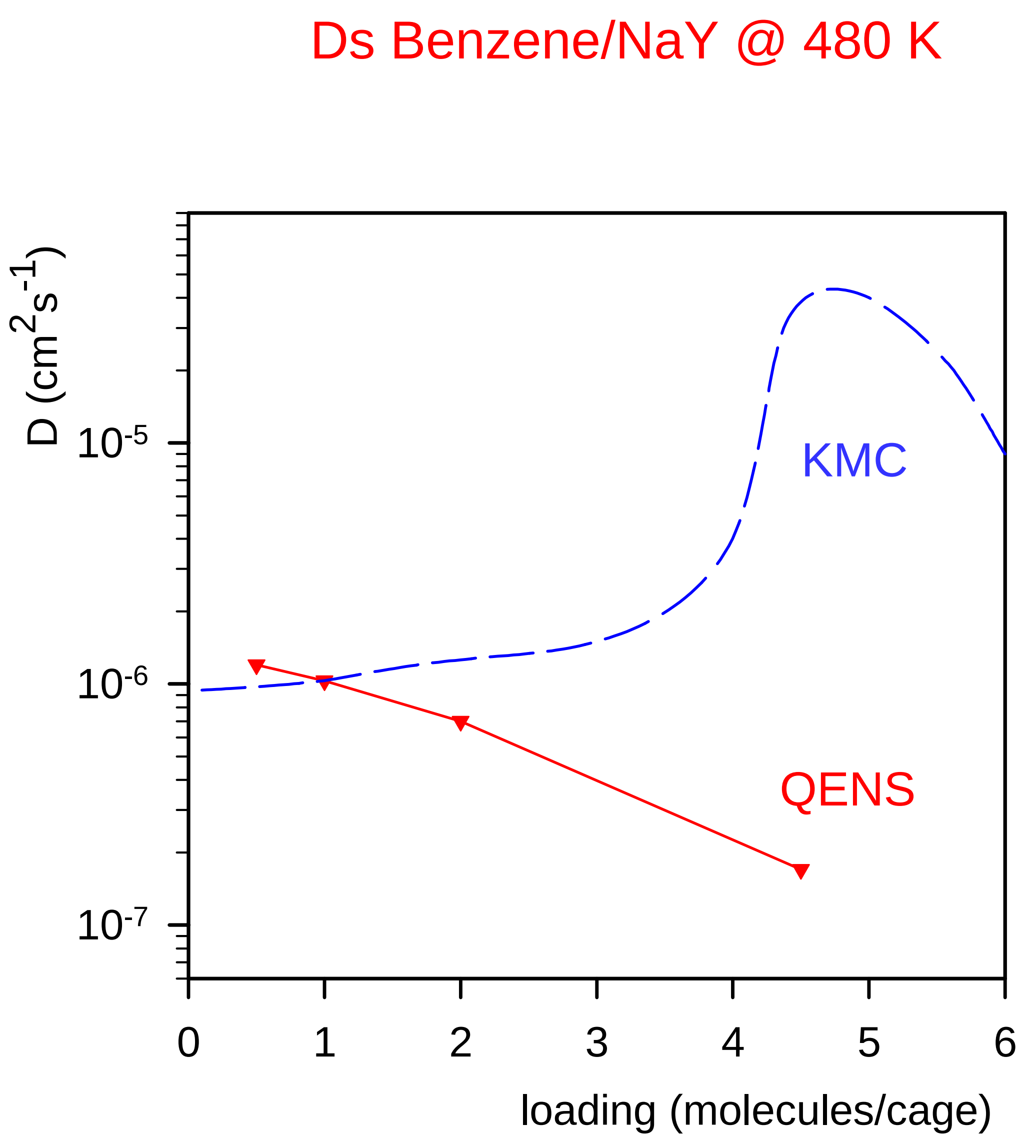
PRL 90 (2003) 245901

Ds Benzene/NaY

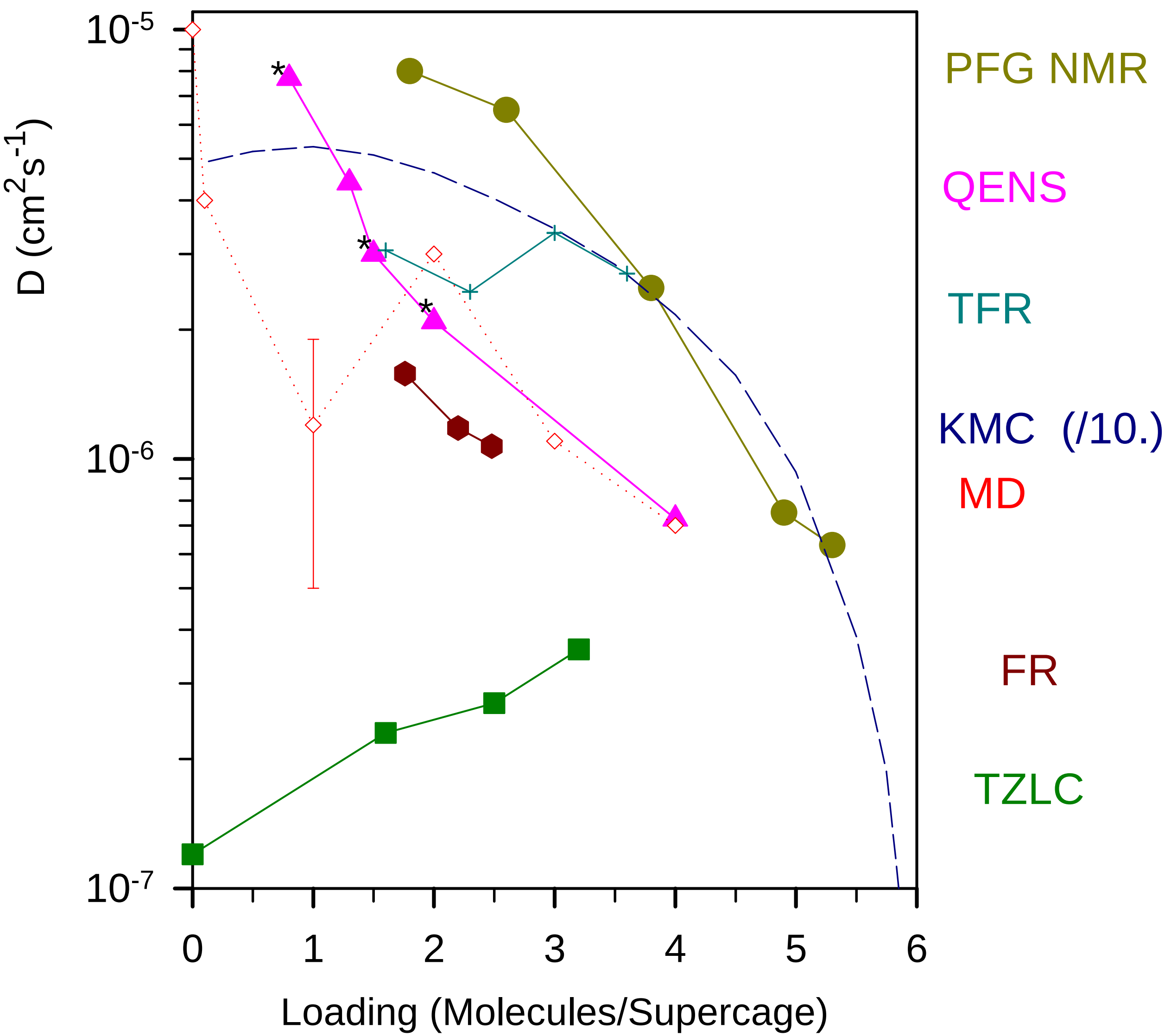


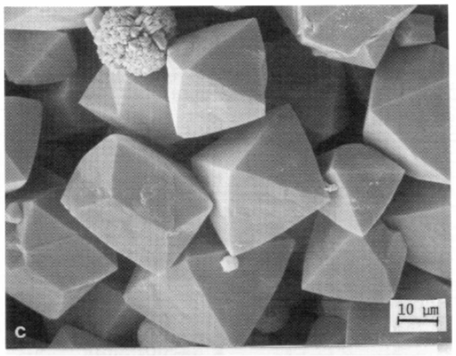




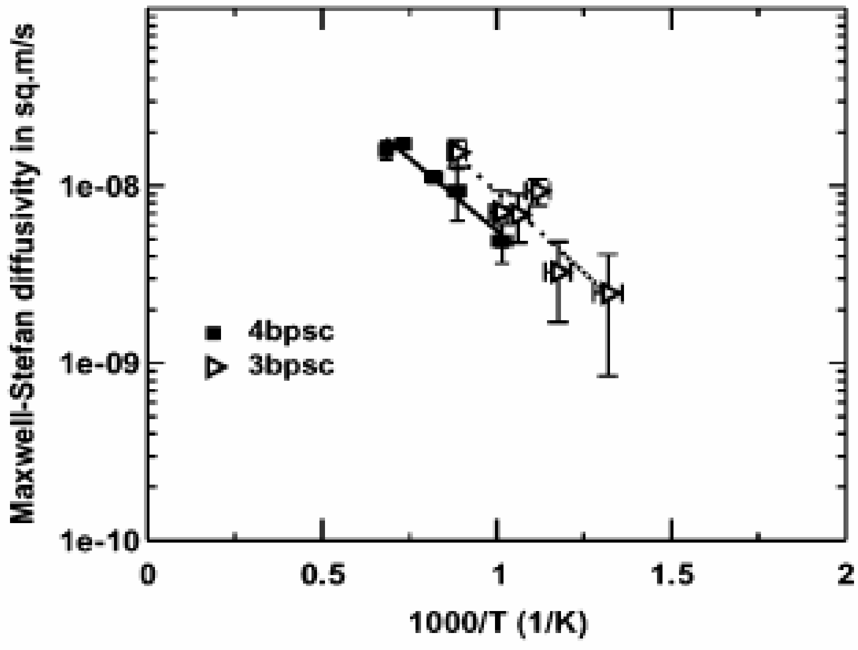

Ds Benzene/NaY @ 480 K
D (cm2s-1)
10-5
10-6
10-7
KMC
QENS
0
1
2
3
4
5
6
loading (molecules/cage)

Ds Benzene / NaX (T = 468 K)

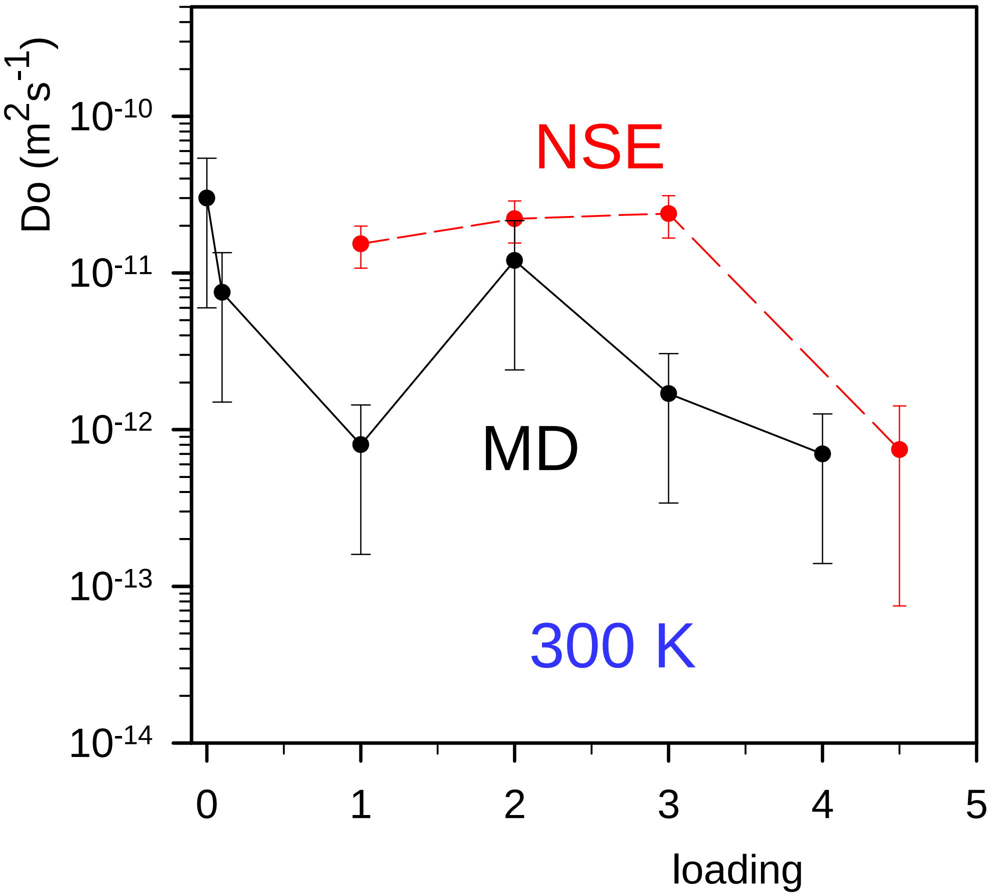




Do Benzene/NaX



JPC B 108 (2004) 17171



Micropor. Mesopor. Mater. (in press)

CONCLUSIONS

Neutron scattering: structure & dynamics of guest-host systems

Methane clathrates: energy resource
geo hazard ?

Hydrogen: energy carrier for the future ? it will not replace oil before several decades

Diffusion in zeolites: Ds, Dt, <d>, τ

comparisons with PFG NMR & macroscopic methods still show large discrepancies

simulations have to be tested by experiment !