



	Experiment title:	Experiment number: CH-1450
Beamline: ID18	Date of experiment: from: 19/05/2003 to: 25/05/2003	Date of report: 14/01/2004
Shifts: 14	Local contact(s): A.I. Chumakov	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): T. Asthalter ^{*1} , J. Villanueva Garibay ^{*1} , V. Olszowka ^{*1} , J. Kornatowski ^{*2} , I. Sergueev ^{2,3} , A.I. Chumakov ^{*3} ¹ Universität Stuttgart, D-70569 Stuttgart, Germany ² Technische Universität München, D-85747 Garching, Germany ³ ESRF, F-38043 Grenoble, France		

Report:

The dynamics of guest molecules in zeolitic and related nanoporous hosts is a topic of high current interest. The motions of guest molecules in zeolites and related hosts were traditionally assumed to be governed by Fick's Law; however, it is now well established [1] that anomalous diffusion may dominate in low dimensions. Moreover, the interplay between reorientational and translational dynamics deserves special attention when it comes to understand chemical reactivities in pores.

A loaded zeolite powder, especially one whose grain size distribution is not very sharp, may not only exhibit dynamics of the molecules in the pores, but other dynamic processes (grain-boundary diffusion) will be superimposed on the intra-channel diffusion to be studied [2]. For this reason, mechanistic studies on diffusion in zeolites are preferably carried out on single crystals, where the external surface is negligible compared with the internal one. Ferrocene loaded into $\text{AlPO}_4\text{-5}$ powder was investigated and suggested to contain quickly rotating molecules [3]. However, only a limited degree of loading could be achieved, and thermal decomposition was reported above 200°C [4].

We therefore studied the dynamics of ferrocene adsorbed in the channels of large single crystals of $\text{AlPO}_4\text{-5}$, a one-dimensional molecular sieve, using quasielastic nuclear forward scattering (QNFS). This method is selective to both translational and rotational motion of molecules containing a Mössbauer nucleus, on the timescale of the natural nuclear lifetime (141.1 ns for ^{57}Fe). *Only the Fe-containing species is observed* since only the resonant nuclei contribute to the signal. The matrix gives a signal only at $t=0$, which is discriminated by the detector electronics. Moreover, full use may be made of X-ray focussing optics and small samples down to μm size may be studied. These two advantages of nuclear resonant scattering are particularly helpful in the present study.

The experiment was carried out at the ID18 beamline, using a four-bounce high-resolution monochromator with 6 meV resolution. The beam was focussed down to a size of $13 \times 6 \mu\text{m}^2$ using Kirkpatrick-Baez optics. The delayed forward scattered quanta were recorded using two stacked avalanche photo diodes having a cross section of $5 \times 5 \text{mm}^2$. The loaded crystals (dimensions $50 \times 50 \times 200 \mu\text{m}^3$) were assembled in a copper grid having parallel grooves of 0.15 mm distance and about 60 μm depth. Their orientation was chosen such that the long crystal axis (which corresponds to the crystallographic c axis of the host lattice) was parallel to the beam.

Spectra were taken both in 16-bunch and in 1-bunch mode, where the time window between two subsequent electron bunches in the storage ring was 176.035 and 2816.56 ns, respectively. The temperature was varied from 60 K to 235 K and a further temperature point was recorded at 296 K.

Assuming that the ferrocene molecules re-orient isotropically in space, the time spectrum for slow rotation can be expressed as

$$I(t) = \left[A e^{-\alpha t/2} \cdot \cos\left(\frac{\Omega_{\text{eff}} t}{2} - \phi\right) \right]^2 \quad (1)$$

where the effective quadrupolar frequency

$$\Omega_{\text{eff}} = \Omega \sqrt{1 - \frac{\lambda^2}{\Omega^2}} \quad (2)$$

is decreased because the Fe nucleus "sees" an effective EFG reduced by rotation, the phase shift ϕ takes into account rotational relaxation, inter-resonance multiple scattering and effects by the timing electronics, and λ is the rotational relaxation rate.

Fig. 1 shows that an almost satisfactory fit of the time spectrum at 215 K using a coherent superposition of two different effective quadrupolar frequencies can be obtained. The deviation from a simple two-line spectrum becomes more pronounced with rising temperature, i.e. one quadrupolar frequency is almost independent of temperature, whereas the other one decreases with rising temperature. Moreover, the fraction of the latter increases with T and becomes equal to 100% at room temperature (see Fig. 2, where the two-line spectrum has almost collapsed into a single-line spectrum). This finding is consistent with the assumption of two species of ferrocene molecules in $\text{AlPO}_4\text{-5}$, an almost stationary one and a rotating one. From the temperature dependence of Ω_{eff} of the rotating species, we obtain an Arrhenius activation energy of (1.97 ± 0.25) meV or (190 ± 24) J/mol. However, it is unclear at the moment whether two different crystallographic sites exist or whether the rotation of the ferrocene molecules in the channels is not isotropic and/or the decreasing Ω_{eff} stems from molecules whose EFG is tilted with respect to the crystallographic c axis. More sophisticated models are being investigated in order to fully explain the observed data, and precise ^2H -quad echo NMR data may help us to verify the validity of our model. Finally, the investigation of the ferrocene dynamics perpendicular to the $\text{AlPO}_4\text{-5}$ channels may help us to verify the anisotropy of the molecular rotation and maybe to separate rotational and translational contributions to the NFS spectrum.

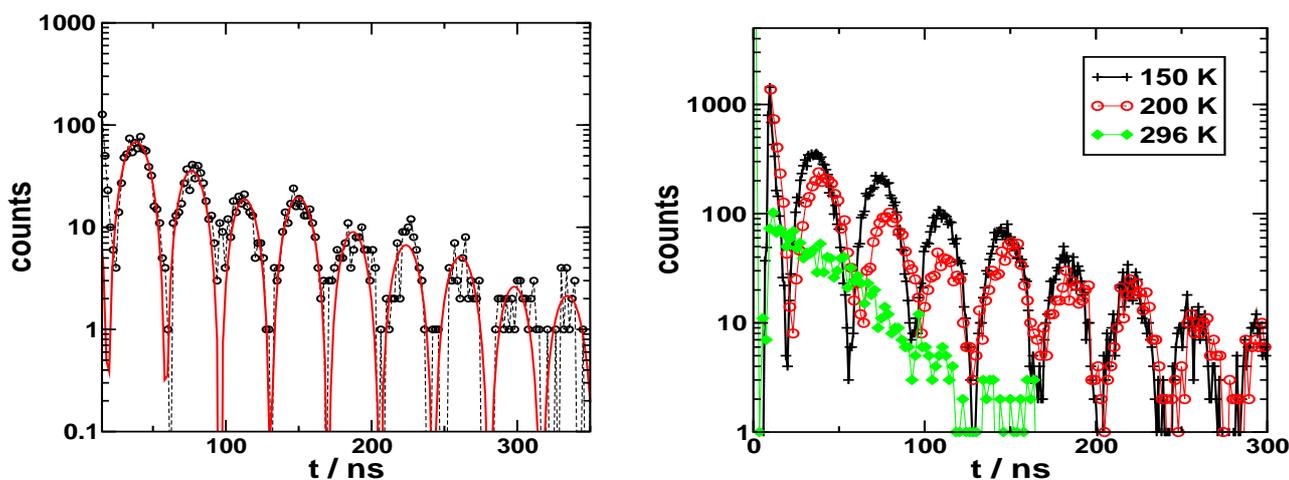


Fig. 1: fit of time spectrum for $T=215$ K, Fig. 2: Time spectra for three temperatures

[1] C. Crabb, *Chem. Eng.* **108** (5), 59 (2001)

[2] J. Kärger, D.M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids*, Wiley, New York 1992

[3] A. Lund, D.G. Nicholson, R.V. Parish, J.P. Wright, *Acta Chem. Scand.* **48**, 738 (1994)

[4] A. Lund, D.G. Nicholson, G. Lamble, B. Beagley, *J. Mater. Chem.* **4**, 1723 (1994)