

## Dynamics of different molecules adsorbed in porous media

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**Abstract.** We present in this paper a comparative study on the dynamics of benzene, cyclohexane, and methanol molecules, confined in the pores of MCM-41 molecular sieve and HZSM-5 zeolite. The quasi-elastic neutron scattering (QENS) measurements revealed that the physical state of these adsorbed molecules depended not only on the structural characteristics of the host matrix but also on the chemical properties, such as dipole moment, of the guest molecules. Thus, while no motion was observed in the time-scale of  $10^{-10}$ – $10^{-12}$  s in the case of methanol, the larger size benzene and cyclohexane molecules are found to perform six-fold and three-fold jump rotation, respectively, when adsorbed inside the cages of HZSM-5 at room temperature. At the same time, all the three molecules are found to undergo a translational motion inside the pores of MCM-41 molecular sieves, the value of diffusion constant being the lowest in case of methanol because of its higher polarity. Translational motion of the guest molecules inside the pores of MCM-41 can be satisfactorily described by Chudley–Elliott fixed jump length diffusion and accordingly the residence time, jump length and diffusion constant are estimated.

**Keywords.** Porous materials; diffusion; neutron scattering.

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### 1. Introduction

The sorption, binding, and the transport characteristics of various adsorbates in zeolitic pore systems have been investigated extensively, both experimentally and theoretically, with an objective to achieve the fundamental understanding of the diffusion behavior of guest molecules in the confined geometries. It is widely reported [1] that the thermodynamic and transport properties of fluids are considerably altered on their physical confinement in well-defined channels and cavity systems of porous materials. Using the quasi-elastic neutron scattering (QENS) and *in situ* Fourier-transform infrared (FTIR) spectroscopy techniques, we demonstrated recently that the benzene molecules existed in a highly compressed non-equilibrium state, when occluded in the micropores of ZSM-5 zeolites [2]. In order to monitor the role played by the symmetry and the chemical nature of the guest molecule, we

have now undertaken this QENS study on room temperature adsorption of benzene, cyclohexane, methanol in two different kinds of porous materials, i.e. MCM-41 and HZSM-5 molecular sieves.

## 2. Experimental details

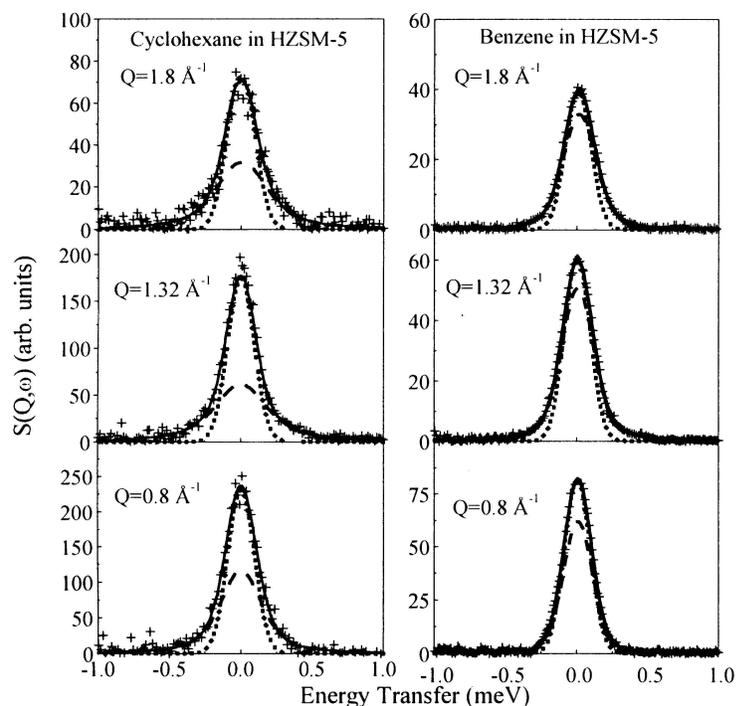
The MCM-41 sample (Si/Al ratio  $\sim 30$ ) used in this study was synthesized by a conventional hydrothermal route; fumed silica and Al-isopropoxide being the source of Si and Al respectively. The  $N_2$  adsorption surface area, pore size and pore volume of a calcined sample were evaluated to be around  $720 \text{ m}^2 \text{ g}^{-1}$ ,  $34 \text{ \AA}$  and  $0.68 \text{ cm}^3 \text{ g}^{-1}$ , respectively. HZSM-5 zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ , surface area  $380 \text{ m}^2 \text{ g}^{-1}$  and pore volume  $0.22 \text{ cm}^3 \text{ g}^{-1}$ ) was obtained from Zeolite International, USA. QENS data were collected prior to and after room temperature adsorption of benzene, cyclohexane and methanol in MCM-41 and HZSM-5, subsequent to a pretreatment (625 K, 48 h) under vacuum ( $10^{-6}$  Torr). A saturation loading of the samples was made for this purpose. The experiments were performed using an incident neutron beam of  $4 \text{ \AA}$  wavelength, and the energy resolution of spectrometer was  $200 \mu\text{eV}$  [3]. The quasielastic spectra were recorded in the wave-vector transfer ( $Q$ ) range of  $0.67$  to  $1.8 \text{ \AA}^{-1}$  at 300 K for bare MCM-41/HZSM-5 and MCM-41/HZSM-5 with sample.

## 3. Results and discussion

In a neutron scattering experiment from homogeneous systems, the observed dynamics mainly corresponds to the self-correlation function of the hydrogen atoms. In that case the incoherent scattering law,  $S_{\text{inc}}(Q, \omega)$ , alone describes the dynamics.  $\mathbf{Q}(=\mathbf{k}-\mathbf{k}_0)$  is the wave-vector transfer and  $\hbar\omega = E - E_0$  is the energy transfer. In general, the incoherent scattering law can be written as

$$S_{\text{inc}}(Q, \omega) \propto A(Q)\delta(\omega) + [1 - A(Q)]L(\Gamma, \omega), \quad (1)$$

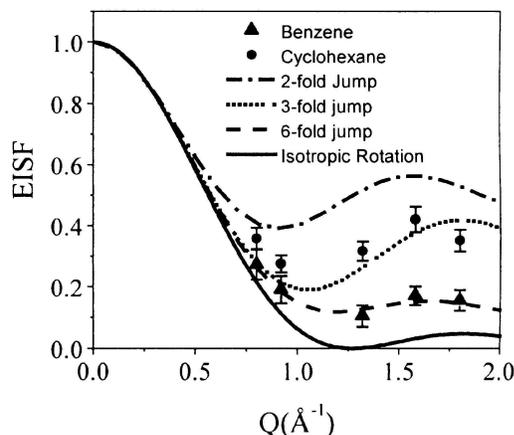
where the first term is the elastic part and the second term is the quasi-elastic part.  $L(\Gamma, \omega)$  is a Lorentzian function and  $\Gamma$  is the half-width at half-maximum (HWHM) of the Lorentzian.  $\Gamma$  is inversely related to the time constant of the motion. It is convenient to analyse the data in terms of elastic incoherent structure factor (EISF) which provides information about the geometry of the molecular motions and is defined as the fraction of elastic intensity in the total spectra. Therefore,  $A(Q)$  in eq. (1) is nothing but the EISF. No quasi-elastic broadening is seen in case of methanol in HZSM-5 zeolite. This indicates that no motion in the time-scale of  $10^{-10}$ – $10^{-12}$  s is occurring in methanol-adsorbed HZSM-5 sample. Since the channel diameter is very small ( $\sim 5 \text{ \AA}$ ) methanol molecules are in a highly compressed state and found to be static in that time-scale inside HZSM-5 zeolite. However, significant broadening is observed in case of benzene and cyclohexane adsorbed in HZSM-5 zeolite. In case of benzene and cyclohexane adsorbed in HZSM-5 zeolite having small pore size, translational contribution will be much less and quasi-elastic data were analysed in terms of rotational motion only. Figure 1 shows the typical QENS



**Figure 1.** Typical QENS spectra at some  $Q$  values for benzene/cyclohexane adsorbed in HZSM-5. Solid lines represent the fitted lines and dotted lines represent the instrument resolution function. Dashed line represents the quasi-elastic component.

spectra for benzene and cyclohexane adsorbed in HZSM-5 zeolite. The variation of EISF with  $Q$  is shown in figure 2. The six-fold rotational jump of benzene with residence time in between jump of 16.5 ps was obtained in case of benzene adsorbed in HZSM-5 sample. However, three-fold rotational jump model and residence time of 8.2 ps were found to be suitable to describe the data of cyclohexane adsorbed in HZSM-5. In case of bulk benzene, residence time of 2.5 ps at RT (liquid state) and 19.2 ps at 277 K (solid state) were reported earlier (references are given in the table 1). Residence time in case of benzene adsorbed in HZSM-5 clearly indicates that the benzene molecules exist in a more compressed form inside HZSM-5 zeolitic cages and behave almost like a solid. Cyclohexane adsorbed in HZSM-5 zeolite are also found to show similar behaviour. The corresponding value of residence time for bulk solid and liquid were reported to be 6.0 ps at 180 K and 1.7 ps at RT respectively. All these values are compared in table 1.

QENS spectra from the dehydrated MCM-41 did not show any QE broadening over the resolution function of the instrument. However, significant broadening was observed from the sample loaded with benzene, cyclohexane and methanol and this may therefore be attributed exclusively to the molecular motions of benzene, cyclohexane and methanol. In order to explore the contribution of occluded molecule,



**Figure 2.** Variation of EISF with  $Q$  for benzene and cyclohexane adsorbed in HZSM-5. Lines are calculated EISF (see text).

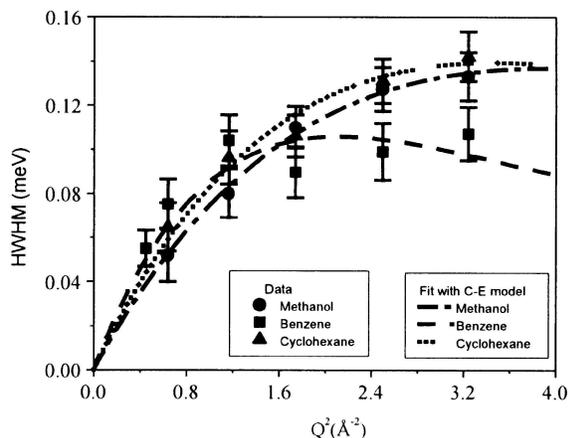
the QENS spectrum of bare molecular sieves was subtracted from the spectrum of the loaded sample. The data thus obtained were separated into elastic and quasi-elastic components by least squares fit of the model scattering law given in eq. (1) with data after convoluted with the instrumental resolution and the parameters ( $A(Q)$  and  $\Gamma$ ) were determined. It was found that the elastic component ( $A(Q)$ ) is almost zero for all the  $Q$ -values suggesting that the observed dynamics does not involve any elastic part. The quasi-elastic part was found to be describable by one Lorentzian only which in turn suggests that no other dynamical event except translational motion contributes to the spectra. The half-width at half-maxima (HWHM) of the Lorentzian function as obtained from the fit is given in figure 3. The simplest model for translational motion is the Brownian motion where it is assumed that the particles move under the influence of the forces arising from the collisions between them. In this case, incoherent scattering law can be calculated by solving Fick's law [4]. The scattering law exhibits a Lorentzian shape whose HWHM increases with the momentum transfer according to a  $DQ^2$  law. However, as can be seen from figure 3, HWHM of the quasi-elastic component does not follow linear behaviour suggesting that simple Fick's law is not adequate in describing the experimental data. A more elaborate model was formulated by Chudley and Elliott [5]. This model assumes that for a time interval  $\tau$ , an atom remains on a given site, vibrating about a centre of equilibrium, building up a thermal cloud. After this time, the atom moves to another site, in a negligible jump time. The jump length  $l$  is assumed to be the same for all such jumps. This model is also called fixed jump model. The powder-averaged scattering law in this case is a Lorentzian with HWHM

$$\Gamma(Q) = \frac{1}{\tau} \left[ 1 - \frac{\sin Ql}{Ql} \right]. \quad (2)$$

One can also find out the diffusion constant,  $D$  from Einstein's relation,  $D = l^2/6\tau$ . In figure 3, the fit of the HWHM values of the Lorentzians as per the Chudley–Elliott

**Table 1.** Dynamical parameters for rotational motion of various molecules adsorbed in HZSM-5. Corresponding parameters reported for bulk solid and liquid are also given for comparison.

Hydrocarbon adsorbed in HZSM-5	Dipole moment (Debye)	Molecular diameter (Å)	Model	Residence time when absorbed in HZSM-5 (ps)	Residence time (bulk) in	
					Solid (ps)	Liquid at RT (ps)
Methanol	1.7	4.5	No broadening is seen	–	–	10.2 [6]
Benzene	0	5.8	Six-fold jump rotation	16.5	19.2 at 277 K [7]	2.5 [9]
Cyclohexane	0	6	Three-fold jump rotation	8.2	6.0 at 180 K [8]	1.7 [10]

**Figure 3.** Variation of HWHM with  $Q^2$  for methanol, benzene and cyclohexane adsorbed in MCM-41. Line is the fit to the Chudley–Elliott model.

model is shown. As seen in figure 3, the experimental values fit quite well with this model. The values of residence time ( $\tau$ ), jump length ( $\langle l \rangle$ ) and the diffusion constant ( $D$ ) are given in table 2. On comparing this diffusion constant with the value reported for the diffusion constant of liquid methanol at 298 K ( $D = 2.6 \times 10^{-5} \text{ cm}^2/\text{s}$  [6]) we may conclude that the translational diffusion constant of adsorbed methanol in MCM-41 is much less than that of bulk liquid methanol. Diffusion constants of benzene and cyclohexane adsorbed in MCM-41 are not changing much from their bulk value. These results can be ascribed to a large dipole moment associated with the methanol molecules resulting in their electronic binding to the framework or extra-framework sites of host matrix thus restraining their molecular motion in the channel system. In the case of non-polar benzene and cyclohexane molecules of almost similar size, the molecular symmetry may play an important role in deciding the diffusion parameters, such as jump length and residence time, as shown in table 2.

**Table 2.** Dynamical parameters for translational motion of various molecules adsorbed in MCM-41 according to Chudley–Elliott model at RT. Corresponding bulk liquid diffusion constants are also given for comparison.

Hydrocarbon adsorbed in MCM-41	Dipole moment (debye)	Molecular diameter (Å)	Jump length, $\langle l \rangle$ (Å)	Residence time, $\tau$ (ps)	Diffusion constant ( $\ell^2/6\tau$ ) ( $\times 10^{-5}$ cm <sup>2</sup> /s) at RT	
					Adsorbed in MCM-41	Bulk liquid
Methanol	1.7	4.5	$2.3 \pm 0.6$	$5.8 \pm 0.5$	$1.5 \pm 0.1$	2.6 [6]
Benzene	0	5.8	$3.1 \pm 0.5$	$7.5 \pm 0.6$	$2.2 \pm 0.6$	2.2 [11]
Cyclohexane	0	6	$2.4 \pm 0.7$	$5.7 \pm 0.7$	$1.7 \pm 0.4$	1.7[12]

#### 4. Conclusions

Quasi-elastic neutron scattering study thus reveals that the methanol molecules adsorbed in HZSM-5 zeolite are not mobile in the time-scale of  $10^{-10}$ – $10^{-12}$  s whereas the benzene and cyclohexane molecules of larger molecular diameter are seen to perform six-fold and three-fold jump rotation, respectively (table 1). It is also of interest to notice that even for adsorption in MCM-41 with larger pore size of 34 Å, the diffusion constant for translational motion of methanol has a much smaller value as compared to the translational motion of the other two molecules in MCM-41 and also as compared to the diffusion constant of bulk methanol (table 2).

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