

## Acetylene diffusion in Na-Y zeolite

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**Abstract.** Study of diffusivity of acetylene adsorbed in Na-Y zeolite by quasi-elastic neutron scattering (QENS) measurements at temperatures of 300, 325 and 350 K is reported. A model in which the acetylene molecules undergo random-walk diffusion characterized by a Gaussian distribution of jump lengths inside zeolite cages describes the data consistently. The diffusion constant, residence time between jumps and root mean square jump length are determined.

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

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### 1. Introduction

Zeolites are useful in a number of industrial processes, principally in petroleum and petrochemical industries, as catalysts and molecular sieves [1]. Consequently the role played by the pore geometry and by the framework acid sites of zeolites in the catalytic activity and selectivity of the guest molecules has been under extensive investigation. Among the experimental methods used for the study of self-diffusivity of hydrocarbons inside zeolite pores, quasi-elastic neutron scattering (QENS) [2,3] and pulsed field gradient NMR (PFG-NMR) [4] are the most important. Studies on the dynamics of propane molecule inside Na-Y zeolite cage was earlier reported by Sayeed *et al* [5].

Zeolites are porous crystals comprising of Al, Si and O atoms. Electrical neutrality is achieved by the inclusion of exchangeable metal cations e.g.,  $\text{Ca}^{++}$ ,  $\text{Na}^+$  etc. Na-Y structure is made up of a network of tetrahedrally connected pores ( $\alpha$ -cages) of diameter  $\sim 11.8$  Å. The pores are interconnected through windows of diameter  $\sim 7.8$  Å. Recent molecular dynamics (MD) simulation studies [6] show a maximum in  $D$  as a function of the length of the guest molecule. Therefore it is of interest to study the variation of the diffusion constant with the length of geometrically linear molecules. Acetylene is the smallest linear hydrocarbon and hence qualifies as an ideal guest molecule to start with. Here we report the results of QENS measure-

ments carried out to study the diffusion of acetylene in Na-Y zeolite at different temperatures.

## 2. Experimental details

The Na-Y zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio (wt%)=2.5) was used for the experiment. The QENS spectra were recorded in both dehydrated and acetylene loaded (to saturation) zeolite samples using the quasi-elastic spectrometer [7] at Dhruva reactor, Trombay. In the present configuration the spectrometer has an energy resolution of  $200 \mu\text{eV}$  with an incident energy of  $5.1 \text{ meV}$ . The quasi-elastic spectra were recorded in the wave vector transfer ( $Q$ ) range of  $0.67$  to  $1.8 \text{ \AA}^{-1}$  at  $300$ ,  $325$  and  $350 \text{ K}$ . Temperature range was chosen on the basis of the sample stability and instrumental resolution. Spectrum from the dehydrated zeolite sample was used to estimate the contribution of bare zeolite to the total spectra.

## 3. Results and discussion

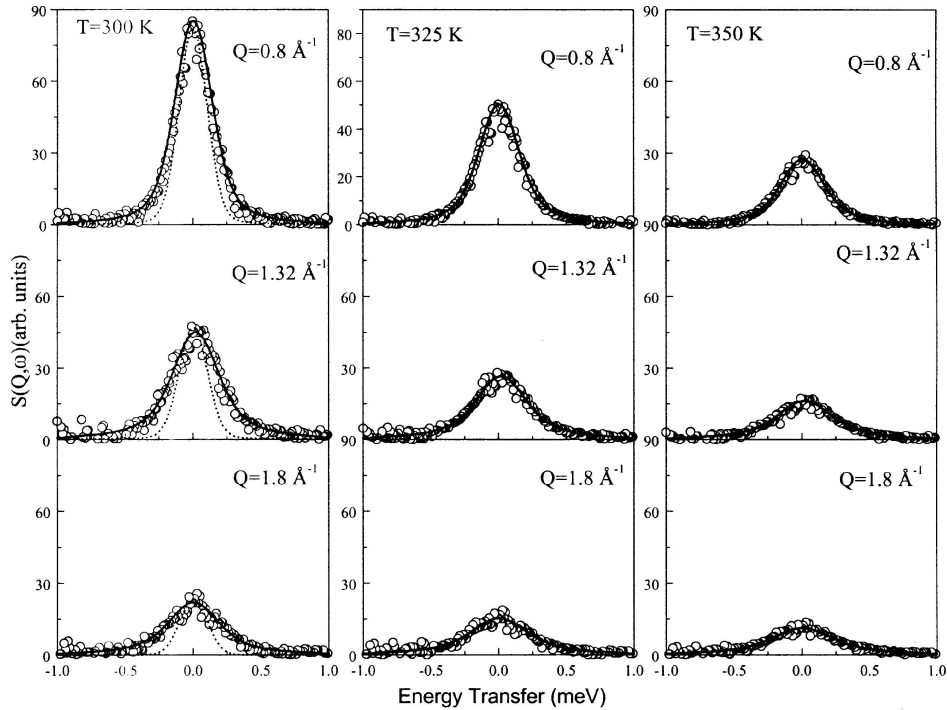
In a neutron scattering experiment from homogeneous systems, the observed dynamics mainly corresponds to the self-correlation function of the hydrogen atoms. In that case the incoherent scattering law,  $S_{\text{inc}}(Q, \omega)$ , alone describes the dynamics.  $\mathbf{Q}(=\mathbf{k}-\mathbf{k}_0)$  is the wave vector transfer and  $\hbar\omega = E - E_0$  is the energy transfer. The QENS spectra from the dehydrated Na-Y zeolite did not show any quasi-elastic (QE) broadening over the resolution function of the instrument, but a large elastic intensity was observed indicating the presence of immobile hydrogens in the sample. QE broadening was observed from the sample loaded with acetylene and this may therefore be attributed exclusively to the molecular motions of acetylene. To estimate the contribution from the acetylene alone, spectra of the dehydrated zeolite were subtracted from the acetylene adsorbed zeolite spectra.

In general, the incoherent scattering law can be written as [8]

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

where the first term is the elastic part and 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)  $A(Q)$  which provides information about the geometry of the molecular motions and is defined as the fraction of elastic intensity in the total spectra. Analysis of the data involves, in the first instant, separating the elastic and quasi-elastic parts in the total spectrum. For that the scattering law given in eq. (1) was convoluted with the instrumental resolution function and the parameters ( $A(Q), \Gamma$ ) were obtained at each  $Q$ -value by least squares fit to the measured data.

Typical fitted QENS spectra at different  $Q$  values and at different temperatures are shown in figure 1. The effect of temperature and  $Q$  is evident in the data. It was found that the elastic component,  $A(Q)$ , is almost zero at all the  $Q$  values suggesting that the observed dynamics does not involve any pure elastic component and

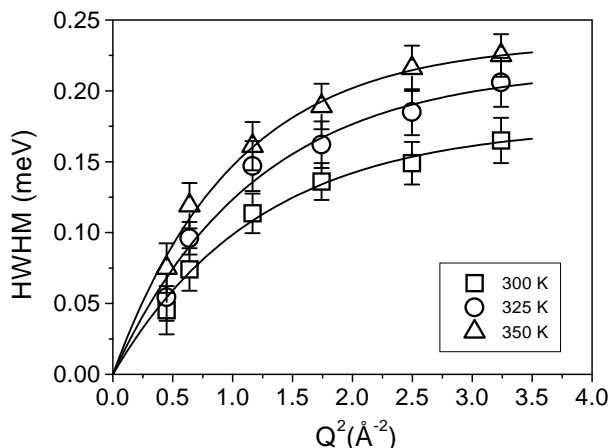


**Figure 1.** Typical fitted QENS spectra from the adsorbed acetylene at some  $Q$  values at different temperatures. Spectra from dehydrated zeolite have been subtracted off. Dashed lines are the instrumental resolution function.

the observed dynamics is mostly due to the translational motion of the acetylene molecules. The variation of  $\Gamma$  with  $Q^2$  is shown in figure 2. Several available models of the dynamics were considered to describe the behaviour of  $\Gamma$ . The simplest motion is the Brownian motion or Fickian motion [8] where the scattering law is a Lorentzian function and whose HWHM increases with the wave vector transfer according to a  $DQ^2$  law and provides a direct method of determining the diffusion constant. However, as can be seen from figure 2, HWHM of the quasi-elastic component deviates from the linear behaviour at high  $Q$  values suggesting that simple Fick's law is not adequate in describing the experimental data. We need to explore more elaborate model to describe the experimental data. One such model was formulated by Hall and Ross [9]. This model assumes that for a time interval  $\tau$ , an atom remains on a given site, vibrating about an average position, building up a thermal cloud. After this time, the atom moves rapidly to another site, in a negligible jump time. The jump length  $l$  is assumed to be Gaussian-distributed for all such jumps under consideration.

The scattering law in this case is a Lorentzian with HWHM,

$$\Gamma(Q) = \frac{1}{\tau} \left[ 1 - \exp\left(-\frac{Q^2 \langle l^2 \rangle}{6}\right) \right], \quad (2)$$



**Figure 2.** Variation of HWHM of the quasielastic component with  $Q^2$ . Solid lines are fit with Hall-Ross model (eq. (2)).

**Table 1.** Values of residence time, root mean square jump length and diffusion constant of acetylene in Na-Y zeolite at different temperatures.

$T$ (K)	$\tau$ (ps)	$\langle l^2 \rangle^{0.5}$ (Å)	$D$ ( $\times 10^{-5}$ cm <sup>2</sup> /s)
300	$3.7 \pm 0.2$	$2.2 \pm 0.1$	$2.2 \pm 0.3$
325	$3.0 \pm 0.2$	$2.2 \pm 0.1$	$2.7 \pm 0.4$
350	$2.8 \pm 0.2$	$2.4 \pm 0.1$	$3.5 \pm 0.5$

where,  $\tau$  and  $\langle l^2 \rangle$  are the residence time and mean square jump length. Very good fit was obtained for the whole  $Q$  range. Solid curves in figure 2 are the variation of HWHM as per the Hall-Ross model as obtained by least squares fit to the experimental HWHM at different temperatures. It is found that this model proposed by Hall and Ross is adequate and consistent with the experimental data. The values of  $\tau$  and  $\langle l^2 \rangle^{0.5}$  obtained from the fit at different temperatures are given in table 1. The estimated values of the diffusion constant  $D$  from,  $D = \langle l^2 \rangle / 6\tau$  are also given in the table 1. The values of diffusion constants can be compared with the diffusivity of propane adsorbed in Na-Y zeolite studied earlier [5] ( $2.3 \times 10^{-5}$  and  $4.0 \times 10^{-5}$  cm<sup>2</sup>/s at 300 K and 350 K respectively). The diffusion constants for acetylene and propane inside Na-Y zeolite are found to be nearly the same.

#### 4. Conclusion

The results of QENS measurements to study the diffusion of acetylene gas in zeolite Na-Y at different temperatures have been reported. The experimental data are found to be consistent with a model in which the acetylene molecules undergo

random diffusion with Gaussian distributed jump lengths inside the zeolite cages. Diffusion constant, residence time in between jumps and root mean square jump lengths are estimated at different temperatures.

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