

## Rotational dynamics of propylene inside Na-Y zeolite cages

V K SHARMA<sup>1,\*</sup>, MALA N RAO<sup>1</sup>, SIDDHARTH GAUTAM<sup>1</sup>, A K TRIPATHI<sup>2</sup>,  
V S KAMBLE<sup>2</sup>, S L CHAPLOT<sup>1</sup> and R MUKHOPADHYAY<sup>1</sup>

<sup>1</sup>Solid State Physics Division; <sup>2</sup>Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

\*Corresponding author. E-mail: sharmavk@barc.gov.in

**Abstract.** We report here the quasielastic neutron scattering (QENS) studies on the dynamics of propylene inside Na-Y zeolite using triple axis spectrometer (TAS) at Dhruva reactor, Trombay. Molecular dynamics (MD) simulations performed on the system had shown that the rotational motion involves energy larger than that involved in the translational motion. Therefore, rotational motion was not observed in our earlier QENS studies on propylene adsorbed Na-Y zeolite using a higher resolution spectrometer at Dhruva. Analysis of the TAS spectra revealed that the quasielastic broadening observed in propylene-loaded zeolite spectra is due to the rotational motion of the propylene molecules. This is consistent with our simulation result. Further, the rotational motion is found to be isotropic. The rotational diffusion coefficient has been obtained.

**Keywords.** Neutron quasielastic scattering; porous materials; molecular dynamics.

**PACS Nos** 78.70.Nx; 66.10.Cd; 78.55.Mb

### 1. Introduction

Dynamics of hydrocarbons adsorbed in zeolitic materials has been of interest because of the potential applications it promises [1]. The catalytic and sieving properties of zeolites depend upon the diffusivity of the adsorbed molecules. This diffusivity in turn is determined by several factors like temperature, size and shape of the adsorbed molecules, the zeolitic void space, the concentration of the adsorbed molecules etc. Several such dependences have been under investigation [2]. We have in particular been investigating the diffusivities of hydrocarbons in Na-Y zeolitic cages. In this context we had earlier reported the translational diffusivities of propane, acetylene and 1,3-butadiene in Na-Y zeolite [3–5]. The translational diffusivities of these molecules are significantly altered by the confinement effect.

We have also studied the translational diffusivities of propylene in Na-Y and Na-ZSM5 zeolites [6] from which it was seen that the diffusivity of propylene in Na-Y is considerably smaller than that of propane in Na-Y obtained earlier [3]. In continuation of the foresaid study we are also carrying out molecular dynamics

simulation studies on this system. Preliminary results from these studies show that the rotational motion is faster than the translational motion similar to the result obtained in the case of propane earlier [3,7]. It is therefore interesting to see if there is a difference in the rotational diffusivities too similar to that in the translational diffusivity. Hence we carried out the rotational dynamics studies on propylene adsorbed in Na-Y zeolite using triple axis spectrometer at Dhruva reactor, Trombay [8].

## 2. Experiment

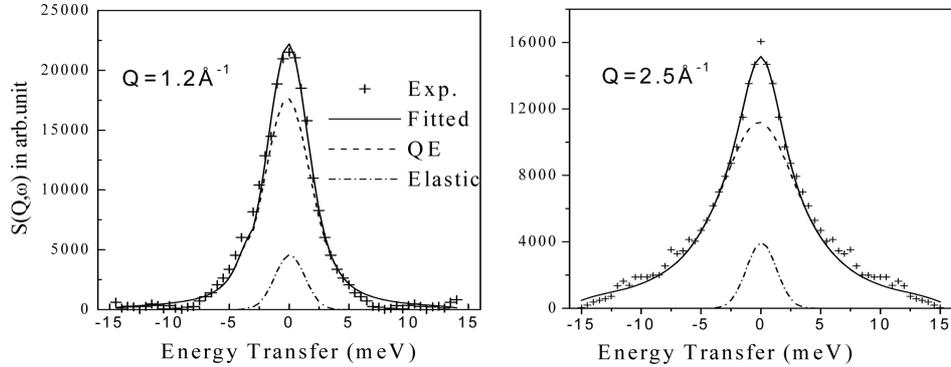
Na-Y sample (8.2 g) with unit cell composition  $\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}(\text{H}_2\text{O})_{264}$  was used in two identical rectangular aluminum containers having dimension 5.7 cm  $\times$  5.4 cm  $\times$  0.4 cm for experiment. The zeolite samples were first dehydrated by evacuating for a period of about 24 h to  $10^{-5}$  torr at a temperature of 573 K. Then one was loaded with propylene gas (purity >99.9%) to saturation at ambient pressure. The propylene loading was estimated with the help of transmission measurements to be 100 mg/g of zeolite, which turns out to be about five propylene molecules per zeolite supercage ( $\alpha$ -cage). In general, rotational motion is expected to be occluded by a high elastic contribution at low  $Q$  values. For propylene with a size of  $\sim 4$  Å, the rotational motion may be seen within a  $Q$  range of 0.5–3.0 Å $^{-1}$ . The QENS experiment was performed using the triple axis spectrometer (TAS) [8] at Dhruva reactor at Trombay, India. TAS was used in inverted geometry, incident energy  $E_i$  was varied and final energy was kept fixed at  $E_f = 20$  meV. TAS provides energy resolution (FWHM – full width at half maximum) of  $\sim 2.8$  meV at elastic position in  $Q$  range 0.8–2.5 Å $^{-1}$ , as obtained from measurements on a vanadium standard sample.

## 3. Results and discussion

The quasielastic spectra was recorded in the wave vector transfer ( $Q$ ) range of 0.8–2.5 Å $^{-1}$  at 300 K for both bare zeolite and propylene-loaded zeolite samples. Bare zeolite sample was used to estimate the contribution of bare zeolite to total spectra. The spectra for bare Na-Y zeolite did not show any broadening while the propylene-loaded zeolite spectra showed quasielastic broadening due to the dynamical motion of propylene molecules. In general, the scattering law can be written as a sum of two components – elastic and quasielastic [9]. The elastic component is represented by a delta function whereas the quasielastic component can be described by a Lorentzian function. The scattering law can be written as

$$S(Q, \omega) = A(Q)\delta(\omega) + [1 - A(Q)]L(\Gamma, \omega), \quad (1)$$

where the coefficient of the delta function,  $A(Q)$ , gives the ratio of elastic component to the total spectra and  $L(\Gamma, \omega)$  is a Lorentzian with half-width at half-maximum (HWHM)  $\Gamma$ . In the case of motion bounded in space-like rotational motion, an elastic contribution is expected to be observed and the EISF in that case has a non-zero value. The behaviour of this term then gives information about the geometry



**Figure 1.** Experimental  $S(Q, \omega)$  (symbol +) and the fit (solid line) using eq. (1). Separated elastic (dash-dot) and quasielastic (dash) parts at  $Q = 1.2$  and  $2.5 \text{ \AA}^{-1}$ .

of motion. The  $\Gamma$  of the Lorentzian can be studied to obtain the time scales of the motion involved. The experimental  $S(Q, \omega)$  from TAS was fitted with eq. (1) convoluted with the instrumental resolution by the method of least squares fit with  $A(Q)$  and  $\Gamma$  as the fitting parameters. The fits are shown in figure 1. Considerable elastic contributions were observed in the spectra. The variation of EISF obtained in TAS data is shown in figure 2. Various models of dynamical motion were envisaged to describe this variation. It was found that the model that describes the EISF variation best is the isotropic rotational diffusion model. In this model the molecule is supposed to rotate about all possible axes of rotation such that after a certain interval of time no preferred orientation of the molecule exists [9]. The EISF in this case can be written as

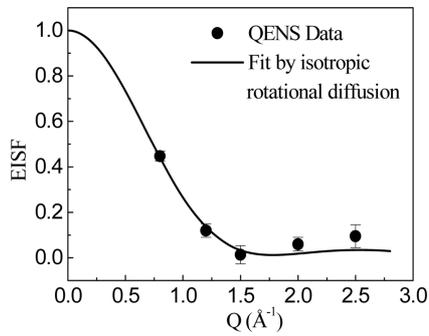
$$A(Q) = j_0^2(Qr), \quad (2)$$

where  $j_0$  is the Bessel function of order zero and  $r$  is the radius of gyration of the molecule. The calculated variation of the EISF is also shown in figure 2. It may be noted that the propylene molecule being asymmetric there exists no preferential orientation and so the isotropic rotational diffusion is the most likely model to describe the rotation of propylene.

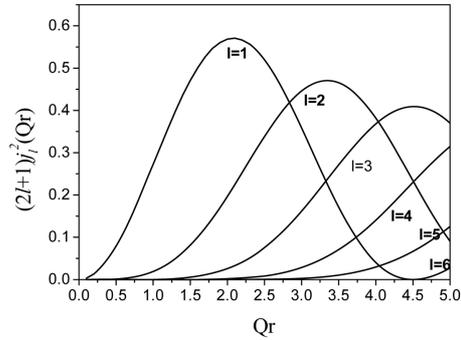
To obtain the time scale of motion one has to analyse the quasielastic broadening as stated above. In the case of isotropic rotation of a molecule, the scattering law can be written as

$$S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{l=1}^{\infty} (2l+1)j_l^2(Qr) \frac{1}{\pi} \frac{l(l+1)D_R}{[l(l+1)D_R]^2 + \omega^2}, \quad (3)$$

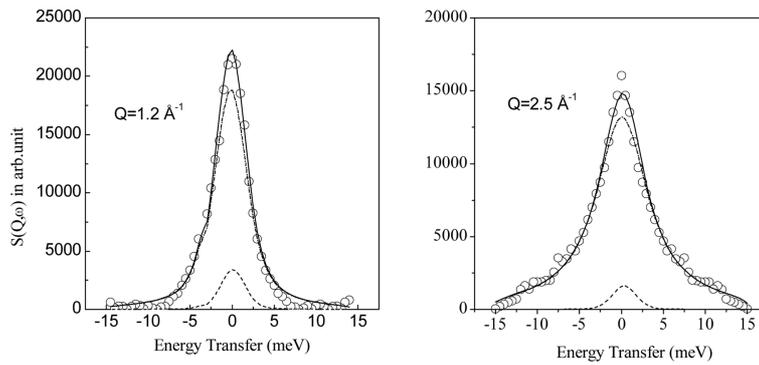
where  $D_R$  is the rotational diffusion coefficient. In practice the summation series in the above equation can be truncated at those values of  $l$  for which the Bessel functions do not contribute up to  $Q_{\max}r$ . In the present case with  $Q_{\max} = 2.5 \text{ \AA}^{-1}$  and  $r = 1.91 \text{ \AA}$  it can be readily seen from figure 3 that terms only up to  $l = 6$  contribute. The experimental spectra were therefore fitted with eq. (3) with the summation truncated after  $l = 6$  with least square fits. The fitted spectra are shown in figure 4. The fits are reasonably good.



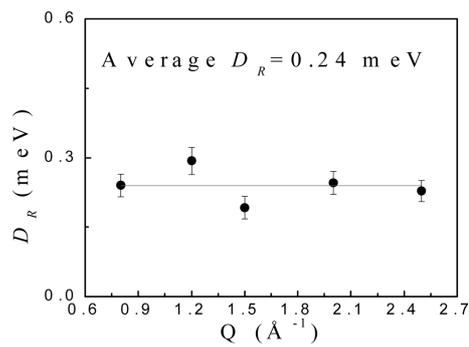
**Figure 2.** Variation of EISF as obtained from QENS data (symbols) with  $Q$ . The calculated EISF assuming isotropic rotational model is shown by a line.



**Figure 3.** Variation of quasielastic structure factor  $(2l + 1)j_l^2(Qr)$  with  $Qr$  for different  $l$ .



**Figure 4.** Fitted  $S(Q, \omega)$  assuming isotropic rotational diffusion model.



**Figure 5.** Variation of diffusion coefficient  $D_R$  with respect to  $Q$ .

**Table 1.** Comparison of rotational parameters of propane and propylene in Na-Y zeolite.

	Propane in Na-Y zeolite	Propylene in Na-Y zeolite
Radius of gyration	1.88 Å	1.91 Å
Average guest concentration (at saturation)	4 molecules per supercage	5 molecules per supercage
Average value of $D_R$ (experiment)	$0.69 \pm 0.06$ meV	$0.24 \pm 0.02$ meV

The diffusion coefficient obtained from the fit showed little variation over different  $Q$ . An average value of  $D_R = (0.24 \pm 0.02)$  meV was obtained. Figure 5 shows the variation of  $D_R$ . The parameters involved in rotational motion of propylene in Na-Y are compared with those obtained for propane in Na-Y zeolite earlier in table 1. It may be noted that the value of average  $D_R$  obtained in the case of propylene in Na-Y zeolite as described above is smaller than that of propane reported earlier. This behaviour can be understood as a consequence of the denser packing in supercages, asymmetric shape and the nature of bonding in propylene.

#### 4. Conclusion

We have carried out the quasielastic neutron scattering studies on propylene adsorbed in Na-Y zeolite. The analysis of the data showed that the quasielastic broadening observed corresponds to the rotational motion as predicted by the MD simulation. Moreover, the rotational motion is found to be isotropic in nature. This is to be expected because of the asymmetry of the molecule. The rotational diffusion coefficient obtained is smaller than that obtained for propane adsorbed in Na-Y zeolite reported earlier which may be due to the combined effect of larger size of propylene molecules ( $r \sim 1.91$  Å), shape (asymmetry of propylene molecules) and higher concentration of propylene molecules in Na-Y zeolite ( $\sim 5$  molecules per supercage).

#### References

- [1] G Tomlinson, *Modern zeolites, structure and function in detergents and petrochemicals* (Traw Tech Publications Ltd., Switzerland, 1998)
- [2] H Jovic, J Karger and M Bee, *Phys. Rev. Lett.* **82**, 4260 (1999)
- [3] A Sayeed *et al*, *J. Phys. Chem.* **B107**, 527 (2003)
- [4] S Mitra *et al*, *Pramana - J. Phys.* **63**, 449 (2004)  
S Gautam *et al*, *Phys. Rev.* **E74**, 041202 (2006)
- [5] S Gautam *et al*, *Chem. Phys. Lett.* **442**, 311 (2007)
- [6] S Gautam *et al*, *Pramana - J. Phys.* **71(5)**, 1153 (2008)
- [7] R Mukhopadhyay *et al*, *Phys. Rev.* **E66**, 061201 (2002)
- [8] S L Chplot *et al*, *Pramana - J. Phys.* **33**, 595 (1989)
- [9] Marc Bee, *Quasielastic Neutron Scattering* (Adam Hilger, Bristol, 1988)