# Simultaneous Measurement of Self- and Transport Diffusivities in Zeolites

H. Jobic,[1] J. Kärger,[2] and M. Bée[3]
[1]*Institut de Recherches sur la Catalyse, CNRS, 2 Avenue Albert Einstein, 69626 Villeurbanne, France*
[2]*Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany*
[3]*Laboratoire de Spectrométrie Physique, Université Joseph Fourier, 38402 St. Martin d'Hères, France*

(Received 1 December 1998)

We have used quasielastic neutron scattering to derive the self- and transport diffusion coefficients of hydrogen molecules adsorbed in Na*X* zeolite. For $H_2$, incoherent scattering is dominant so that self-diffusion is measured. For $D_2$, the coherent and incoherent contributions are of the same order of magnitude so that both collective and individual motions can be characterized. At low $D_2$ concentration, the self- and transport diffusivities have similar values. For higher loadings, the transport diffusivity increases rapidly and exceeds the self-diffusivity. Only close to the saturation of the zeolite does the transport diffusivity start to decrease. To our knowledge this is the first time that transport and self-diffusion coefficients have been measured simultaneously for an adsorbed molecule. In contrast to numerous examples where discrepancies have been stated, these results are in agreement with each other. [S0031-9007(99)09209-1]

PACS numbers: 68.35.Fx, 61.12.Ex

As crystalline "sponges" with pores of molecular dimension, zeolites have become popular as environmentally friendly key materials for numerous industrial applications, including adsorption, catalysis, and ion exchange. In many cases, their efficiency is controlled by intracrystalline diffusion [1,2]. However, there is a remarkable mystery about its rate: The diffusivities measured at equilibrium are often found to be much larger than under nonequilibrium conditions [3,4], though standard theory would allow only the reverse situation [1,5]. Over many years, it has been a matter of controversy whether this discrepancy is but an artifact generated by the different temporal and spatial scales of observation of the experimental techniques. Applying quasielastic neutron scattering to the diffusion of hydrogen molecules in zeolite Na*X*, for the first time this source of discrepancy could be excluded.

Diffusivities which are measured under the influence of concentration gradients, i.e., under nonequilibrium conditions, are generally referred to as transport diffusivities, $D_t$. They are determined by macroscopic methods like gravimetry, volumetry, chromatography, or frequency response techniques. By contrast, self-diffusivities $D_s$ are measured under equilibrium conditions by microscopic techniques, viz. quasielastic neutron scattering (QENS) and pulsed-field gradient (PFG) NMR, which cover molecular displacements over nanometers and micrometers, respectively. Good agreement has been observed in recent years between the results obtained from the two microscopic techniques and from equilibrium molecular dynamics (EMD) simulations (e.g., Refs. [6,7]).

For comparison with the self-diffusivities, the transport diffusivities are often represented in terms of the so-called corrected diffusivity, $D_0$, which is defined by the relation,

$$D_t(c) = D_0(c)\left(\frac{d\ln p}{d\ln c}\right), \qquad (1)$$

where $c$ denotes the adsorbate concentration in equilibrium with the pressure $p$. The term $(d\ln p/d\ln c)$ is the thermodynamic factor. Adsorption by zeolites is generally described by a Langmuir-type isotherm so that the thermodynamic factor is equal to or larger than 1. The behavior of non-Langmuir systems is impossible to predict so that more experimental and theoretical work is needed in this case. In first order approximation (i.e., neglecting cross-correlation effects) one can assume $D_0 \approx D_s$. Thus one has to expect that $D_t \geq D_s$, which is in contrast to a series of experimental studies [3,4].

For unveiling the origin of the violation of Eq. (1), one needs an experimental technique which allows the simultaneous measurement of transport and self-diffusion. QENS is at the time being the only technique where both $D_s$ and $D_t$ can be measured. The self-diffusivity is obtained by following the motion of tagged molecules. The transport diffusivity measures the evolution of local concentration gradients. We have applied the QENS technique to a molecule adsorbed in a zeolite, to measure for the first time both diffusivities simultaneously.

For the hydrogenous molecules studied so far (e.g., Ref. [8]), the scattering is essentially incoherent because of the large incoherent cross section of the hydrogen atom. This means that the motion of one individual proton, and therefore, of one given molecule, will be followed. Neutrons are Doppler shifted by molecules moving on a comparable time scale, typically $10^{-8}$–$10^{-12}$ s. If the diffusion is isotropic, like in Na*X*, the energy spectra of the scattered neutrons correspond to Lorentzian functions. At small values of the neutron momentum transfer, $Q$, corresponding to large distances, their half width at half maximum (HWHM) is simply $D_s Q^2$, where $D_s$ is the self-diffusion coefficient [9].

If the scattering from the molecule is predominantly coherent, collective motions are probed. First, coherent scattering involves time-dependent pair correlations, which can be related to $D_0$ [10]. Second, the thermodynamic factor is related to the quasielastic intensity at small $Q$ values. Therefore the transport diffusivity $D_t$, defined by Eq. (1), can be determined. This coefficient can be obtained from measurements at equilibrium, because there are natural density fluctuations in the system.

If a scatterer with both incoherent and coherent contributions is selected, it is then possible to measure $D_s$ and $D_t$ simultaneously. This has been accomplished by Ross and co-workers with deuterium in niobium [11–13].

We have performed such an experiment with $D_2$ adsorbed in Na$X$ zeolite. A molecule with a small radius was selected to minimize the rotational contribution to the scattering (for a molecule, the broadening due to the translation is convoluted with the rotation). For small $Q$ values, the quasielastic spectra can be analyzed using two Lorentzians, due to the incoherent and coherent cross sections of $D_2$. However, even in this simple case, we found that it was difficult to fit reliably the spectra with two Lorentzians and a background. The difficulty was resolved by studying the diffusion of $H_2$ at the same concentrations: It was then possible to fix the width of the incoherent contribution of $D_2$ after correcting from the mass difference between the two isotopes.

The measurements were performed at 100 K (the zeolite acts as a catalyst to reach thermal equilibrium), at six different loadings: from 0.8 to 7.5 molecules per supercage, on average. At this temperature, orthopara mixtures are obtained. At 100 K, the ortho/para ratio is 1.6 for $H_2$ and 2.1 for $D_2$. The scattering cross sections of the mixtures were calculated by taking into account the spin correlations and the rotational levels of the molecules [14]. For $H_2$, the ratio coherent/incoherent scattering is 0.03 so that incoherent scattering dominates and only the self-diffusion is measured. For $D_2$, the ratio coherent/incoherent is 4.43; therefore the two contributions will contribute to the scattering, and both $D_s$ and $D_t$ can be determined.

The QENS spectra of $H_2$ at the different loadings were obtained after subtraction of the signal of the zeolite. The data could accurately be fitted with a Lorentzian function, convoluted with the instrumental resolution. The HWHM of the Lorentzians is reported in Fig. 1 as a function of $Q^2$. All the spectra could reasonably be fitted simultaneously with a jump diffusion model [15]. There are two parameters in this model: the time between jumps (the residence time on a given site) and the jump length. The broadening behavior calculated from this model is shown in Fig. 1 as a continuous line. We have derived the self-diffusion coefficients from the broadenings determined at small $Q$ values, in a range where the molecular motion follows Fick's law (linear variation of the width). The first $Q$ value corresponds to a length scale of 30 Å; this is larger than the cage-to-cage distance so that one is really measuring long range diffusion. The mobility of $H_2$ in Na$X$ has also been obtained by PFG NMR [16]; the diffusivities are the same within experimental error, which confirms the validity of the QENS analysis. On the other hand, the neutron diffraction experiments performed so far on this system [17] did not locate the adsorption sites so that the interpretation of the jump mechanism is still preliminary. The values of $D_s$ reported in Fig. 2 correspond to the self-diffusivities of $H_2$ divided by $\sqrt{2}$; the estimated error is of 20%. There is clearly an increase of the diffusivity for larger concentrations, a result also found by PFG NMR [16]. This shows that there is no gaslike diffusion and that the molecules are in interaction with the sodium cations, in agreement with a jump diffusion model. As the concentration increases, the residence time determined by

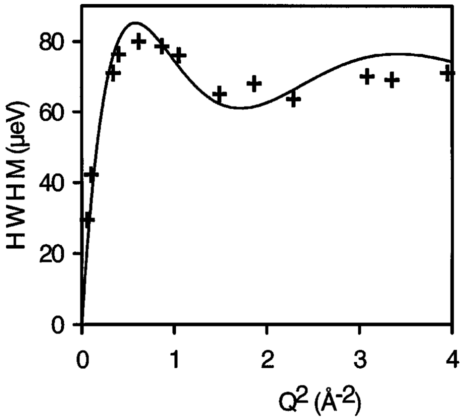

FIG. 1. Broadenings of the elastic peak vs $Q^2$ for $H_2$ in Na$X$ zeolite ($T = 100$ K, 7.5 molecules per supercage, on average). The crosses (+) are obtained from individual fits of the spectra. The curve corresponds to a simultaneous fit to all spectra, with a jump diffusion model: jump length = 5.9 Å; residence time = 9 ps.

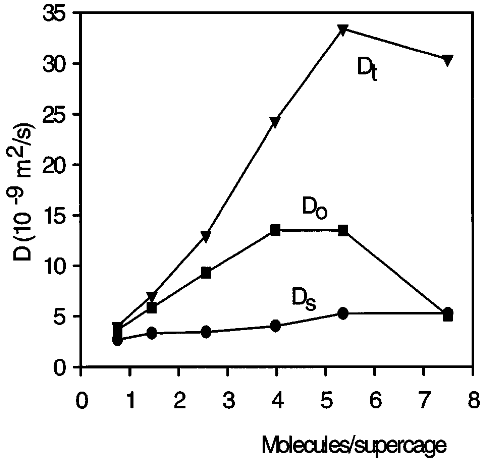

FIG. 2. Different diffusion coefficients obtained for $D_2$ in Na$X$ zeolite, as a function of loading. $D_s$, $D_0$, and $D_t$ are, respectively, the self-, the corrected, and the transport diffusion coefficients.

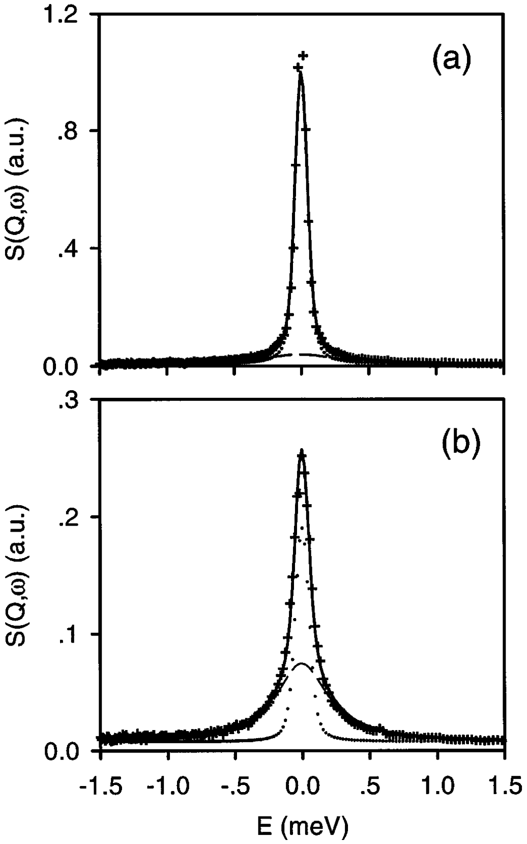

FIG. 3. Comparison between experimental (+) and calculated QENS spectra obtained for $D_2$ in Na*X* zeolite at (a) $Q = 0.58$ Å$^{-1}$ and (b) $Q = 1.22$ Å$^{-1}$. The dotted line corresponds to the incoherent contribution, the dashed line to the coherent one, and the solid line is the sum of both contributions ($T = 100$ K, 2.6 molecules per supercage, on average).

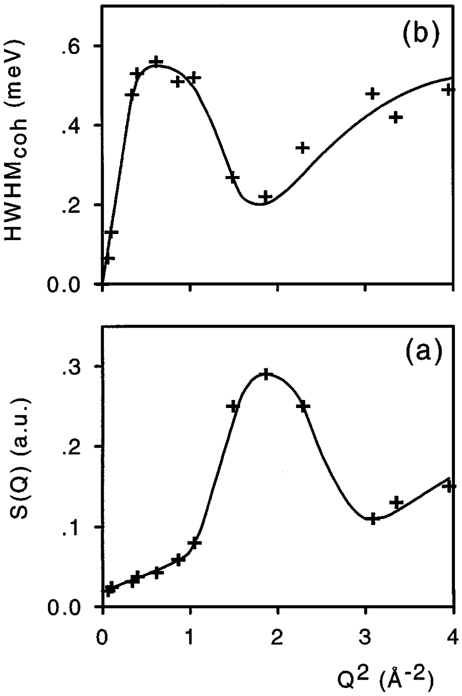

FIG. 4. (a) Coherent intensity for $D_2$ in Na*X* as a function of $Q^2$; (b) width of the coherent scattering vs $Q^2$ ($T = 100$ K, 4 molecules per supercage).

QENS decreases so that $D_s$ increases, indicating a weaker interaction with the cations.

For $D_2$, two contributions were taken into account (Fig. 3). The HWHM of the Lorentzian due to the incoherent part of the scattering was fixed. The HWHM and the relative intensity of the Lorentzian corresponding to the coherent part was fitted to the spectra. The relative intensity of the coherent scattering is proportional to a structure factor $S(Q)$. This quantity is shown in Fig. 4(a) as a function of $Q^2$, to visualize the dip in the width of the coherent scattering for the maximum of the structure factor [Fig. 4(b)]. This effect was first predicted by de Gennes [18] and is designed pictorially as the de Gennes narrowing. The maximum of $S(Q)$ at $Q^2 = 1.9$ Å$^{-2}$ corresponds to an intermolecular distance of 4.6 Å (the position of the maximum is hardly affected by the loading). The HWHM in Fig. 4(b) corresponds qualitatively to a jump diffusion model (cf. Fig. 1), narrowed by $S(Q)$. The solid line in Fig. 4(b) is just a guide for the eye, since it is not possible to describe analytically the $Q$ dependence of the broadening because of correlation factors [11,12], and because the model with a fixed jump length does not fit perfectly the data (this can be seen in Fig. 1). The transport diffusivity is determined at small $Q$ values, so that it is independent of any model, as for $H_2$. The values obtained at the different loadings are reported in Fig. 2; the estimated error is of 50%.

It appears from Fig. 2 that the self- and transport diffusivities are comparable at low loadings, but there is a very large increase of $D_t$ with the loading. Such an increase of the transport diffusivity has been calculated from nonequilibrium molecular dynamics (NEMD) [10,19], but it has never been observed experimentally so far. For a concentration of 5.4 molecules per supercage, on average, the ratio $D_t/D_s$ is of 6.4. Close to the saturation of the zeolite (9 molecules per supercage in our experimental conditions), the transport diffusivity decreases which means that the collective motions become affected by the packing density. The corrected diffusivity, $D_0$, was obtained from $D_t$ and from the thermodynamic factor calculated by fitting a Langmuir isotherm to the adsorbed quantities. It appears that the corrected diffusivity is not constant, this assumption being often made in the interpretation of macroscopic data [4].

Our experimental results provide clear evidence that, for $H_2$ in Na*X*, the transport diffusivities exceed the self-diffusivities, except at low loadings. The behavior of more complex adsorbates remains to be tested. However, by filling the gap between microscopic equilibrium methods and macroscopic nonequilibrium techniques, coherent QENS has the potential to determine what the correct diffusivities are.

The neutron experiments were performed at the Institut Laue-Langevin, Grenoble, France, using the IN6 spectrometer. We thank this institute for the allocation of beam time and Dr. A. J. Dianoux for his help during the measurements. Support by the Deutsche Forschungsgemeinschaft (SFB 294) and the European Community (Joule programme CT95-0018) is gratefully acknowledged.

---

[1] J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York, 1992).
[2] N. Y. Chen, T. F. Degnan, and C. M. Smith, *Molecular Transport and Reaction in Zeolites* (VCH, New York, 1994).
[3] H. Jobic, M. Bée, J. Kärger, H. Pfeifer, and J. Caro, J. Chem. Soc. Chem. Commun. **1990**, 341 (1990).
[4] O. Talu, M. S. Sun, and D. B. Shah, AIChE. J. **44**, 681 (1998).
[5] D. N. Theodorou, R. Q. Snurr, and A. T. Bell, in *Comprehensive Supramolecular Chemistry,* edited by G. Alberti and T. Bein (Pergamon, Oxford, 1996), Vol. 7, p. 507.
[6] E. J. Maginn, A. T. Bell, and D. N. Theodorou, J. Phys. Chem. **100**, 7155 (1996).
[7] C. Saravanan, F. Jousse, and S. M. Auerbach, Phys. Rev. Lett. **80**, 5754 (1998).
[8] H. Jobic, M. Bée, and G. J. Kearley, J. Phys. Chem. **98**, 4660 (1994).
[9] M. Bée, *Quasielastic Neutron Scattering* (Hilger, Bristol, 1988).
[10] E. J. Maginn, A. T. Bell, and D. N. Theodorou, J. Phys. Chem. **97**, 4173 (1993).
[11] R. Hempelmann, D. Richter, D. A. Faux, and D. K. Ross, Z. Phys. Chem. Neve Folge **159**, 175 (1988).
[12] J. C. Cook, D. Richter, O. Schärpf, M. J. Benham, D. K. Ross, R. Hempelmann, I. S. Anderson, and S. K. Sinha, J. Phys. Condens. Matter **2**, 79 (1990).
[13] S. K. Sinha and D. K. Ross, Physica (Amsterdam) **149B**, 51 (1988).
[14] J. A. Young and J. U. Koppel, Phys. Rev. **135**, A603 (1964).
[15] C. T. Chudley and R. J. Elliott, Proc. Phys. Soc. London **77**, 353 (1961).
[16] N. K. Bär, H. Jobic, and J. Kärger, in *Proceedings of the 12th International Zeolite Conference, Baltimore, 1998,* edited by M. M. J. Treacy, B. K. Marcus, M. E. Bisher, and J. B. Higgins (MRS, Warrendale, 1999), p. 77.
[17] M. P. Fang, P. E. Sokol, and Y. Wang, Phys. Rev. B **50**, 12 291 (1994).
[18] P. G. de Gennes, Physica (Utrecht) **25**, 825 (1959).
[19] D. Nicholson (private communication).