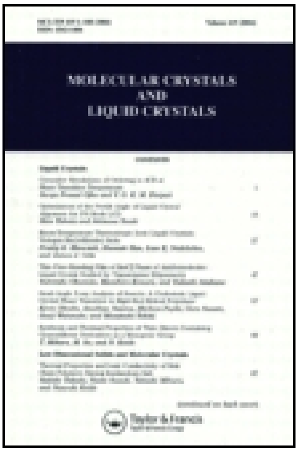

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NEUTRON SCATTERING STUDIES OF HOST-GUEST INTERACTION IN ZEOLITES

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Abstract : Neutrons are coupled with all the degrees of freedom of the molecules, and particularly suitable to study molecular dynamics. They provide at the same time spatial and dynamical informations and allow a good representation of the guest behaviour in the host topology. Experiments have shown the mobility and diffusivity of protonated molecules (CH_4, H_2 and HD) and the location of several hydrocarbons in zeolite crystals.

Introduction

In condensed matter, interactions between particles determine their relative equilibrium positions and orientations and their dynamical behaviour. Then the study of topology and dynamics of "host and guest" systems is a way for evaluating interaction forces.

Zeolites are microporous crystals presenting channels and cavities regularly distributed over the lattice(1). These cavities communicate through pores or windows. Consequently these materials offer to the physicists an interesting tool insofar as the cavities may be utilized to isolate one or several molecules, thus constituting a simple physical model.

Many techniques are applied to the study of inclusion compounds in zeolites. Few of them provide a physical insight at microscopic scale. Infrared spectrometry sees the guest molecule through its internal vibrations(2). For the observation of intermolecular relations, neutron spectrometry is a powerful technique(3,4,5). Thermal neutrons are coupled with all the degrees of freedom of the molecules; their wavelength is of the order of magnitude of the intermolecular distances. They provide *at the same time spatial and dynamical informations* (6). Complementary to X-Rays, since sensitive to hydrogen atoms, neutron diffraction can give the structural organization of the guest in the host. Complementary to N.M.R., neutron scattering allows the determination of the guest diffusion with a view on the local translational motion. Despite the complexity of the data analysis, neutron experiments are very attractive for experimentalists who benefit of the overall experimental set-up available at research reactors.,

Zeolites

Many structures exist, presenting rather complex channel frameworks. Natural zeolites and most of the synthesized forms are aluminosilicate materials. Their anionic framework is a tridimensional network of SiO_4 and AlO_4 tetrahedra linked to each other by the oxygens. It contains channels and interconnected voids. The negative charge due to the substitution of Si by Al is compensated by cations. The general formula is $M_{x/m}(AlO_2)_x(SiO_2)_y$ (m valence of the cation). The most common forms are the A, X and Y types. Their anionic frameworks are regular arrays of sodalite units (built of 12 Si or Al tetrahedra). Figure 1 shows two arrangements : simple cubic array and diamond-like array. The void volume and specially the pore opening depend on the sodalite arrangements. In *A-type* , the window connecting two cavities is an eight-oxygen ring of 5 Å diameter; the "unit cell" has 12.3 Å parameter and contains one cavity with an internal diameter of 11.4 Å. In NaA, because of the presence of a cation in each window, the effective pore size is equal to 4 Å; the exchange with divalent cations leaves the window unoccupied; in CaA the pore size is equal to 5 Å. The *X* and *Y-type* differ by their Si/Al ratio and exhibit the same topology :a large unit cell of 25 Å parameter contains 8 cavities (internal diameter 12Å) connected through 12-oxygen rings of 8 Å.

One can easily adjust the temperature and pressure values in order to prepare samples containing a given number of guest molecules per unit cell. The containers must be checked for leaks in order to avoid any rehydration during the experiments.

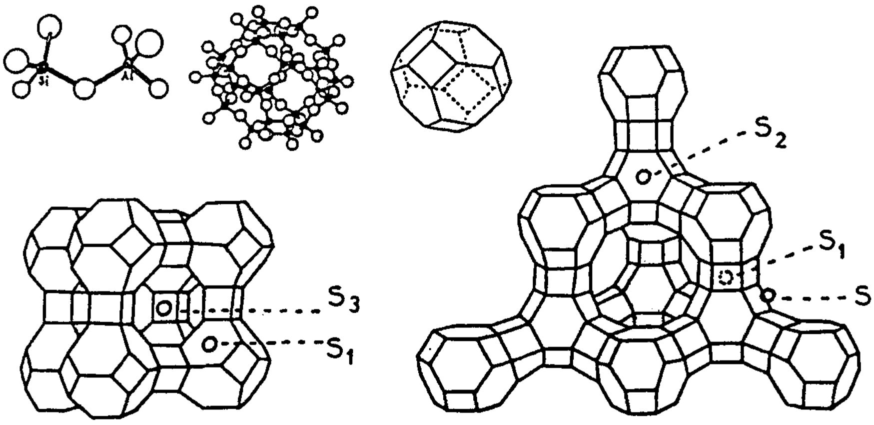

FIGURE 1 Shematic representation of A and X-type zeolites. SiO_4 and AlO_4 tetrahedra. Sodalite unit with and without oxygens. S_1, S_2, S_3 cationic sites.

Neutron Scattering

In neutron spectrometry one measures the change in both energy and direction of the neutrons scattered by the target because of the interaction with the sample nuclei. The probability that a neutron leaves the sample in a solid angle $d\Omega$, around the direction Ω, with an energy comprised between E and E + dE is the *double differential cross section* $\partial^2\sigma/\partial\Omega\partial E$.

For different reasons the scattering may be coherent or incoherent. The relative magnitude of the coherent and incoherent structure factors b depends on the nature of the nuclei. In general $b_{coh} >> b_{inc}$. The principal exception is the H atom. For structural analysis, it is preferable to work with deuterated instead of protonated samples. On the contrary dynamical measurements of individual guests requires a highly incoherent scatterer and hydrogen is the best candidate.

The *coherent* part contains all the *partial dynamical structure factor* . For periodic systems such as crystals, the integration over energy contains the *static structure factor* F_{hkl}. The corresponding spectrum is a series of Dirac peaks in well defined **q** directions whose position and intensity gives the symmetry of the lattice and the atom positions in the elementary cell$^{(4)}$. The intensity of a Bragg peaks in the scattering angle θ contains the structure factor of the hkl reflection : $F_{hkl} = \sum_{\alpha} b^{\alpha}_{coh} \exp -2\pi i\,(hx_{\alpha} + ky_{\alpha} + lz_{\alpha})$; $x_{\alpha}\ y_{\alpha}\ z_{\alpha}$ are the coordinates of the atom α. The diffraction patterns are analysed by standard refinement method developped for X-Ray scattering (7).

The *incoherent part* gives the *positional correlation* of the same atom at time 0 and t.

$$S^{\alpha}_{inc}(q,\omega) = \int dt\, e^{-i\omega t} \sum_{j=1} \left\langle e^{iq.R^{\alpha}_{j}(0)}\ e^{-iq.R^{\alpha}_{j}(t)} \right\rangle$$

The term in bracket , relates the positions of the same atom at different times. The investigation of the *dynamical* behaviour of sorbed molecules requires an analysis of the motion of each individual proton. To be useful it is necessary to define what kinds of motion are possible in order to define the relevant scattering functions. The intensity of the purely elastic component is the spatial Fourier transform of the trajectory of the atom, weighted by a probability of occupation. It has the dimension of a structure factor and is called the Elastic Incoherent Structure Factor (EISF) of the corresponding motion$^{(3)}$.

Equilibrium position of the guest in the host

The diffraction pattern of the loaded zeolite corresponds to the positions of the N ions of the host unit cell plus the M atoms of the guest molecule.When one consider that the guest does not perturb the zeolite lattice, the structure factor is :

$F_{hkl} = F^{zeolite}_{hkl} + F^{molecule}_{hkl}$. In general $F^{zeolite}$ is known from X-Rays analysis.

Until now, the most powerful contribution of neutron diffraction, even on powders, has been the guest location, especially for deuterated hydrocarbon molecules. The advantage of neutron comes from the fact that deuterium and carbon have similar scattering length which involves participation of all the nuclei of the guest molecules to the structure factor.

This has first been shown on methane and acetylene in NaA zeolite$^{(8)}$ in order to compare the experimental data with potential energy calculations. Working with samples containing less than 1 molecule per cavity, at temperatures such that the molecules are trapped$^{(2)}$, we determined the most energetic sorption site, analysing successively the diffraction patterns of the empty zeolite and the ones with the molecules. The locations of CD_4 and C_2D_2 (Figure 2) are found close to the less coordinated Na^+ cation (Na_{III}) but not far from two other Na^+ cations of the framework. The orientation of acetylene is perpendicular to the direction of the Na_{III} cation in agreement with X-Ray determination and potential energy calculation, showing that the triple bond C-C is in front of the cation. Other hydrocarbon molecules are under study such as n-alkanes in X-zeolites. Propane in NaX has been found in front of the four oxygen ring, the CH_3 groups beingdirected towards the framework walls (Figure 3).The heptane molecule has been found in a non linear conformation and located in front of the window(9) .

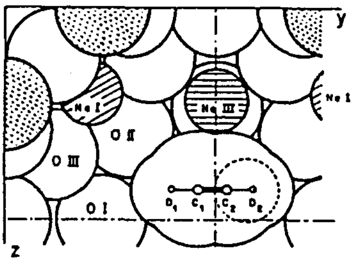

FIGURE 2 Position of acetylene in NaA zeolite.

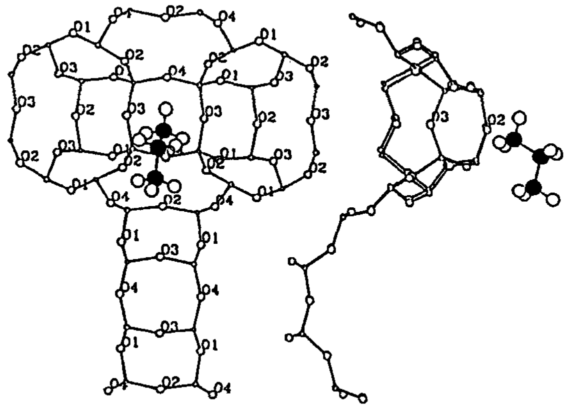

FIGURE 3 Position of propane in NaX. Stereo view.

Dynamical measurements

Neutron scattering allows to follow the motions of the whole molecule over distances comparable to the channel dimensions. Available neutron spectrometers measure energy transfer from a few tens of meV down to fractions of a μeV and momentum transfer in the range 10^{-2} - 10 $Å^{-1}$. This corresponds to distances $10^{-1} < r < 100$ Å, over time scale 10^{-14} - 10^{-8} s. This time range contains the characteristic times of the internal and external vibrations and of the rotational and translational motions.

In order to compare the dynamical behaviour of CH_4 in NaA with informations given by potential energy calculations (life-time in the potential wells, translational barriers),

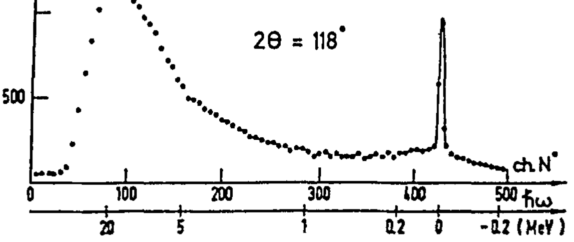

FIGURE 4 Neutron time-of-flight spectra of CH_4 in NaA, for two scattering angles

we worked on samples containing less than one molecule/cavity, from room temperature down to 4 K, with an elastic resolution of 25 μeV(10) (Figure 4). The long range translation was not accessible, meaning that the molecule remains in the same cavity for times longer than 10^{-10} s. The most interesting result is the evidence for the temperature dependence of the mobility of the molecule inside the cavity; this is reflected in the volume where the molecule moves. Figure 5 shows the change with temperature of the shape of the E.I.S.F. curves, revealing that: the molecule moves within the entire volume of the cavity at room temperature (motion in a sphere of radius R_1); when the temperature decreases, the trajectory gets closer and closer to the walls (volume comprised between R_1 and R_2, $R_2 \to R_1$) with increasing trapping time in sorption sites (non zero value of the EISF). Below 80 K the molecule is seen immobile during the time larger than the time resolution. Accordingly the frequency distribution of the external vibrations is broad and flat at high temperature, showing that the molecule vibrates with respect to the walls during very short times; at 4 K two broad peaks appear at 70 and 180 cm^{-1}(11).

In order to measure the long range translation, further experiments were performed on a neutron spin-echo spectrometer (time resolution 10^{-8} s)(12). In CaNaA zeolite the mean life-time of CH_4 inside a cavity is found equal to 4.10^{-10} s whereas it is longer than 10^{-8} s in NaA; this increase in the residence time shows the influence of the Na cations located in the windows connecting two cavities which block the intracrystalline diffusion. A diffusion-jump model, involving discrete sites (the cavities) on a cubic lattice of 12Å parameter, leads to an intracrystalline diffusion coefficient equal to 6 ± 1.5 $10^{-10} m^2 s^{-1}$ for CH_4 in CaNaA at 300 K (in agreement with N.M.R.). This experiment emphasized the interest of neutron spectrometry for the determination of the real diffusion coefficient (insofar as the translational motion of a particle is followed along few nanometers, the macroscopic defects of the crystallites do not interfere in the determination of the intracrystalline diffusion coefficient).

The ensemble of experimental data collected on CH_4 in NaA have been compared to calculated results from a numerical simulation of the dynamics(13). This has been a great support for checking the validity of the potential model involved in the calculation.

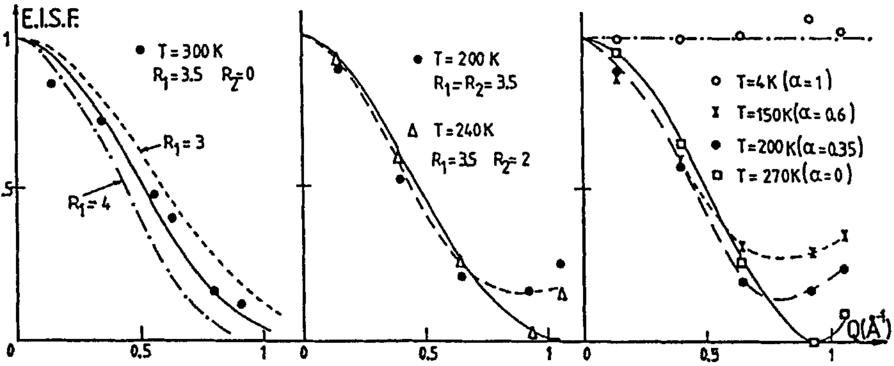

FIGURE 5 Elastic incoherent structure factor vs the momentum transfer Q, for CH_4 in NaA at several temperatures.

The dynamical behaviour of **H_2 and HD** sorbed in NaA zeolite has been measured by incoherent quasi-elastic scattering(14,15). The experiment was carried on samples loaded with 1.2 mol/cav and analyzed as the superposition of scattering from two populations : one made up of molecules with a motionless centre of mass (i.e. with characteristic time $>10^{-10}$ s.), the others having a long range translational motion; the proportion of each varies with temperature, the molecules being all at rest below 50 K (no quasielastic scattering) and fully-translating above 150 K (no elastic peak). These temperatures are only a little bit lower than for methane in NaA. This is not very surprising since the interactions of these molecules with the zeolite framework similar. The quasi-elastic part of the spectrum is satisfactorily fitted with a single Lorentzian, its width Δ varying with the momentum transfer q and with the temperature. A liquid-like jump diffusion model, where the molecule undergoes isotropic jumps of mean length $\bar{l}$ and is at rest for a time τ_0 accounts for the width Δ in the entire (q,T) range (Figure 6). The mean jump length $\bar{l}$ his independent of temperature and equal to 0.39 nm for H_2 and 0.33 for HD (in the ratio of the square root of their masses), τ_0 increasing when T decreases (τ_0=10.8 ps at 100K).

On the other hand the temperature dependence of the diffusion coefficients points out an unexpected feature. As a matter of fact each result can be represented on an Arrhenius plot but this leads to different D_0 values and different activation energies, and to $D_{HD} > D_{H2}$ at high temperature. This result has no physical meaning since the interaction of the zeolite with isotopic species must be identical, and heavy molecules diffuse more slowly than light ones. The explanation has been found from quantum mechanics(16). Expansion of the free energy of a particle evolving in a potential U(r) provides the temperature dependence of the diffusion coefficient :

$$D = D_0 \exp\left[\frac{E}{RT} - \frac{A}{m(RT)^2}\right] \quad \text{with} \quad A = \frac{h^2}{24}\ \Delta(U(\mathbf{r}))$$

In zeolites, the correction term of quantum origin A is considerably enhanced because of the very strong and very rapid change with distance to the cavity walls of the electric field created by the cations. In this way it must be taken into account even at temperatures as high as 100 K for such light molecules. The fit to the experimental data can be done with a unique set of parameters : D_0 = 16.4 $10^{-9}m^2s^{-1}$ and $E_{H_2} = E_{HD}$ = 450 K (Figure 7). From the value of the second derivative of U(r), one deduces the external vibrations, 350 and 290 cm^{-1} for H_2 and HD.

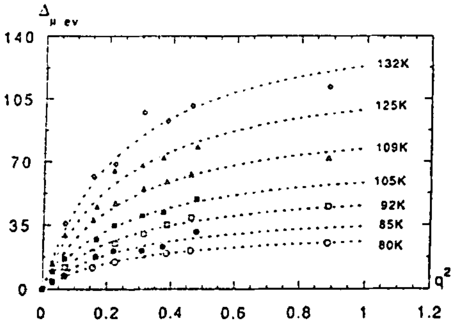

FIGURE 6 Width vs q^2 of the quasielastic scatteringof hydrogen in NaA and fit with a liquid-like diffusion model .

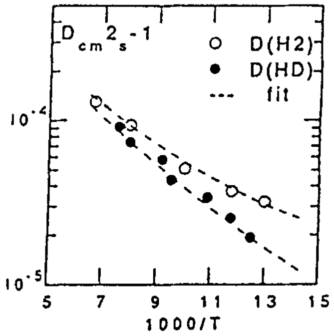

FIGURE 7 Variation with temperature of the coefficients of H_2 and HD and fit with the quantum correction.

Conclusion

Neutron diffraction found to be a method by which it is possible to locate the guest molecule in zeolites since all the atoms contribute to the structure factor, especially for hydrocarbon molecules after substitution of hydrogen with deuterium. Measurements in a large range of temperatures allow the determination of the most energetic sorption site.

Concerning the dynamical behaviour, the specific advantage of neutron scattering is the ability to determine the volume in which the guest (essentially protonated molecules) evolves during a given time interval. On the time scale of 10^{-10} s, the motion of the methane molecule is restricted to the volume of a NaA cavity whereas the H_2 molecule acts as a quasi free particle in the crystal. Nevertheless these different behavior cannot be attributed to different strength of the host-guest interaction; they have been related to the difficulty of CH_4 in crossing the windows connecting two cavities. The experiments have shown that their local diffusive motions have similar activation energies. The major difference between these two molecules comes from their size (4 Å and 2.2 Å) relative to the size of the window aperture (4 Å)in NaA zeolite.

The last but not the least advantage of neutron spectroscopy is its ability to measure *long-range* translational motions over *short* distances, of the order of a few unit cells. Therefore diffusion coefficient measurements are free of spurious effects due to defects in the crystals.

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* Neutron experiments performed at Institut Laue Langevin (ILL) and Laboratoire Léon Brillouin (LLB).