Molecular Motion of Ferrocene in a Faujasite-Type Zeolite: A Quasielastic Neutron Scattering Study

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We study the molecular motion of ferrocene $Fe(C_5H_5)_2$ locked up in the supercages of KY zeolite at temperatures 22 K ≤ *T* ≤ 238 K by means of quasielastic neutron scattering. The geometry of the motion is determined to be a 5-fold internal jump reorientation of the cyclopentadienyl C_5H_5 rings around the symmetry axis of the ferrocene molecule. We also obtain the mean residence time for these jumps as well as the activation energy for the process. We compare with NMR results on ferrocene in faujasite-type zeolites and with quasielastic neutron scattering results on pure ferrocene.

Introduction

Recently, Overweg et al.[1] have studied the molecular motions of ferrocene molecules $Fe(C_5H_5)_2$ locked up in the supercages of faujasite-type zeolites by means of NMR spectroscopy. They concluded that for temperatures *T* below 225 K the ferrocene molecules have no translational freedom, the only motion being a, on the time scale of NMR experiments (∼microseconds), very rapid internal jump rotation of the cyclopentadienyl C_5H_5 rings about their 5-fold axes. The actual value of the residence time τ of the rings at each site was determined by NMR to be much smaller than microseconds. Here we study at various temperatures the dynamics of ferrocene in a KY zeolite by means of quasielastic neutron scattering with which we can probe motions at time scales of the order of nanoseconds as well as the geometry of the motion. For ferrocene in a KY zeolite it is found that the motion is consistent with an internal jump rotation of the rings about their 5-fold axes. The residence time $\tau(T) = 62$ ps at $T = 202$ K. From the temperature dependence of $\tau(T)$ we determine an activation energy $E_a = 5.96$ kJ mol^{-1} needed for the rotations. We compare our results with those obtained by Overweg et al. and with quasielastic neutron scattering results on pure ferrocene.[2]

Quasielastic Neutron Scattering

The theoretical incoherent dynamic structure factor $S(Q,\omega)$, i.e., the scattered neutron intensity as a function of momentum *Q* and energy ω transfer, is for a powder sample and 5-fold jump diffusion over a circle with radius *R* given by[3]

$$S(Q,\omega) = A_0(Q)\, \delta(\omega) + B(Q,\omega) \qquad (1)$$

where the amplitude $A_0(Q)$ of the delta function $\delta(\omega)$ is the so-called elastic incoherent structure factor (EISF). $B(Q,\omega)$ is the quasielastic broadening

$$B(Q,\omega) = 2A_1(Q)\frac{1}{\pi}\frac{\lambda_1}{\omega^2 + \lambda_1{}^2} + 2A_2(Q)\frac{1}{\pi}\frac{\lambda_2}{\omega^2 + \lambda_2} \quad (2)$$

Here the amplitudes $A_l(Q)$ with *l* = 0, 1, 2 are given by

$$A_l(Q) = \frac{1}{5} + \frac{2}{5}j_0\!\left(2QR\sin\frac{\pi}{5}\right)\cos\!\left(\frac{2\pi l}{5}\right) + \frac{2}{5}j_0\!\left(2QR\sin\frac{2\pi}{5}\right)\cos\!\left(\frac{4\pi l}{5}\right) \quad (3)$$

with $j_0(x)$ the spherical Bessel function of zeroth order, and the half-widths λ_l with *l* = 1, 2 are given by

$$\lambda_l = \frac{2}{\tau}\sin^2\frac{\pi l}{5} \qquad (4)$$

where τ is the mean residence time of the molecule at one site. We note that τ depends on *T* but not on *Q*, as we will need below. We will also need that $A_0(Q) + 2A_1(Q) + 2A_2(Q) = 1$ for all *Q*, due to the normalization of $S(Q,\omega)$, i.e., $\int S(Q,\omega)\, d\omega = 1$ for all *Q*. We remark that the neutron spectrum observed in experiments is given by eq 1 folded with the resolution function $R(Q,\omega)$ of the spectrometer.

Experiment

The sample consisted of ferrocene $Fe(C_5H_5)_2$ loaded into the supercages of dehydrated KY zeolite, prepared similar to the way described by Overweg et al.[1] There is one ferrocene molecule in each supercage. The sample was contained in an indium sealed aluminum flat plate sample chamber.
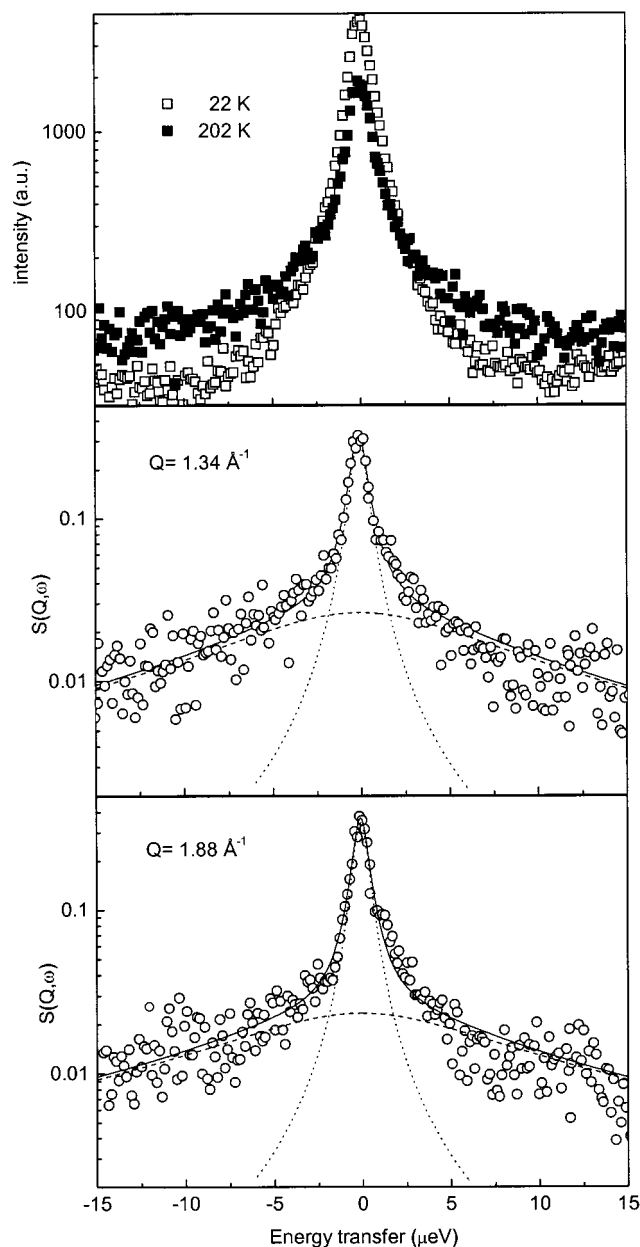
The neutron scattering measurements have been performed on the backscattering spectrometer BSS of the Forschungszentrum Jülich, Germany. First we used the Si(111) monochromator, resulting in an energy window $-15 \le \omega \le 15$ μeV and an energy resolution $\Delta\omega(Q) \approx 0.5$ μeV (hwhm), depending slightly on the momentum transfer *Q*. Second, the energy window was

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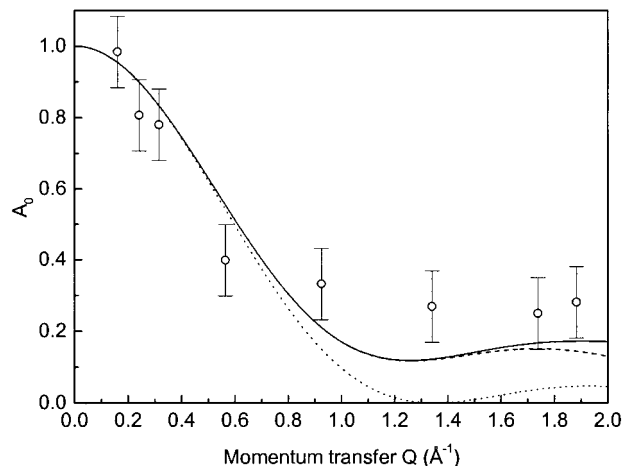† Delft University of Technology.
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Figure 2. Fitted values for the area of the central line A_0, the incoherent elastic structure factor EISF, for ferrocene in KY zeolite (open circles). The solid line gives the theoretical EISF according to a 5-fold jump reorientational model on a circle with radius $R = 2.33$ Å (cf. eq 1) and the dashed line for 10-fold and the dotted line for ∞-fold jumps (cf. Bée[3]).
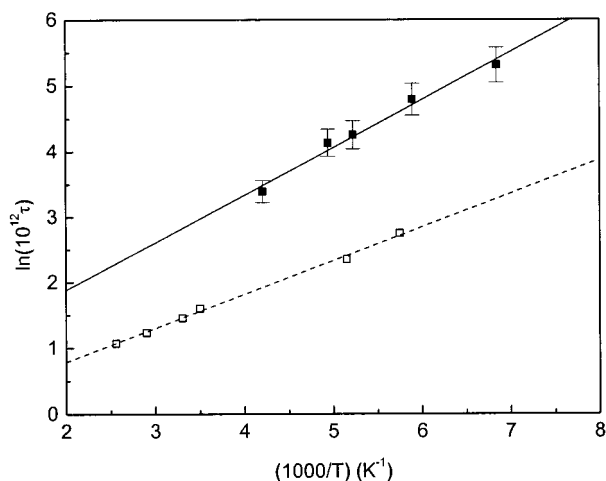
Results

Below 100 K no quasielastic broadening in the spectra of ferrocene in KY zeolite is observed; i.e., the spectra $S(Q,\omega)$ are indistinguishable from the resolution function $R(Q,\omega)$. Above 140 K a broadening starts to appear which is very clear at $T = 202$ K. In Figure 1a the spectra for momentum transfers $Q = 1.8$ Å^{-1} at $T = 22$ and 202 K are plotted. Clearly the central peak at $T = 202$ K is lower than the peak at $T = 22$ K, whereas the side wings have more intensity at $T = 202$ K than at $T = 22$ K. This means that at 22 K $B(Q,\omega) = 0$ and $A_0(Q) = 1$ while at 202 K $B(Q,\omega) > 0$ and $A_0(Q) < 1$ (cf. eq 1). The spectra at $T = 202$ K were subsequently fitted with the 5-fold jump reorientational model according to eqs 1−4, where $\delta(\omega)$ is replaced by the normalized resolution function $R(Q,\omega)$. A_0 and τ were taken as two independent fit parameters while A_1 and A_2 were determined by the relations $A_0 + 2A_1 + 2A_2 = 1$ and $A_2(Q)/A_1(Q)$ as given by eq 3 and $R = 2.33$ Å (i.e., the actual radius of the cyclopentadienyl rings[4]). The fits for $Q = 1.34$ and 1.88 Å^{-1} are shown in Figure 1b,c. We find that all the spectra $S(Q,\omega)$ can be fitted perfectly (like in Figure 1) with the 5-fold jump model where τ depends on T, but not on Q, as theoretically predicted.

The fitted values for the area of the central line A_0, the elastic incoherent structure factor, are represented in Figure 2 as a function of Q, as well as the theoretical EISF according to eq 3 with $R = 2.33$ Å. We also show (cf. Bée[3]) the theoretical predictions for 10-fold jumps and for continuous diffusion over a circle (i.e., ∞-fold jumps). The agreement between theory and experiment is sufficient to ascertain that one indeed observes a 5-fold jump rotation of the cyclopentadienyl rings of ferrocene over a circle with radius $R = 2.33$ Å. From the present experiment we find for the mean residence times $\tau(T) = 203$ ps (146 K), 121 ps (170 K), 71 ps (191 K), 62 ps (202 K), and 30 ps (238 K) as shown in Figure 3. The dependence of the mean residence times $\tau(T)$ on temperature T is well-described by an Arrhenius law:

$$\tau(T) = \tau_\infty \exp[E_a/k_B T] \qquad (5)$$

with E_a being the activation energy for a jump reorientation, to be determined from the slope of the curve in Figure 3. We find

Figure 1. Top: Neutron scattering spectra on ferrocene Fe(C$_5$H$_5$)$_2$ in KY zeolite for momentum transfer $Q = 1.8$ Å^{-1} at temperatures $T = 22$ K (open squares) and $T = 202$ K (solid squares) as measured on the BSS spectrometer in Jülich. Middle and bottom: Incoherent dynamic structure factors $S(Q,\omega)$ for momentum transfers $Q = 1.34$ and 1.88 Å^{-1} of ferrocene in KY zeolite (open circles), together with fits according to a 5-fold jump reorientational model (as explained in the text). The dotted line gives the central peak of the fit, and the dashed line gives the quasielastic broadening.

shifted to $-5 \leq \omega \leq 30$ μeV by using the Si$_{0.9}$Ge$_{0.1}$(111) monochromator, resulting in an energy resolution $\Delta\omega(Q) \approx 1.2$ μeV, again slightly depending on Q. In both setups the momentum transfer Q ranged from 0.2 to 1.9 Å^{-1}. We also performed in both setups measurements on vanadium to determine the full resolution function $R(Q,\omega)$ of the spectrometer, which, in good approximation, is of Lorentzian shape with hwhm $\Delta\omega(Q)$. Measurements on pure KY zeolite show quasielastic spectra also proportional to $R(Q,\omega)$. From the intensity we conclude, as expected, that the scattering from KY zeolite is far less than from ferrocene. Its (small) contribution is accounted for in the modeling procedure.

Figure 3. Residence times τ obtained from fits on neutron spectra with the 5-fold jump reorientational model as a function of temperature T for ferrocene in zeolite (solid squares, present work) and solid ferrocene (open squares, by Gardner et al.[2]). The solid line is a fit with an Arrhenius type law.

for E_a a value of $E_a = 5.96$ kJ mol^{-1} and for the preexponential factor $\tau_\infty = 1.63$ ps.

Discussion

We conclude that the geometry of the motion of the ferrocene molecules locked up in the supercages of KY zeolite is a 5-fold jump reorientation of the cyclopentadienyl C_5H_5 rings around the symmetry axis of the ferrocene molecule. Quasielastic neutron scattering spectra at different temperatures are perfectly fitted with such a model. Furthermore, the experimental elastic incoherent structure factor as a function of Q is in good agreement with the theoretical curve according to the 5-fold jump reorientational model. For small Q values we find that the radius of the circle is in agreement with the actual radius of the cyclopentadienyl rings (i.e., 2.33 Å), whereas for large values we find that the EISF tends to 1/5, where five is the number of sites used in the 5-fold model. These conclusions are consistent with those obtained by Overweg et al.[1]

We are also able to determine the mean residence time of the ferrocene molecule at one site, being 62 ps at 202 K. From the temperature dependence of the mean residence time we determine the activation energy for a jump reorientation of the cyclopentadienyl rings of the ferrocene molecule around their 5-fold axes to be 5.96 kJ mol^{-1}. The values of the mean residence times and for the activation energy are considerably larger than those obtained for pure ferrocene (as shown in Figure 3), meaning that the ferrocene molecule is more tightly bound in the supercages of the zeolite than in the pure solid state.

According to Brot,[5] the frequency ω_{libr} of libration of the ferrocene molecule in its potential well is of the order of $\pi\tau_\infty^{-1}$, where $\tau_\infty = 1.63$ ps is the prefactor in eq 5. Thus, one expects a libration peak in $S(Q,\omega)$ at $\omega \sim \omega_{libr} \sim 1.3$ meV, far outside the energy window of the BSS spectrometer used in the present work. We prepare experiments on the IRIS spectrometer of ISIS (UK) to confirm the existence of such a libration peak.

References and Notes

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