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Classification

Physics Abstracts

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Segmental motion of alkyl chains grafted on silica gel, studied by neutron scattering

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Résumé. — Les spectres de diffusion quasi-élastique de neutrons par C_nH_{2n+1} greffé sur silice, ont été mesurés pour $n = 4, 8, 12, 16, 18, 22$. La masse d'échantillon dans le faisceau est déterminée en utilisant la fonction de diffusion élastique et quasi-élastique, intégrée et extrapolée à $q = 0$, après correction de la diffusion cohérente. On obtient ainsi les fonctions de diffusion molaires des chaînes $S_n(q, \omega)$. En admettant que toutes les chaînes, quel que soit n , contiennent à leurs extrémités un même nombre n_e de maillons contribuant la même quantité S_e à S_n et que les CH_2 restant au milieu sont tous équivalents et contribuent chacun S_m , on obtient $S_n = S_e + (n - n_e) S_m$. Cette relation est vérifiée pour le facteur de structure incohérent élastique et utilisée pour calculer S_m . L'échantillon $n = 22$ a un comportement anormal en raison de l'interaction entre chaînes voisines qui devient possible. Les données sont en accord avec un modèle de saut impliquant 3 ou 5 liaisons à condition que la conformation à 5 liaisons dure trop peu pour pouvoir effectuer plusieurs sauts consécutifs. Le temps moyen entre sauts est, à température ambiante, $1,9 \times 10^{-11}$ s.

Abstract. — The quasielastic neutron scattering spectra of C_nH_{2n+1} grafted on silica are obtained for $n = 4, 8, 12, 16, 18, 22$. The well known difficulty in determining the mass in the beam is overcome by using (as a reference) the integrated elastic and quasielastic scattering function, extrapolated to $q = 0$. A correction for the coherent scattering contribution is applied. It is thus possible to determine the molar scattering functions of the chains $S_n(q, \omega)$. Assuming that in all chains there is a constant number n_e of end atoms contributing S_e to S_n for all n and that the remaining middle CH_2 are all equivalent, each contributing S_m to S_n , we obtain $S_n = S_e + (n - n_e) S_m$. This relationship is verified for the elastic incoherent structure factor and used to calculate S_m . The $n = 22$ case is left apart, its anomalous behaviour is explained by interaction between neighbouring chains. The data agree with a 3-bonds jump model with a time between jumps equal to 1.9×10^{-11} s at room temperature.

Alkyl chains of fixed length chemically bonded to the surface of high specific area porous silica gel offer interesting features for the study of the segmental motion of the chains by neutron scattering. Since the chains are bound to the solid, their mutual interaction is strongly restricted and they are expected to behave as if they were in a vacuum. The length of the chains being well defined, it is possible, by comparing chains of different lengths, to separate the contribution of the extremities from that of the middle. Alkyl grafted silica gels have been prepared

for a variety of purposes. They have been used for gas phase chromatography. The most important application is their use as stationary phases for high performance liquid chromatography and it is thought, at present, that 80 % of separations are performed *via* this method. In view of this importance precise synthesis methods have been developed on the basis of a detailed study of the grafting mechanism [1] and guarantee the reproducibility of the preparation.

Neutrons are scattered by all parts of the chains as well as by the silica itself. The spectrum obtained is the sum of contributions from the various scatterers.

(*) ERA CNRS 952.

To separate the contribution of the silica, a spectrum of bare silica is measured and subtracted after proper normalization taking into account its mass in the neutron beam. The same method is extended to the case of the chains : if one considers that the only difference between a C_8 and a C_{12} chain is the presence of 4 additional middle CH_2 for C_{12} , the rest of the CH_2 and CH_3 group behaving exactly the same way in each chain the difference of the properly normalized spectra will give the spectrum of the middle CH_2 . However, the spectrum of C_8 is not a minor correction as is the spectrum of silica and we had to devise a method to evaluate the mass of the sample in the beam for that case. Finally models for the CH_2 motion are discussed.

1. Preparation of samples. — The n alkyl chains are grafted onto a silica having a specific area of $520 \text{ m}^2/\text{g}$, via Si-O-Si bonds, by means of the reaction of silica silanol groups with n alkyltrichlorosilane [2]. One or two Si-O-Si bonds per chain can be formed. The main steps of the preparation are : acidic treatment of the silica, outgassing under vacuum at 180°C , reaction with a silane solution in xylene, washing with xylene to eliminate silane excess, hydrolysis of the non reacted Cl and elimination of residual solvent by heating at 80°C . The coverage is limited to $1.3 \text{ chains nm}^{-2}$ because only 30 % of the surface OH react. At the end of the preparation, two types of undesired scatterers may be left on the sample : silanol groups, which either didn't react or were created by hydrolysis, and solvent adsorbed on the chains.

The presence of silanol groups is apparent on bare silica neutron spectra, where they give a quasi-elastic peak. We shall see later that the silica correction is simpler because it is an almost purely coherent scatterer. This would not be true if too many OH were left. To avoid this, silica is exchanged with D_2O before outgassing. The incoherent quasielastic peak is then no longer visible.

In the case of grafted silica, the chains hide the silanol groups and it is doubtful that a D_2O exchange can take place. Even so the contribution of silanol groups is expected to be small compared to that of the chains. To check this, we have compared two grafted samples prepared with the same reactants according to the same procedure, except for the following two differences. One silica was exchanged with D_2O between acidification and outgassing, and the hydrolysis on this sample was carried out using D_2O . Thus the samples differed only by the replacement of H by D in silanols. It was found that the spectra obtained from these two samples were identical.

Finally it was important to check that all solvent was eliminated by a heat treatment at 80°C . This is because chromatographic evidence suggests that in different conditions some solvent is strongly held by the chains. Three samples of the same grafted

silica treated respectively with benzene, methanol and perdeuteromethanol before the final heating showed identical spectra, confirming that our procedure was sufficient to remove all solvent.

2. Neutron scattering experiments. — The neutron scattering experiments were performed with the IN5 time of flight spectrometer at ILL. The sample containers were tight aluminium boxes having the shape of discs with a thickness of 1 or 2 mm and a diameter 5 cm, which was larger than the cross-section of the neutron beam. The transmission of the sample and its container was always larger than 90 %, so that no multiple scattering correction was needed. The sample container was perpendicular to the beam, and it was left at room temperature.

The wavelength of the incident neutrons was 1 nm, giving a resolution of 0.018 meV. The counting time was of the order of 12 hours for each sample. A vanadium sample was used to normalize the counter efficiencies and check the resolution. The normalization of spectra and the correction for self-shielding were done with the IN5PDP program [3]. We thus obtained $S_n(q, \omega)$ for silica carrying C_nH_{2n+1} chains and $S_0(q, \omega)$ for bare silica, where q is momentum transfer, ω is energy transfer and S is the differential cross-section multiplied by the ratio of incoming and outgoing wave-vectors, called in the following the corrected cross-section (CCS) to avoid confusion with the usual scattering law, which is not practical for chemical systems.

3. Mass of chain in the beam and silica correction. — The mass of the sample in the neutron beam can be assumed to be proportional to the total mass of sample in the box, because the position of the box in the beam is very reproducible and the cross-section of the beam by the box is constant. However, this is true only if the sample is evenly spread in the box.

One can also measure the transmission of the sample. The counts on two monitors, M1 before the sample, M2 after the sample, are recorded and compared to the counts on the same monitors with an empty box, $M1_z$ and $M2_z$. The transmission is

$$T = \frac{M2}{M1} \frac{M1_z}{M2_z} = \exp[-\sigma m], \quad (1)$$

σ : total neutron scattering cross-section for 1 g of sample.

m : mass of sample in 1 cm^2 of the beam.

Only the part of the sample seeing neutrons which reach the second monitor is taken into account with this method.

We found that the ratio of the mass determination by these two methods showed variations of 20 %. It is thus not possible to rely on the even distribution of the sample in the box to calculate the mass in the beam.

We therefore used another method more directly related to the sample actually in the beam. According

to the definition and properties of the CCS, for incoherent scattering we have :

$$\int_{-\infty}^{+\infty} S(q, \omega) d\omega = M\sigma, \quad (2)$$

M : mass of sample in the beam.

Unfortunately, we cannot use time of flight spectra to calculate integral (2), because it is obtained at a fixed angle and not at a fixed value of q . For a fixed angle, q is a function of ω and equation (2) is not valid for $S(q(\omega), \omega)$. We may however restrict the integration in (2) to a small range of ω around $\omega = 0$. In that range q is nearly constant. Let $I(q)$ be this integral. It refers only to the quasielastic and elastic spectrum after subtraction of the coherent contribution. The loss of the inelastic part of the spectrum is taken into account by the Debye-Waller factor :

$$I(q) = M\sigma \exp[-Aq^2]. \quad (3)$$

The plot of $\text{Log } I(q)$ as a function of q^2 allows the extrapolation of $I(q)$ to $q = 0$, giving M .

Integration of experimental data over a small range of ω around the elastic peak gives $J_n(q)$ for C_n chains and $J_0(q)$ for bare silica. Coherent and incoherent scattering are mixed in these integrals. Coherent scattering varies from one sample to the other, and when the sample is crystalline, it is concentrated in Bragg peaks and can often be neglected in the regions between these peaks. In our case silica is amorphous and is practically a purely coherent scatterer. Thus, $J_0(q)$ can be subtracted from $J_n(q)$ after proper normalization, to give $I_n(q)$. However, the chains also contribute to the coherent scattering. To evaluate this contribution, we assume that the q dependence of the coherent scattering is the same for the chains and for the silica. Thus it should be possible to obtain the total coherent correction by multiplying $J_0(q)$ by an appropriate coefficient C_R .

To justify this we consider that the chains form a layer of uniform thickness around the grains and in the pores of the silica. This thickness should not exceed 0.5 nm which is 15% of the characteristic dimension of the pores and grains of the texture. The coherent scattering density is nearly the same for chains and for silica under these conditions, so that there is no contrast between the silica and the chain layer. Adding the chains is thus approximately equivalent to putting more scattering power in the same volume. The coefficient C_n is the ratio of the coherent total cross-section for silica with chains to that without them. The incoherent integrated CCS is then given by

$$I_n(q) = J_n(q) - C_n \frac{m_n}{m_0} J_0(q), \quad (4)$$

where m_n and m_0 are the masses of silica in the beam for the grafted and bare silica respectively.

$J_0(q)$ is determined by numerical integration in a

range of ω just sufficient to cover the elastic peak. $J_n(q)$ could be determined in the same way. However this procedure would involve two errors. Firstly a background which varies from counter to counter and from one experiment to another would be unavoidable. Secondly, the wings of the quasielastic peak would have to be cut off somewhere. Since the shape of the quasielastic peak is nearly that of a single Lorentzian, we determine the parameters of this Lorentzian plus a constant background by a fit of the data and calculate from these parameters the area of the quasielastic peak. The area of the elastic peak is determined by numerical integration and corrected for the Lorentzian quasielastic contribution on the same basis.

Although the physical basis of the calculation, summarized in equations (3) and (4), is simple, the practical procedure is complicated for two reasons. Firstly, the masses which we want to evaluate in equation (3) must be known in order to use equation (4). (Notice that the mass of silica m_n and the mass of chain M_n are connected through the chemical composition of the sample.) Secondly silica being a purely coherent scatterer our method cannot be applied to calculate m_0 . These difficulties are overcome since we do not want the exact masses m_n and M_n but quantities proportional to these masses in order to be able to compare the spectra of various chain lengths.

In addition the term $C_n \frac{m_n}{m_0} J_0(q)$ is much smaller than $J_n(q)$, except at low q so that an error on m_0 will not have too strong an effect on $I_n(q)$. This can be seen on table I where figures concerning the less favourable case $n = 16$ have been given.

Accordingly we proceed in the following way. A first value k_n of the ratio m_n/m_0 is calculated using the total mass in the boxes of grafted and bare silica. $I_n(q)$ is calculated and extrapolated to $I_n(0)$. We thus obtain a new set of values for m_n . We calculate a new set of values of k_n such that the k_n are proportional to the new m_n and that the average of k_n taken on all the samples is the same as before. This procedure leading from an old k_n to a new k_n is iterated. The value of the average k_n can also be improved by modifying m_0 . m_0 is adjusted with the requirement that the plots of $\text{Log } I_n(q)$ as functions of q^2 are the best straight line possible because this linearity indicates that the coherent scattering, that would not fit the straight line, has been correctly subtracted. We check that the adjustment of m_0 has little effect on the relative values of the m_n .

Finally, we obtain a set of k_n and use it to calculate also the incoherent CCS of the chains :

$$S_n^i(q) = S_n - C_n k_n S_0(q). \quad (5)$$

Table I.

q	0.26	0.37	0.48	0.59	0.70	1.13
J_n	283	214	212	201	208	124
$J_0 C_n k_n$	190	64	36	24	22	14

We also obtain a set of values of M_n practically independent of the adjustment of m_0 , and use it to calculate the specific scattering functions of the chains : $S'_n(q)/M_n$. Multiplied by the molar mass of the chains this gives the molar scattering functions $S_n(q)$ or S_n . These molar scattering functions are known only within an unknown constant factor but can be compared.

4. Contribution of the middle of the chains. — The scattering function of a chain is the sum of the scattering functions of one CH_3 and $n - 1$ CH_2 . We can consider the rotations around the C-C bonds as independent. Starting from the free end we take the rotation of CH_3 around the first C-C bond, then the rotation of $\text{CH}_2\text{-CH}_3$ around the second C-C bond and so on. As we progress inside the chains, the inertia of the moving part will increase and the motion will become slower. However it is well known [4] that other motions are possible, involving the displacement of a few atoms and synchronized rotation around several C-C bonds. In these movements the two ends of the chain are kept approximately immobile. It is then reasonable to assume that the characteristics of these movements of the middle of the chain are independent of the length of immobile chain on both sides. If we increase the length of the chain, the number of scatterers in the middle of the chain, capable of this type of motion, will increase. The behaviour of the extremities with one end free and the other blocked by silica, will be unchanged. Thus if n_e is the number of CH_2 or CH_3 groups belonging to the ends and if S_n, S_e, S_m are the molar scattering functions for the chain, the end part and one middle CH_2 respectively, we expect

$$S_n(q, \omega) = S_e(q, \omega) + (n - n_e) S_m(q, \omega). \quad (6)$$

The statistical accuracy of individual points of the surface $S(q, \omega)$ is not sufficient to allow a good test of this equation. However, an important feature of these quasielastic studies is the separation of the elastic and quasielastic part of the spectrum :

$$S_n(q, \omega) = B e^{-Aq^2} [EISF(q) \delta(\omega) + (1 - EISF(q)) L(\omega)]. \quad (7)$$

e^{-Aq^2} is the Debye-Waller factor of equation (3), $\delta(\omega)$ is the δ function representing the elastic peak, $L(\omega)$ is the broadened part, normalized to unity as is $\delta(\omega)$. $EISF$ is the elastic incoherent structure factor. The $EISF$ can be determined experimentally as the ratio

$$f = \frac{EL}{EL + QU}, \quad (8)$$

where EL and QU are the integrated intensities of the elastic and quasielastic peaks respectively [5].

In the ratio f , many factors common to EL and QU are eliminated and the statistical error on integrated intensities is small. In the case of the IN5 spectrometer the instrumental function into which the $\delta(\omega)$ function

is transformed has a triangular shape so that the distinction between the elastic and the quasielastic part is very clear. For all these reasons the best test of (5) is done with f equation (6) gives

$$EL_n = EL_e + (n - n_e) EL_m. \quad (9)$$

Let $\sigma_n, \sigma_e, \sigma_m$ be the total cross-sections of the complete chain, the end part and a CH_2 respectively. Another expression for equation (1) appropriate for the molar quantities now used, is

$$\frac{EL_n + QU_n}{\sigma_n} = \frac{EL_e + QU_e}{\sigma_e} = \frac{EL_m + QU_m}{\sigma_m} = K. \quad (10)$$

Dividing equation (4) by K we obtain

$$\sigma_n \frac{EL_n}{EL_n + QU_n} = \sigma_e \frac{EL_e}{EL_e + QU_e} + (n - n_e) \sigma_m \frac{EL_m}{EL_m + QU_m}, \quad (11)$$

or

$$\sigma_n f_n = \sigma_e f_e + (n - n_e) \sigma_m f_m. \quad (12)$$

Figure 1 represents the plot of $\frac{\sigma_n}{\sigma_m} f_n$ as a function of n , $m = \text{CH}_2$.

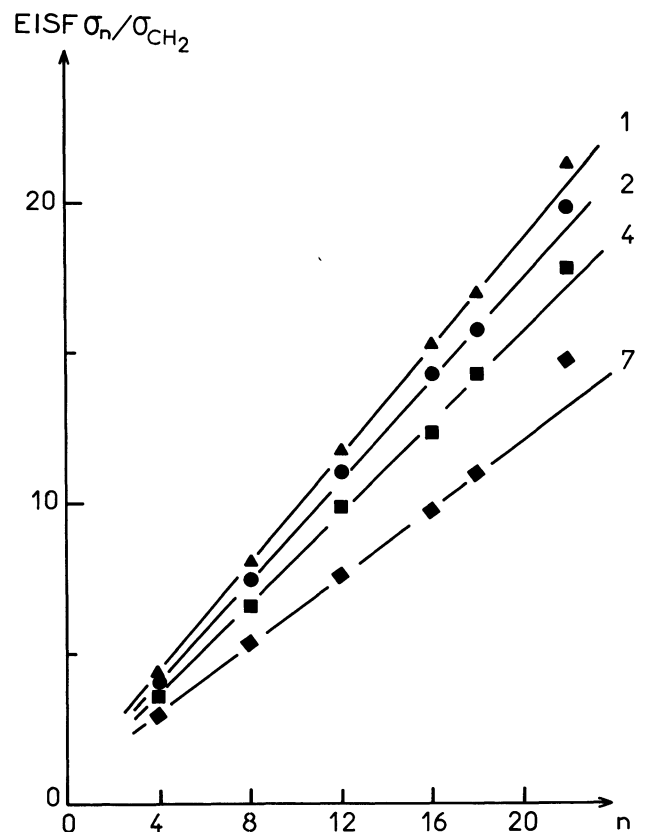


Fig. 1. — $EISF \sigma_n/\sigma_{\text{CH}_2}$ function of n : $q = 0.25 \text{ \AA}^{-1}$, $q = 0.37 \text{ \AA}^{-1}$, $q = 0.59 \text{ \AA}^{-1}$, $q = 1.13 \text{ \AA}^{-1}$.

The plot is linear for n between 4 and 18, in agreement with our hypothesis. When we add four CH_2 to a chain we increase the length of the middle chain. Therefore the contribution to $S_n(q, \omega)$ or to $\sigma_n f_n$ is the same. This is observed in passing from 4 to 8, 12 and 16. On the other hand, the C_4 chain by itself makes a different contribution to the $EISF$ because it is constituted of end parts. No anomalous behaviour is observed in passing from 4 to 8, and we conclude that the end parts involve at most four carbon atoms. Eight carbon atoms are sufficient to observe the middle CH_2 motion. The anomalous behaviour of $n = 22$ can be interpreted by the fact that these chains can, more so than the others, interact with each other and with the silica surface, especially inside the pores. This interaction slows down the motion, thus giving a larger $EISF$.

5. Model of the middle CH_2 motion. — Although the verification of equation (6) would be less conclusive because of poorer statistics, it can be used to calculate the complete spectrum of a middle CH_2 , discarding the $n = 22$ sample. The $EISF$ of a middle CH_2 can thus be calculated in two ways : either a Lorentzian fit of S_n to calculate f_n followed by determination of a slope, or else the reverse. The difference between the two is only a few percent, however, this is significant for an $EISF$. We think that the second procedure is more correct because, as we shall see, the single Lorentzian fit is fully justified for S_m whereas it is not for an S_n which involves contributions of the ends. The correct $EISF$ is given in table II.

The basic idea of models of intramolecular motion is that a chain spends most of its time in most stable conformations and, after an average time τ in one conformation, jumps rapidly to another [6a]. For an alkyl chain, the most stable conformations are obtained as part of a diamond lattice [4]. A jump involves the simultaneous movement of at least 3 C-C bonds. The 4-bonds motion is not considered for alkyl chains because it requires a conformation which is very improbable (pentane exclusion) for steric reasons. When the end atoms of the 3-bonds conformation are held fixed, the jump can occur only at the expense of some strain. This is not so for a special case of the 5-bonds motion, called the crankshaft motion [7].

The theory of jump models predicts a Lorentzian shape for the ω dependence $L(\omega)$ [6b], with a width $2/\tau$ independent of q and an $EISF$ of the form

$$EISF = \frac{1}{2} \left(1 + \frac{\sin qs}{qs} \right) = f_2(s), \quad (13)$$

Table II.

q	0.26	0.37	0.48	0.59	0.70	1.13
$EISF$ exp.	0.905	0.892	0.770	0.814	0.752	0.583
$EISF$ 3-bonds	0.955	0.913	0.862	0.805	0.747	0.575
$EISF$ 5-bonds (short lived)	0.950	0.903	0.847	0.786	0.726	0.558

where s is the jump length and the scatterer has only two positions available. When the scatterer can occupy three equidistant positions on a circle [5]

$$EISF = \frac{1}{3} \left(1 + \frac{\sin qs}{qs} \right) = f_3(s). \quad (14)$$

The three-bonds motion involves two positions for each scatterer whereas the 5-bonds motion involves three. The motion of all scatterers being synchronous, their contributions to $EISF$ can simply be added on, giving the general formula

$$EISF = \frac{1}{2^p} \sum_{j=1}^{2^p} f(s_j), \quad (15)$$

where

$$p = \text{number of moving } \text{CH}_2, \\ s_j = \text{jump length of the } j\text{th hydrogen atom.}$$

The jump distances are deduced from the bond lengths and angles. In both the 3- and 5-bonds cases there are

$$4 \text{ protons with } s_1 = 0.178 \text{ nm,} \\ 4 \text{ protons with } s_2 = 0.373 \text{ nm, and}$$

in the 5-bonds case there are in addition

$$2 \text{ protons with } s_3 = 0.224 \text{ nm,} \\ 2 \text{ protons with } s_4 = 0.429 \text{ nm.}$$

$$f = f_2 \text{ for the 3-bonds model,} \\ f = f_3 \text{ for the 5-bonds model.}$$

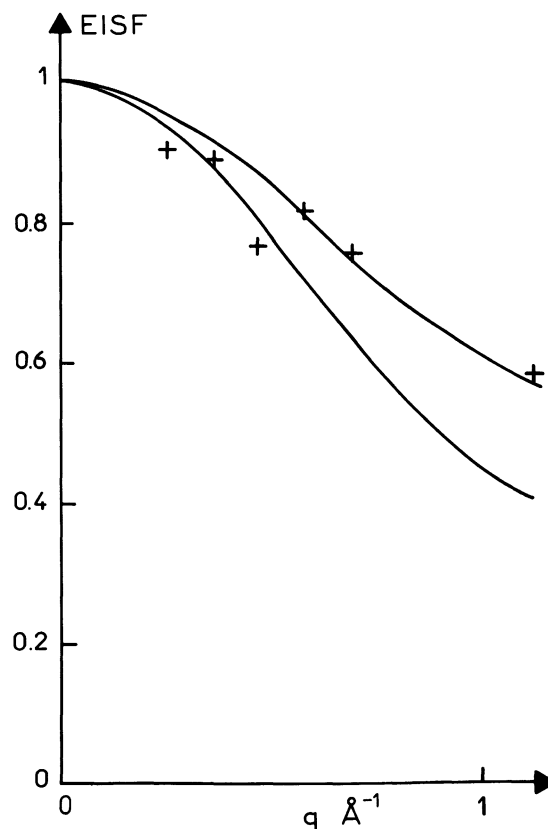


Fig. 2. — $EISF$ function of q : higher curve : 3-bonds model; lower curve : long lived 5-bonds model; + experimental points.

Figure 2 gives the curves of *EISF* for 3- and 5-bonds model together with experimental points. At low q the accuracy is poor because statistics are poor. At large q where the data are more reliable it is clear that the 3-bonds model is preferred. Notice however that if, in the 5-bonds model, we replace f_3 by f_2 in equation (15) we obtain an *EISF* which is very close to that of the 3-bonds model. The difference between these two versions of the 5-bonds model is the following : using f_3 means that the lifetime of the crankshaft conformation is sufficient to allow several $2\pi/3$ rotations, using all the possible positions. Using f_2 means that, after one jump, it is probable that another jump involving only a part of the crankshaft will take place and destroy this particular crankshaft. Our conclusion is that the longlived 5-bonds model is excluded whereas the short lived 5-bonds model cannot be distinguished unambiguously from the 3-bonds model.

Figure 3 shows for the shape of the quasielastic peak, a good agreement between the jump model prediction and experiment. More precisely we have fitted a single Lorentzian with constant background to the data for the highest q (Fig. 3). The width corresponds to a time between jumps equal to 1.9×10^{-11} s. For other q values the statistics are poorer and the fit was done using the same value for the width. There is no indication of any variation of the width with q .

6. Conclusion. — The method of data treatment presented in this paper is quite general, although the problem of the coherent contribution to the scattering has to be solved in each case. Our results show that, whenever a mixture of different chemical species is studied, it is possible to separate the contribution of one species to the neutron scattering by comparing spectra of samples containing different amounts of that species. This can apply for instance to adsorption when the coverage is changed, to solutions of various concentrations and to isotopic substitutions. The limitation of the technique is that these changes in coverage, concentration, etc. must not by themselves modify the behaviour of the studied species. Otherwise, the partial molar scattering functions determined by the experiment will be different from simple molar scattering functions and the interpretation will be more difficult.

For the chains grafted on silica studied here a clear conclusion concerning the model of motion of the middle CH_2 can be drawn. It is now possible to envisage the study of these solids in conditions closer to those of chromatography. Here the chains move freely whereas, with liquid chromatography, a solvent surrounds them. The effect of adsorbed molecules on the motion of the chains would help in understanding the retention mechanism of chromatography, that is the holding by the chains of molecules to be analysed,

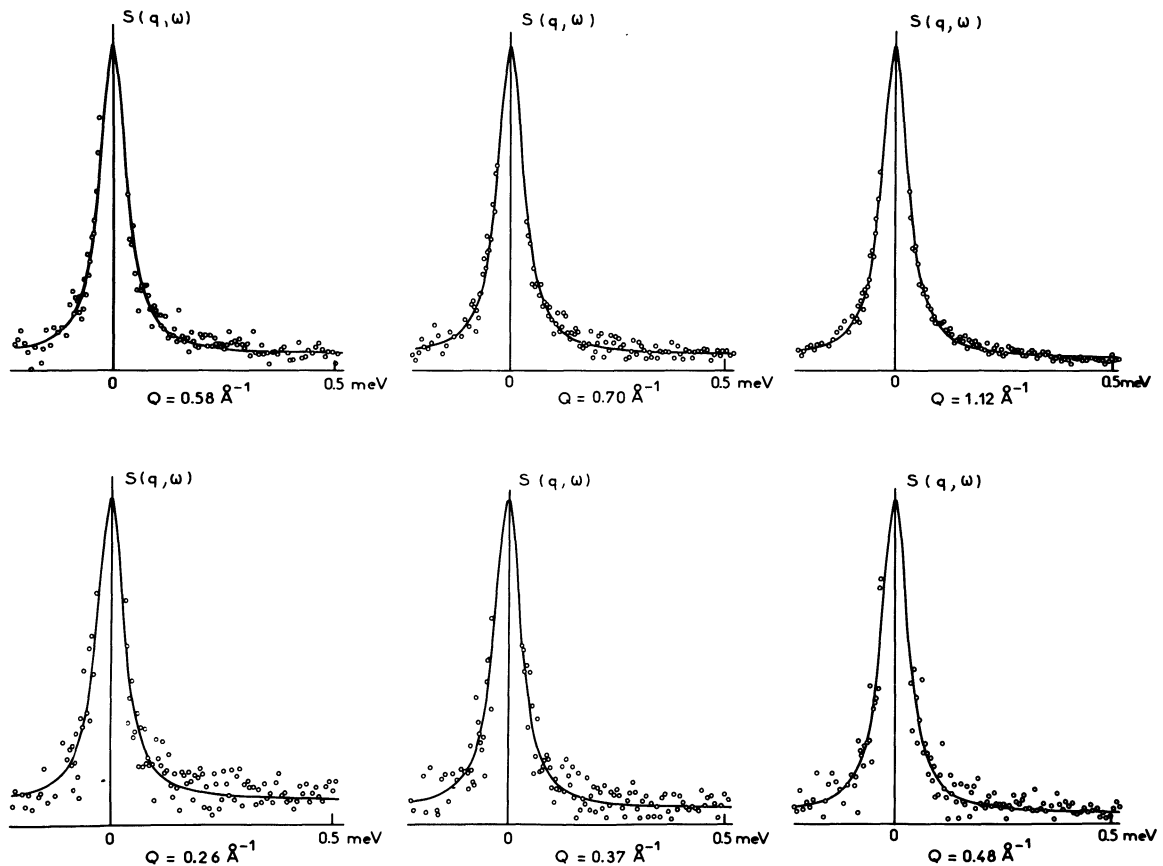


Fig. 3. — $S_m(q, \omega)$ (arbitrary units) function of ω (meV). (—) Calculated Lorentzian, (+) experimental points. The elastic peak is not represented.

in competition with the eluting solvent. In that respect a recent NMR study [8] dealing with polyethylen indicates that the observed motion shifted from 3-bonds to 5-bonds jumps when the temperature was increased. In the 3-bonds jump the chain is more strained than in the 5-bonds jump, the activation energy should therefore be larger for 3-bonds jump and they should dominate at high temperature. This is not the case and another reason has to be considered, the effect of the neighbouring molecules or local unfolding of the chain favoured by high temperature. The comparison of the motion of chains with and without adsorbed molecules would therefore be very interesting.

Finally comparison with chain motion in polyethylen seems difficult because the motion is strongly altered by the environment. A study on polyethylene gives a time which is an order of magnitude larger than the one we find [9]. Another study on $n\text{-C}_{33}\text{H}_{68}$ illustrates the complexity of the problem [10].

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