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dibromoalkane-urea inclusion compounds

Neutron scattering investigations of guest molecular dynamics in α, ω-dibromoalkane–urea inclusion compounds

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Abstract. Incoherent quasi-elastic neutron scattering (IQNS) has been used to investigate the dynamic properties of α, ω-dibromoalkane (guest) molecules (Br(CH$_2$)$_n$Br) constrained within the urea channel structure (host) in the crystalline α, ω-dibromoalkane–urea inclusion compounds. These investigations have been carried out on samples of urea inclusion compounds containing urea-d$_4$ to ensure that the incoherent scattering is dominated by the α, ω-dibromoalkane molecules, and the two experimental geometries of semi-oriented polycrystalline samples have been considered (specifically, with the channel axes of all crystals either parallel or perpendicular to the momentum transfer vector), allowing translational motions of the guest molecules along the channel to be investigated separately from reorientational motions of the guest molecules about the channel axis. The experiments have been performed as a function of firstly the experimental geometry, secondly the length of the α, ω-dibromoalkane molecule ($n = 8$–10) and thirdly the temperature (with particular interest in changes in the dynamic properties above and below the well established phase transition temperatures for these inclusion compounds). It is shown that in the low-temperature phase there is an oscillatory motion along the channel axis which becomes overdamped above the phase transition temperature. Above the phase transition temperature, the dynamic properties of the guest molecules can be understood in terms of translational motions along the channel (modelled as continuous diffusion between rigid impermeable boundaries) and reorientational motions about the channel axis (modelled as uniaxial rotational diffusion in a onefold cosine potential). Quantitative dynamic information relating to these motional models is presented.

1. Introduction

We are currently interested in the structural, dynamic and chemical properties of urea inclusion compounds containing a diverse range of organic 'guest' molecules. In these inclusion compounds, the urea molecules form an extensively hydrogen-bonded 'host' structure containing parallel one-dimensional channels that are densely packed with guest molecules [1, 2]. Within the urea channels the guest molecules are constrained to adopt an almost fully extended all-*trans* conformation [3]. In general, there is an incommensurate structural relationship [2, 4] between the periodic repeat distance c_h of the host structure along the channel axis and the periodic repeat distance of the guest molecules along the channel axis. We have shown recently [5, 6], by x-ray diffraction and other techniques, that urea inclusion compounds containing functionalized n-alkane guests exhibit new structural

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properties, particularly concerning the three-dimensional packing arrangement of the guest molecules. In particular, it has been shown [6] by single-crystal x-ray diffraction that, at room temperature, the guest molecules in the α, ω-dibromoalkane–urea inclusion compounds with $n = 7$–10 exhibit a characteristic three-dimensionally ordered packing arrangement in which $\Delta_g = \frac{1}{3}c_g$, where Δ_g denotes the offset, along the channel axis, between the positions of guest molecules in adjacent channels. This guest structure is rhombohedral, and a given single crystal of the inclusion compound usually contains two domains of this guest structure, differing in orientation from the host structure. Furthermore, the α, ω-dibromoalkane–urea inclusion compounds *also* contain regions in which the guest molecules are ordered only along the channel axis; the periodic repeat distance is the same (within experimental error) for the one-dimensionally ordered regions and the three-dimensionally ordered regions discussed above. We discuss these structural properties further in section 6. It is relevant to note that, in contrast with this situation for the α, ω-dibromoalkane guests, the molecular packing in the three-dimensionally ordered regions of the guest structure in n-alkane–urea inclusion compounds corresponds to $\Delta_g = 0$. It is interesting and important to speculate whether the presence of terminal Br atoms *vis-à-vis* CH_3 groups on the guest molecule gives rise to a similarly marked difference in the dynamic properties of the guest molecule.

It is known [8–10] that n-alkane–urea inclusion compounds undergo a phase transition from a low-temperature (LT) phase in which the host channel structure is orthorhombic to a high-temperature (HT) phase in which the host channel structure is hexagonal. This transition is also believed to be associated with an abrupt change in the dynamic properties of the n-alkane molecules, and it has been shown that these molecules undergo considerable *motion in the* HT *phase.*

Differential scanning calorimetry has shown that the α, ω-dibromoalkane–urea inclusion compounds undergo a phase transition similar to the well established phase transition for the n-alkane–urea compounds, and powder x-ray diffraction [15] has demonstrated the structural change in the host associated with the transition in the 1,10-dibromoalkane–urea inclusion compound is the same as that established previously [10] for the n-hexadecane–urea inclusion compound. To our knowledge, there have been only two previous studies of the guest molecular dynamics in α, ω-dibromoalkane–urea inclusion compounds. Early ^{1}H NMR studies of $Br(CH_2)_{10}Br$–urea by Bell and Richards [16] suggested, on the basis of $T_1(^1H)$ measurements, that there is rapid rotation of the guest molecules even at low temperatures. It was also suggested that, at higher temperatures, there are additional dynamic processes which were assigned as either segmental motions of the guest molecule *or reorientational motions of the urea molecules. Recent* ^{2}H NMR *studies of* n-*alkane–urea-*d_4 [17] and α, ω-dibromoalkane–urea-d_4 [18] inclusion compounds have indeed provided direct evidence for the occurrence of the latter motion at higher temperatures. Dielectric loss spectroscopy has also been used [19] to study the dynamic properties of $Br(CH_2)_{10}Br$–urea, and the fact that a signal is indeed detected for this inclusion compound suggests that the two end groups of the guest molecule are undergoing independent motions. A preliminary ^{2}H NMR study of $Br(CD_2)_{10}Br$–urea-h_4 [18] has also alluded to the existence of appreciable molecular motion in the HT phase of this material.

Although the dynamic properties of the guest molecules in n-alkane–urea inclusion compounds have been studied in detail via a wide range of experimental techniques (previous detailed neutron scattering investigation [11–14] of the n-nonadecane–urea-d_4 inclusion compound have been carried out, and we consider the results of these studies in comparison with our results on the α, ω-dibromoalkane–urea inclusion compounds in section 6), surprisingly little attention has so far been devoted to studying the dynamic properties

of functionalized guest molecules within the urea channel structure. In this paper, we report incoherent quasi-elastic neutron scattering results for semi-oriented polycrystalline samples of α, ω-dibromoalkane–urea-d_4 inclusion compounds; deuteration of the host molecules in these samples minimizes the incoherent scattering from the host, allowing the results to be interpreted in terms of the dynamic properties of the guest molecules alone. In these investigations, the neutron scattering was measured as a function of firstly the experimental geometry (momentum transfer vector either parallel or perpendicular to the urea channel axis), secondly the length of the guest molecule ($Br(CH_2)_n Br$; $n = 8$–10) and thirdly the temperature (with particular regard to differences in motional properties above and below the phase transition temperatures, indicated by differential scanning calorimetry, for these materials). The use of semi-oriented polycrystalline samples in these investigations allows motions of the guest molecules *along* the channel axis to be studied independently from reorientational motions of the guest molecules *about* the channel axis. The following two experimental geometries (figure 1) were considered.

(i) Momentum transfer Q parallel to the channel axis. This geometry allows motions of the guest molecules *along* the channel axis to be studied and is denoted $Q_{\parallel}$. In this geometry, the channel axes of all the crystals lie in the scattering plane. When these axes are aligned at an angle of 135° with respect to the incident neutron beam, the condition that the momentum transfer vector is parallel to the channel axis is satisfied for the scattering angle $2\theta = 90°$.

(ii) Q perpendicular to the channel axis. This geometry allows reorientational motions of the guest molecules *about* the channel axis to be studied and is denoted $Q_{\perp}$. In this geometry, the channel axes of all crystals are perpendicular to the scattering plane, and the momentum transfer vector is perpendicular to the channel axis for all values of 2θ.
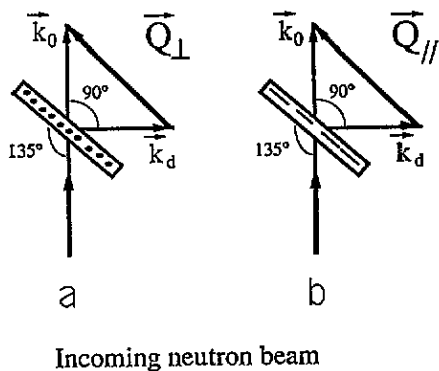

Figure 1. Experimental geometries: (*a*) momentum transfer vector Q perpendicular to the channel axis; (*b*) Q parallel to the channel axis for $2\theta = 90°$.

Theoretical models have been developed to describe the reorientational and translational dynamic properties of the α, ω-dibromoalkanes constrained within the urea channel structure, and the results from fitting these models to the experimental data are presented in this paper. A preliminary report of some of the main results in this work has been published in the *Proceedings of the International Conference on Neutron Scattering* held in Oxford (UK) in August 1991 [7].

2. Experimental details

Inclusion compounds containing α, ω-dibromoalkanes ($Br(CH_2)_nBr$; $n = 8$–10) in urea-d_4 were prepared by slowly cooling warm solutions of the α, ω-dibromoalkane and urea-d_4 in CH_3OD. The degree of deuteration of the urea molecules was shown by infrared spectroscopy to the greater than about 98%. Incoherent scattering arising from the included guest molecules therefore represents more then 92% of the total incoherent scattering from the sample. Powder x-ray diffraction confirmed that the crystals had the characteristic channel host structure of the conventional urea inclusion compounds.

For the neutron scattering experiments, single crystals (typical dimensions 0.5 mm × 0.5 mm × 5 mm) were placed in grooved aluminium containers such that the urea channel axes (crystallographic c axis of the host structure; prism axis of the hexagonal prismatic morphology [2]) of all crystals were parallel to each other. However, the orientations of the crystals with respect to rotation about this axis were random. The sample thickness was chosen to correspond to a transmission of about 90%, thus ensuring that the effects of multiple scattering could be neglected for large scattering angles in the data analysis. Neutron scattering experiments were carried out on these semi-oriented polycrystalline samples (for the two experimental geometries discussed above) using the time-of-flight spectrometer IN5 ($\lambda_{inc} = 6$ Å; spectral resolution (FWHM) = 67 μeV) at the Institut Laue–Langevin (ILL) in Grenoble [20]. The resolution function of IN5 is essentially triangular.

The spectrum of a vanadium standard (with the same dimensions as the samples of the α, ω-dibromoalkane–urea inclusion compounds) was recorded at 5 K, for both the $Q_{\parallel}$ and the $Q_{\perp}$ geometries, to determine the instrumental lineshape. The detectors were normalized using these vanadium spectra, and background subtraction was performed using conventional procedures.

The $Br(CH_2)_9Br$–urea-d_4 inclusion compound was studied as a detailed function of temperature (in both the LT and the HT phases), and the $Br(CH_2)_8Br$–urea-d_4 and $Br(CH_2)_{10}Br$–urea-d_4 inclusion compounds were studied at 120 K and 240 K. The phase transition temperatures for all these compounds are in the range 120–140 K (as shown by differential scanning calorimetry). At each temperature, spectra were recorded for both the $Q_{\parallel}$ and the $Q_{\perp}$ geometries.

3. Description of results

Spectra recorded in the $Q_{\parallel}$ geometry for the LT phase are shown in figure 2; quasi-elastic broadening is negligible, but inelastic peaks ('side peaks') are observed at about 0.7 meV. The intensity of the side peaks depends on the scattering angle 2θ (as a consequence of the variation in the orientation and the amplitude of the momentum transfer vector with 2θ whereas the observed mean frequency of the side peaks does not change with 2θ). In the HT phase (figure 3), these side peaks are broadened considerably (corresponding to an oscillatory motion which has become heavily damped above the phase transition temperature) and there is appreciable quasi-elastic broadening (corresponding to a translational motion of the guest molecules along the channel axis).

Spectra recorded in $Q_{\perp}$ geometry for the LT phase have negligible quasi-elastic broadening and there is no evidence for side peaks. In the HT phase, there is considerable quasi-elastic broadening, corresponding to a reorientational motion of the guest molecules about the channel axis (figures 4 and 5). The 'experimental' elastic incoherent structure factors (EISFs) for the reorientational motions are reported in figure 6. Clearly, on the
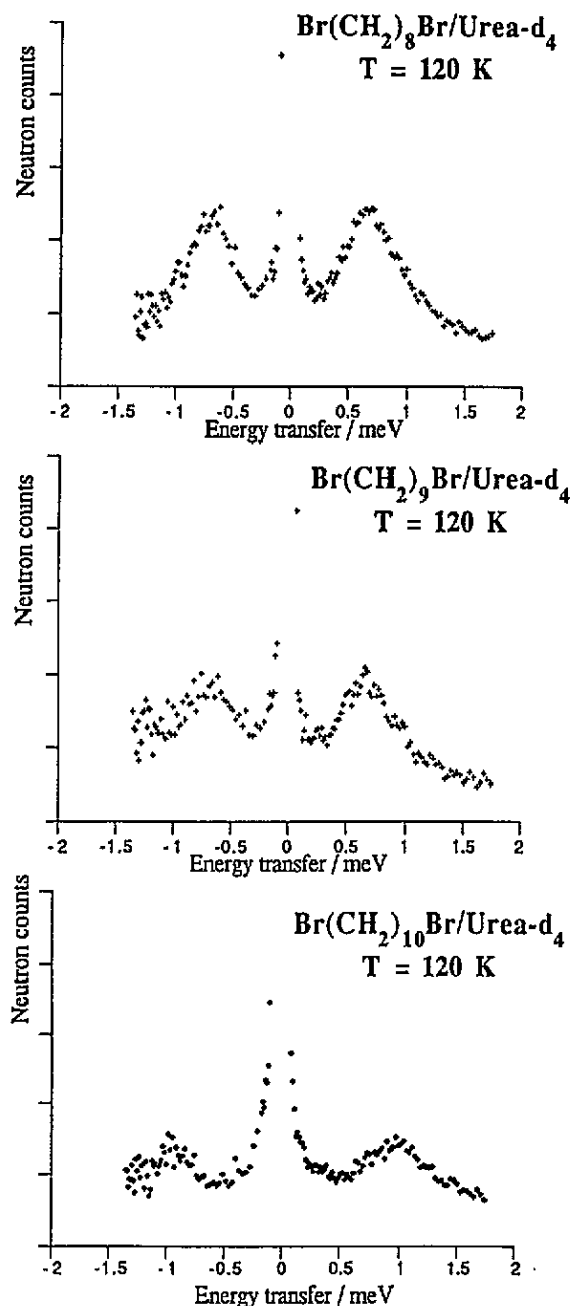
Br(CH$_2$)$_8$Br/Urea-d$_4$
T = 120 K

Neutron counts

-2   -1.5   -1   -0.5   0   0.5   1   1.5   2
Energy transfer / meV

Br(CH$_2$)$_9$Br/Urea-d$_4$
T = 120 K

Neutron counts

-2   -1.5   -1   -0.5   0   0.5   1   1.5   2
Energy transfer / meV

Br(CH$_2$)$_{10}$Br/Urea-d$_4$
T = 120 K

Neutron counts

-2   -1.5   -1   -0.5   0   0.5   1   1.5   2
Energy transfer / meV

Figure 2. $Q_{\parallel}$ spectra at 120 K (LT phase) for the Br(CH$_2$)$_n$Br–urea-d$_4$ inclusion compounds with $n = 8, 9, 10$. The scale expansion factor for these spectra is 100.

characteristic time scale of the experiments, the temperature dependence of the EISFs reveals the diffusive nature of the reorientational process, the amplitude of which increases with increasing temperature. This is consistent with a model of a particle moving in a potential with a barrier height which is temperature dependent. It is also noteworthy that the molecules do not perform uniform reorientations about the channel axis, as shown by comparing the experimental EISFs with the theoretical EISF for $2\pi/6$ jumps (or, equivalently, for a model of uniform rotational diffusion) calculated [23] taking a radius of gyration of 1.39 Å for the

CH$_2$ groups in an all-*trans* α, ω-dibromoalkane molecule rotating about its long molecular axis.

4. Development of models for the dynamic properties

We now consider the dynamic models for the α, ω-dibromoalkane guest molecules which have been found successfully to explain the experimental results discussed above. A detailed description of the models used in this paper can be found in [13].

4.1. Motions along the channel axis

Our IQNS results suggest that the motions of the α, ω-dibromoalkane molecules along the channel axis can be separated into two components: a diffusive translatory motion and an oscillatory motion, These motions are assumed to be uncorrelated with respect to times and the corresponding scattering law is then

$$S^t(Q, \omega) = S^{OSC}(Q, \omega) \otimes S^{trans}(Q, \omega) \tag{1}$$

where $S^{OSC}(Q, \omega)$ refers to the oscillatory motion, $S^{trans}(Q, \omega)$ refers to the translatory motion and $\otimes$ denotes convolution. The following scattering law has thus been derived [13] (for Q parallel to the displacement vector of the protons (valid considering spectra recorded at the $2\theta = 90°$ scattering angle only)):

$$S^t(Q, \omega) = \exp(-Q^2 \langle r^2 \rangle)[S^{trans}(Q, \omega) + F_1^{OSC}(Q, \omega) + F_2^{OSC}(Q, \omega)]. \tag{2}$$

In this expression, $F_1^{OSC}(Q, \omega)$ and $F_2^{OSC}(Q, \omega)$ define the side peaks and represent the one-phonon and two-phonon terms, respectively, in the phonon expansion of the intermediate scattering function [13]. The truncation of the series at the second order is valid if $Q^2 \langle r^2 \rangle$ is significantly less than unity. However, as the autocorrelation function $G(t)$ is close to its limiting value of unity only at short times, the error due to the truncation will affect only the wings of the profile. We have therefore used a flat background to take account of the higher phonon terms in the series expansion. Describing the oscillatory motion giving rise to these side peaks as a damped harmonic oscillator, the following are derived:

$$F_1^{OSC}(Q, \omega) = \frac{Q^2 \langle r^2 \rangle K_0 \Omega_0^2}{\pi (\Omega_0^2 - \omega^2)^2 + \pi K_0^2 \omega^2}$$

$$F_2^{OSC}(Q, \omega) = \frac{[Q^2 \langle r^2 \rangle]^2}{2\pi} \frac{K_0}{1 - q^2} \left(\frac{1}{\omega^2 + K_0^2} + \frac{16\Omega_0^2(1 - q^2) - (4\Omega_0^2 + \omega^2)}{(4\Omega_0^2 - \omega^2)^2 + 4K_0^2\omega^2} \right) \tag{3}$$

where $\langle r^2 \rangle$ represents the mean square amplitude of the oscillations (along the channel axis), K_0 is the damping factor, Ω_0 is the mean frequency of the oscillator and $q = K_0/2\Omega_0$.

The translatory component of the motion has been modelled successfully as continuous linear diffusion between two rigid impermeable boundaries and is represented by the following scattering law [21]:

$$S^{trans}(Q, \omega) = A_0^{trans}(Q)\delta(\omega) + \sum_{n=1}^{N} A_n^{trans}(Q)L_n(\omega) \tag{4}$$

with

$$A_0^{\text{trans}}(Q) = j_0^2(\tfrac{1}{2}QL)$$

$$A_n^{\text{trans}}(Q) = \frac{4(QL)^2[1 - (-1)^n \cos(QL)]}{[(QL)^2 - (n\pi)^2]^2}. \tag{5}$$

In these equations, j_0 denotes the spherical Bessel function of zero order ($j_0(x) = (\sin x)/x$) and $L_n(\omega)$ represent Lorentzians with half-width at half-maximum height given by

$$\Delta\omega_n = D_t \left(\frac{n\pi}{L}\right)^2. \tag{6}$$

In fitting this scattering law to the experimental spectra, the fitted parameters are the translation length L and the translational diffusion coefficient D_t. For the experimental Q-range investigated in our experiments, it was found sufficient to consider only two functions $L_n(\omega)$, thus giving $N = 2$ in equation (4).

4.2. Reorientational motions about the channel axis

According to the qualitative discussion in the previous section, we need to consider a model for diffusive reorientational motions according to the following observations. First, the amplitude of the reorientational motion is temperature dependent and does not correspond to a uniform reorientation. Second, regarding the EISFs at 160 and 200 K, the amplitude of the reorientational motion is small so that the minima of the potential (for a reorientational motion in a twofold or threefold potential) are close to each other; we can therefore predict that, at higher temperatures, the barriers are small enough to avoid a clear distinction (in the Q-range investigated in the present experiments) between these various models. We have already shown [26] that, for a model of diffusion within a potential with two minima separated by 90°, the motion becomes rapidly (when the temperature increases) equivalent to diffusion in a onefold potential.

Finally, for simplicity, we shall assume in the following that the reorientational motions of the guest molecules about the channel axis can be modelled as uniaxial rotational diffusion in a onefold cosine potential, using the following scattering law developed by Dianoux and Volino [22]:

$$S^{\text{r}}(Q, \omega) = A_0^{\text{rot}}(Q)\delta(\omega) + \sum_{m=1}^{M} A_m^{\text{rot}}(Q)L_m(\omega). \tag{7}$$

The functions $L_m(\omega)$ represent Lorentzians with half-width at half-maximum height given by

$$\Delta\omega_m = D_r m^2 \tag{8}$$

where D_r is the rotational diffusion coefficient.

Because the crystals in our semi-oriented polycrystalline samples had random orientations with respect to rotation about the channel axis (specified by rotation angle φ), it is necessary to average over φ, giving the following expression for the EISF:

$$A_0^{\text{rot}}(Q) = \frac{1}{\pi[I_0(\gamma)]^2} \int_0^{\pi} J_0(2Qr \sin\varphi)I_0(2\gamma \cos\varphi)\,d\varphi. \tag{9}$$

In fitting this scattering law to the experimental spectra, the fitted parameters are D_r and γ. The parameter γ is related to V_0 (the effective potential barrier for the rotations) and to $\bar{\phi}$ (the mean angle of fluctuations about the channel axis) via the following equations:

$$V_0 = 2k_B T \gamma \tag{10}$$

$$\bar{\phi} = \cos^{-1}\left(\frac{I_1(\gamma)}{I_0(\gamma)}\right) \tag{11}$$

where k_B is the Boltzmann constant, T is the temperature, r is the radius of gyration (1.39 Å) for protons in the CH_2 group of an alkane molecule rotating about its main molecular axis, J_0 is the Bessel function of zero order and first kind, and I_0 and I_1 are the modified Bessel functions of zero order and first order, respectively.

For the Q-range investigated in our experiments (0–2 Å^{-1}), it was found sufficient to consider this scattering law with six functions $L_m(\omega)$, giving $M = 6$ in equation (7).

4.3. Fitting procedure

Theoretical scattering laws for fitting to the experimental $Q_\parallel$ and $Q_\perp$ spectra were obtained by convoluting equations (2) and (7), respectively, with the instrumental resolution function as follows:

$$S^{\text{theory}}(Q, \omega) = A_0(Q)V(Q, \omega) + \sum_{i=1}^{N} A_i(Q)[L_i(\omega) \otimes T(Q, \omega)] \tag{12}$$

where $V(Q, \omega)$ denotes the spectrum of the vanadium standard at 5 K (representing the instrumental lineshape function for the elastic peak), and $T(Q, \omega)$ denotes a triangular instrumental resolution function determined by fitting the experimental spectrum for the vanadium standard at 5 K.

For the $Q_\parallel$ geometry, only the data from the detector at $2\theta = 90°$ were fitted, since it is only at this scattering angle that Q is exactly parallel to the channel axis. For the $Q_\perp$ geometry, the scattering law was fitted simultaneously to all the individual spectra recorded in the range $30° < 2\theta < 120°$ (excluding those containing significant coherent scattering), thus implicitly taking into account the Q-dependence of the scattering law. We shall therefore obtain direct information on the purely translational and purely rotational components of the dynamics of the guest molecules; an inherent limitation of our analysis is that correlations between these motions cannot be analysed.

5. Discussion of results

5.1. Motions along the channel axis

The fitted spectra are shown in figure 3, and the best-fit parameters are listed in table 1. There is some uncertainty in the fitted parameters relating to the oscillatory motion. This is due, in part, to the very low intensity of the side peaks, but it is also related to the fact that the parameters Ω_0 and K_0 become correlated at sufficiently high temperatures (it can be shown readily that, when K_0 is sufficiently large relative to Ω_0 (in practice, this situation arises at a sufficiently high temperature), equation (3) becomes a function of Ω_0^2/K_0, and the parameters Ω_0 and K_0 therefore cannot be refined independently). For this reason, the values of Ω_0 and K_0 at 280 K were determined by fixing Ω_0 at the value (0.8 meV) obtained

Table 1. Best-fit parameters for $Br(CH_2)nBr$–urea-d_4 samples for the $Q_{\parallel}$ geometry (experimental data collected on the detector at $2\theta = 90°$).

n	T (K)	$Q^2\langle r^2\rangle$	Ω_0 (meV)	K_0 (meV)	D_t (10^6 cm^2 s^{-1})	L (Å)	$\sqrt{\langle r^2\rangle}$ (Å)
8	120	0.7	0.9	0.5	—	—	0.6
8	240	2.1	0.9	0.7	5.8	2.1	1.0
9	120	0.8	0.8	0.5	—	—	0.6
9	160	1.2	0.9	0.9	0.7	0.9	0.7
9	200	1.2	0.8	1.0	1.3	1.3	0.7
9	240	1.4	0.8	1.0	2.4	1.6	0.8
9	280	1.5	0.8	0.8	7.0	2.3	0.8
10	120	0.7	1.0	0.7	—	—	0.6
10	240	1.4	0.8	1.16	2.7	1.8	0.8

at 240 K and refining K_0 in the usual way. There is therefore greater uncertainty in the values of Ω_0 and K_0 determined at the higher temperatures studied.

For $Br(CH_2)_9Br$–urea-d_4 in the temperature range 120–280 K, Ω_0 decreases slightly and K_0 increases as the temperature is increased: this explains the overdamped nature of the oscillatory motion in the HT phase. As expected, the mean squared amplitude $\langle r^2\rangle$ of the oscillations increases as the temperature is increased. The parameters L and D_t relating to the translational diffusion process both increase as the temperature is increased and are in the ranges 0.9 Å $< L <$ 2.3 Å and 0.7×10^{-6} cm^2 s^{-1} $< D_t < 7.0 \times 10^{-6}$ cm^2 s^{-1}. On the assumption of an Arrhenius behaviour for D_t the variation in D_t with temperature in the HT phase corresponds to an activation energy of 6 ± 1 kJ mol^{-1} for the translational motion of the guest molecules.

Considering the set of $Br(CH_2)_nBr$ guest molecules with $n = 8$–10 at 240 K, Ω_0 remains approximately constant whereas K_0 increases with increase in n. For L and D_t it is difficult to assign a well defined trend with n, and these parameters *may* depend on the odd–even character of n. However, restricting the discussion to the even guest molecules $Br(CH_2)_8Br$ and $Br(CH_2)_{10}Br$, it is clear that both L and D_t decrease as the length of the guest molecule is increased.

Despite the uncertainty in the parameters relating to the oscillatory motion, it is nevertheless clear from the fact that the quasi-elastic broadening is of the order of a few tens of microelectronvolts, whereas the oscillation frequency Ω_0 is in the range 0.8–0.9 meV that the oscillatory and translatory motions are not coupled in time. We must therefore point out that the large damping of the oscillatory motion gives rise to a diffusive component which overlaps with the narrow component owing to the translational diffusion. It is very likely that both motions are correlated and that ideally a single model should describe the short-time (oscillatory behaviour) and the long-time (diffusive motion) limits of the translational motion.

5.2. Reorientational motions about the channel axis

The experimental EISFs $A_0(Q)$, determined at various temperatures, are shown in figure 6. The experimental variation in $A_0(Q)$ with temperature indicates that the amplitude of the rotational motion of the guest molecules increases with increasing temperature and the absence of low-frequency inelastic features in the $Q_{\perp}$ spectra for both the LT and the HT phases suggests that the motion is diffusive rather than oscillatory in nature. The uniaxial rotational diffusion model developed by Dianoux and Volino [22] has been found to be applicable at all the temperatures studied.
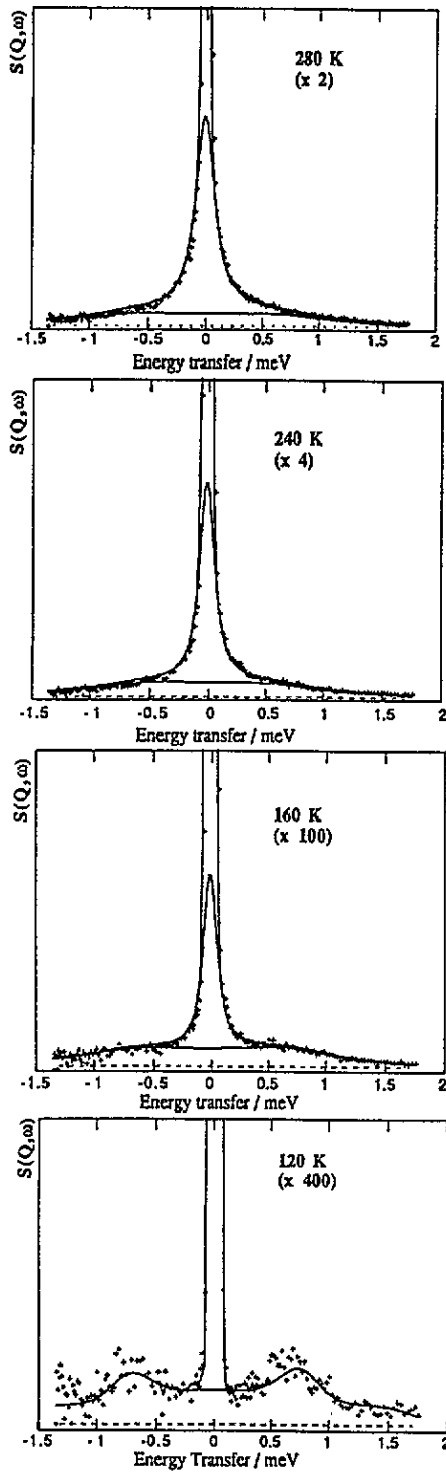
Figure 3. Evolution of the $Q_\parallel$ spectra at $2\theta = 90°$ ($Q_0 = 1.5$ Å^{-1}) for Br(CH$_2$)$_9$Br–urea-d$_4$ as a function of temperature in both the LT and the HT phases. The solid curves represent the fitted scattering law given in the text (equation (2)).
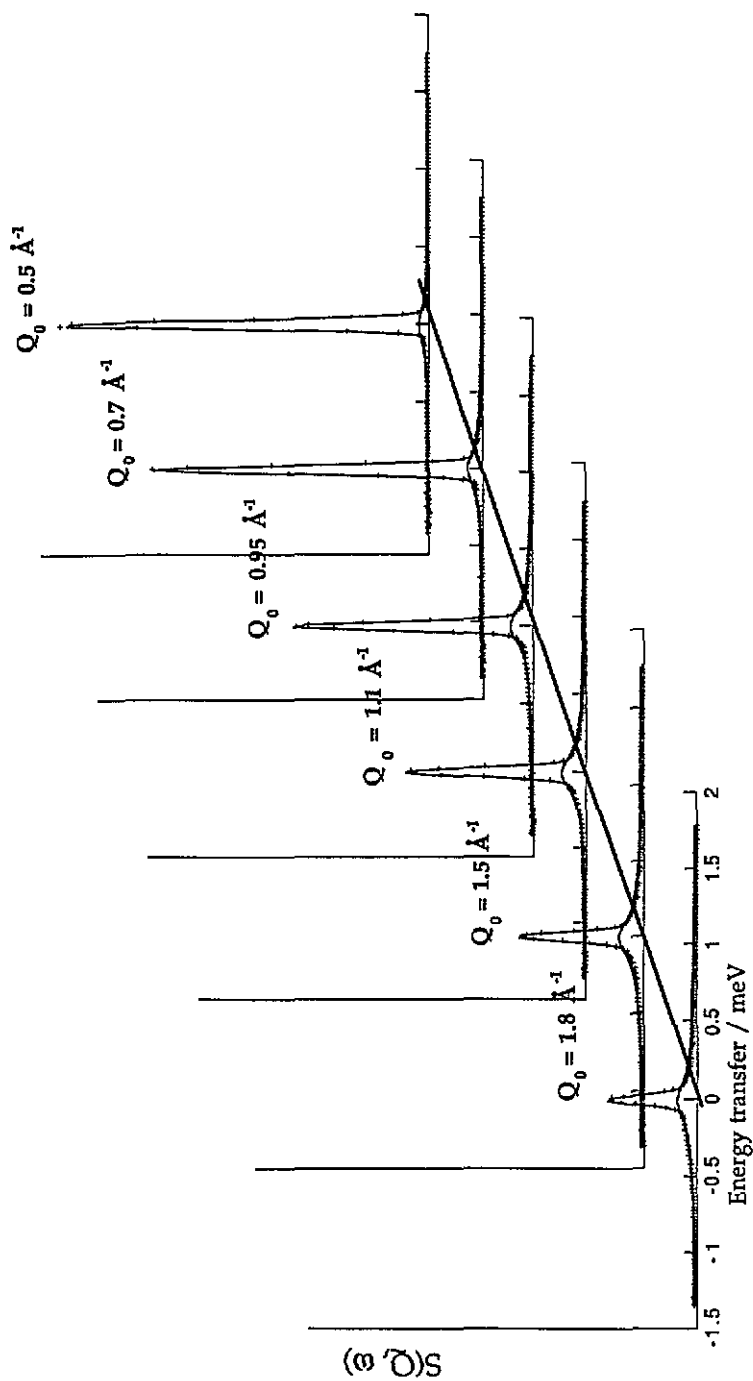
Figure 4. Q-dependence of the experimental and fitted spectra for $Br(CH_2)_9Br$–urea-d_4 in the $Q_\perp$ geometry at 280 K.

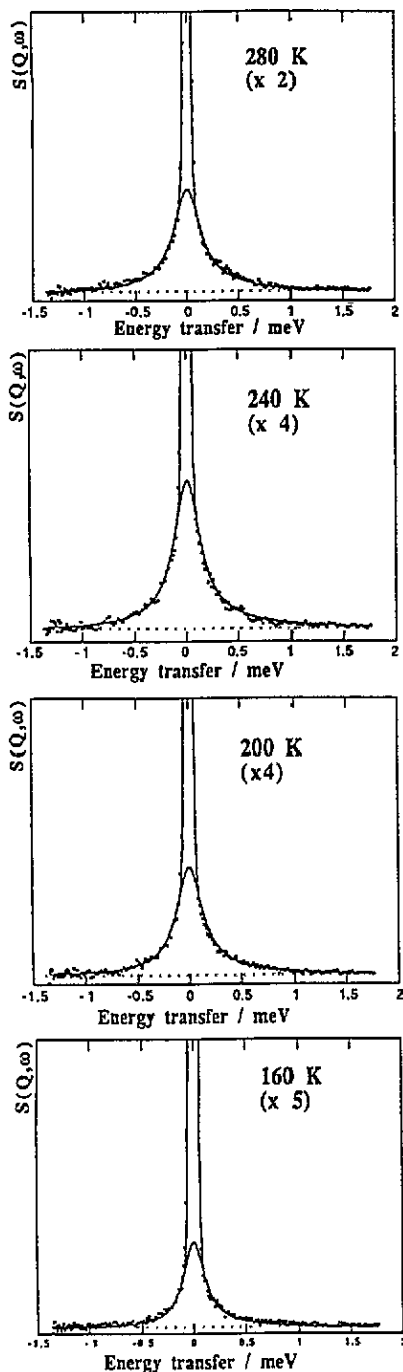**Figure 5.** Temperature dependence of the experimental and fitted spectra for $Br(CH_2)_9Br$–urea-d_4 in $Q_\perp$ geometry at $Q_0 = 1.5$ Å^{-1}.

The fitted $Q_\perp$ spectra shown in figure 4 as a function of the scattering angle and the temperature dependence of the spectra at $Q_0 = 1.5$ Å^{-1} is shown in figure 5. The best-fit parameters are listed in table 2. The theoretical values for the EISF derived from these parameters are compared with the experimental values in figure 6. From table 2 it is clear that D_r increases as the temperature is increased, and $\bar{\phi}$ increases (and V_0 decreases) with

Table 2. Best-fit parameters for $Br(CH_2)_nBr$–urea-d_4 samples for the $Q_\perp$ geometry. In each case, the parameters were derived by simultaneously fitting the theoretical model to all the experimental spectra (each corresponding to a different Q_0) in the range $30° < 2\theta < 120°$.

n	T (K)	γ	D_r (ps^{-1})	$\bar{\phi}$ (deg)	V_0 (kJ mol^{-1})
8	240	1.9	0.23	47	7.6
9	160	6.0	0.16	21	15.9
9	200	3.2	0.19	33	10.6
9	240	2.4	0.20	41	9.6
9	280	1.9	0.21	54	8.8
10	240	2.4	0.19	41	9.6

increase in temperature. From the data at 240 K, D_r decreases and $\bar{\phi}$ increases as the length of the guest molecule is increased. The values of these parameters are in the ranges 0.16 ps$^{-1} < D_r < 0.23$ ps^{-1} and $21° < \bar{\phi} < 54°$. Because the value of V_0 varies with temperature, it is not valid to apply the Arrhenius equation to describe the temperature dependence of D_r in order to derive an activation energy for the reorientational motion.
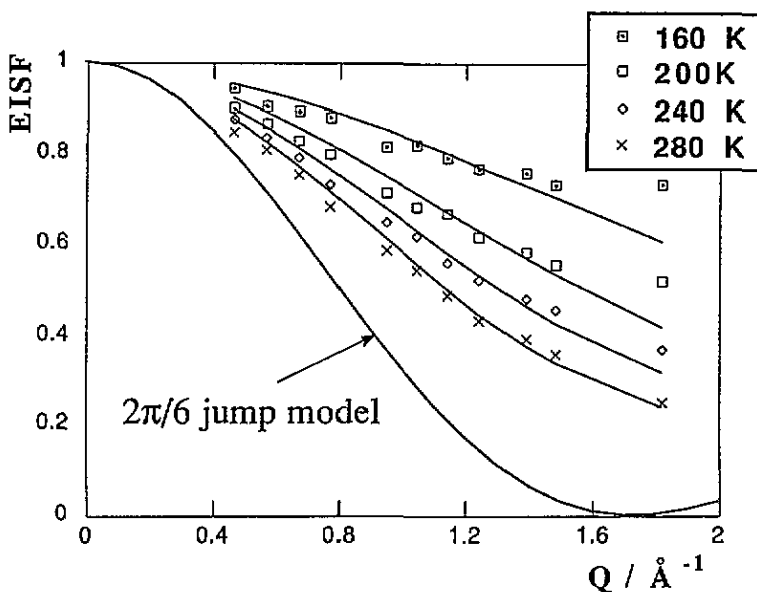

Figure 6. Comparison between the experimental (⊡, □, ◊, ×) EISFs for $Br(CH_2)_9Br$–urea-d_4 in the $Q_\perp$ geometry at various temperatures and the theoretical (———) EISFs calculated using equation (9). For comparison, the theoretical curve for the $2\pi/6$ jump model is also shown (———).

6. Concluding remarks

The results reported here have revealed new and detailed insights into the dynamic properties of the guest molecules in the $Br(CH_2)_nBr$–urea-d_4 inclusion compounds over a wide temperature range, and some of the wider implications of these results are now discussed.

First, it is clear that qualitatively the dynamic properties of *n*-alkane and α, ω-dibromoalkane guest molecules in the urea channel structure are essentially the same. Furthermore, there is a marked similarity in some quantitative aspects of the dynamics for the *n*-nonadecane and 1,9-dibromononane guests (the only systems that have so far been studied as a detailed function of temperature). These qualitative similarities observed suggest that replacing CH₃ end groups by Br end groups has no *significant* effect on the mechanism of motion of the whole guest molecule. However, at this stage it might be not valid to use a direct quantitative comparison between the results for these systems to assess the effects of the CH₃ end group *vis-à-vis* the Br end group on the dynamic properties of the guest molecule in view of the different molecular lengths (i.e. different numbers of methylene groups) of these guests. In contrast with these observations, preliminary experiments performed on urea inclusion compounds where the guest contains other functional groups (such as the diacyl peroxide functional group [29]) revealed a new kind of motional behaviour. There is a distinct paucity of previous reports on the dynamic properties of the guest molecules in α, ω-dibromoalkane–urea inclusion compounds; in recognizing the different scope of the techniques which have been employed, there is encouraging agreement between the results reported here and the previous ¹H NMR study by Bell and Richards [16].

Second, we now consider the guest molecular dynamics in relation to the known average structural properties of the guest structure in α, ω-dibromoalkane–urea inclusion compounds established from our x-ray diffraction studies [6]. We recall that the guest molecules are densely packed along each individual channel (the interaction between adjacent guest molecules in the same channel is probably repulsive [24]) and there is a well defined positional relationship between the positions of guest molecules in neighbouring channels (in the three-dimensionally ordered regions of the guest structure). The IQNS results have been interpreted successfully on the basis that all guest molecules in the structure exhibit the same dynamic behaviour, suggesting that, if there *are* any differences in the dynamic behaviour of the guest molecules in the one-dimensionally ordered and three-dimensionally ordered regions of the guest structure, then these differences are small.

On the other hand, it could be proposed that the two dynamic processes (oscillations and diffusion) are associated with the two different types of guest structure (i.e. the regions of one-dimensional ordering and three-dimensional ordering). The neutron scattering law would therefore correspond to the simple superposition of the spectrum containing the inelastic side peaks (the intensity of which is proportional to both the amplitude of the oscillations and the relative size of the domains of three-dimensional ordering) and the quasi-elastic spectrum arising from the translational diffusion of the guest molecules within the regions of one-dimensional ordering. Furthermore, the side peaks clearly do not correspond to a propagative mode of the three-dimensionally ordered regions, since dispersion of this mode is not observed. We have not assessed, from our x-ray diffraction data, the relative numbers of guest molecules present within these two different types of guest structure, and it is conceivable that one of these regions may be present in a sufficiently small amount that the guest molecules within it do not give rise to a significant contribution to the IQNS spectrum.

In view of the dense packing of guest molecules along the channel, and in the knowledge of the appreciable translation lengths (of the order of about 2 Å) deduced from our IQNS studies, it is probable that the translational motions of neighbouring guest molecules within a given channel are highly correlated. Because of the repulsive intrachannel guest–guest interaction, it is also likely that the reorientational motions of neighbouring guest molecules in the same channel are highly correlated.

Alternatively, it is also conceivable that translation of a given guest molecule towards

its neighbour in the same channel might be associated with the production of a *gauche* end group in one of these molecules, it having been established recently by Raman spectroscopy [25] that a significant number of *gauche* end groups do indeed exist for α, ω-dibromoalkane guest molecules in urea inclusion compounds. Such a proposal clearly requires the translational motion and the interconversion of *gauche* and *trans* end groups to occur on the same time scale.

Focusing attention now on the relative motions of guest molecules in neighbouring channels, we recall that, in the three-dimensionally ordered regions of the guest structure, there are well defined positional correlations between the guest molecules in adjacent channels, even at ambient temperature. On the assumption that all the guest molecules perform the same motions, independent motions of guest molecules with translation lengths of greater than about 2 Å would inevitably mean that a well defined value of Δ_g would not be detected from the x-ray diffraction patterns, and correlated translational motions of the guest molecules in adjacent channels are therefore implicated (at least for the regions of the crystal containing a three-dimensionally ordered guest structure). From the evidence at present available, we cannot assess whether the reorientational motions of the guest molecules in adjacent channels are correlated.

Third, we discuss in more detail the origin of the side peaks observed in the $Q_{\parallel}$ spectra. We recall that such side peaks were not observed in the IQNS spectra of the crystalline phase of pure n-nonadecane [26] nor for n-heptane and n-octane guest molecules in TANO inclusion compounds [27]. Because of the very low energy of these inelastic features, we assign the underlying motion as a collective excitation of the guest molecules along the channel axis rather than an intramolecular oscillation. Such a collective excitation might correspond to an acoustic mode originating from the three-dimensionally ordered domains of the guest structure, as discussed above. Alternatively, it is important to recall that the urea inclusion compounds investigated here are incommensurate composite systems [6]. The side peaks might therefore be assigned to a new type of excitation, called a 'sliding mode' [28], corresponding to antitranslations of one substructure with respect to the other substructure along the incommensurate axis c^*.

In view of the results reported in this paper, and the interesting comparison that they provide in relation to previous IQNS results for urea inclusion compounds containing n-alkane guests, we are currently extending this work to consider the dynamic properties of urea inclusion compounds containing a wide range of other types of guest species. In this regard, preliminary experiments [29] have shown that the guest molecular dynamics in the $I(CH_2)_8I$–urea-d_4 inclusion compound are qualitatively similar to the dynamic properties of the α, ω-dibromoalkane–urea inclusion compounds reported here. Future work will consider other types of guest molecule, with particular emphasis on those that are known to adopt three-dimensionally ordered packing arrangements that are different from the arrangement characteristic of the α, ω-dibromoalkane guests.

Finally, we discuss future developments in the methodology for interpreation of the experimental spectra. The scattering laws considered here for the $Q_{\parallel}$ and $Q_{\perp}$ spectra did not take into account the possibility of coupling between the translational and reorientational motions of the guest molecules. Since these motions occur on the same time scale, and in view of the fact that the urea molecules are arranged in a helical manner in forming the walls of the channel [1, 2], it may be proposed that these motions are correlated and could be described as a screw-type motion. Furthermore, since the urea channel structure is essentially invariant for the inclusion compounds containing the different guest molecules considered here, it is plausible that the form of the coupling between the translational and reorientational motions should be independent of the identity of the guest molecule. This

issue represents an important area for future investigation in this field, and development of appropriate theoretical models for correlated translational and reorientational motions is required; recent theoretical developments in a related subject [30] are relevant in this regard. We also note that the $Q_\parallel$ spectra have been fitted only for one value of Q_0 (corresponding to the scattering angle $2\theta = 90°$). An important improvement in our ability to model the motions along the channel axis will consider the measurement of $Q_\parallel$ spectra for different values of Q_0, thus allowing the Q-dependence of the scattering law to be taken into account in the fitting procedure. Experimental measurements using a triple-axis spectrometer are clearly relevant in relation to this and other aspects of our continuing research into the molecular dynamics of urea inclusion compounds.

Acknowledgments

References

[1] Smith A E 1952 *Acta Crystallogr.* 5 224
[2] Harris K D M and Thomas J M 1990 *J. Chem. Soc. Faraday Trans.* 86 2985
[3] Kobayachi M, Koizumi H and Cho Y 1990 *J. Chem. Phys.* 93 4659
[4] Rennie A J O and Harris K D M 1990 *Proc. R. Soc* A 430 615
[5] Harris K D M and Hollingsworth M D 1990 *Proc. R. Soc* A 431 245
[6] Harris K D M, Smart S P and Hollingsworth M D 1991 *J. Chem. Soc. Faraday Trans.* 87 3423
[7] Smart S P, Guillaume F, Harris K D M, Sourisseau C and Dianoux A-J 1992 *Physica* B 180–1 687
[8] Parsonage N G and Pemberton R C 1967 *Trans. Faraday Soc.* 63 211 and earlier references cited therein
[9] Chatani Y, Anraku H and Taki Y 1978 *Mol. Cryst. Liq. Cryst.* 48 219
[10] Harris K D M, Gameson I and Thomas J M 1990 *J. Chem. Soc. Faraday Trans.* 86 3135
[11] Guillaume F 1988 *Thesis* Université de Bordeaux I
[12] Guillaume F, Sourisseau C and Dianoux A-J 1990 *J. Chem. Phys.* 93 3536
[13] Guillaume F, Sourisseau C and Dianoux A-J 1991 *J. Chim. Physique* 88 1721
[14] Guillaume F, Harris K D M and Dianoux A-J 1992 *Institut Laue–Langevin (Grenoble) Annual Report 1991* pp 74–7
[15] Shannon I J and Harris K D M 1993 unpublished results
[16] Bell J D and Richards R E 1969 *Trans. Faraday Soc.* 65 2529
[17] Heaton N J, Vold R L and Vold R R 1989 *J. Am. Chem. Soc.* 111 3211
[18] Aliev A E, Smart S P and Harris K D M 1993 *J. Mater. Chem.* at press
[19] Meakins R J 1955 *Trans. Faraday Soc.* 51 953
[20] Blank H and Maier B (ed) 1988 *The Yellow Book: Guide to Neutron Research Facilities at the ILL* (Grenoble: Institut Laue–Langevin) pp 52–3
[21] Hall L and Ross D K 1981 *Mol. Phys.* 42 673
[22] Dianoux A-J and Volino F 1973 *Mol. Phys.* 34 1263
[23] Bee M 1988 *Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, Biology and Materials Science* (Bristol: Adam Hilger)
[24] Rennie A J O and Harris K D M 1992 *J. Chem. Phys.* 96 7117
[25] Smart S P, Harris K D M, Guillaume F and El Baghdadi A 1992 *Mol. Cryst. Liq. Cryst.* 211 157
[26] Guillaume F, Doucet J, Sourisseau C and Dianoux A-J 1989 *J. Chem. Phys.* 91 2555
[27] Bée M, Renault A, Lajzérowicz-Bonneteau J and Le Bars-Combe M 1991 *J. Chem. Phys.* 97 7730
[28] Guillaume F, El Baghdadi A and Dianoux A-J 1993 *Phys. Scr.* T 49 691
[29] Harris K D M, Guillaume F and Dianoux A-J 1993 *ISIS Experimental Report* RB/3412; 1993 *ISIS Annual Report* A325
[30] Guillaume F 1994 *Mol. Phys.* at press