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Citation: The Journal of Chemical Physics **109**, 4078 (1998); doi: 10.1063/1.477008 View online: http://dx.doi.org/10.1063/1.477008 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/109/10?ver=pdfcov Published by the AIP Publishing

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# Dynamic properties of dioctanoyl peroxide guest molecules constrained within the urea tunnel structure: A combined incoherent quasielastic neutron scattering and solid state <sup>2</sup>H nuclear magnetic resonance investigation

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(Received 19 February 1998; accepted 20 May 1998)

The dynamic properties of dioctanoyl peroxide guest molecules within the urea host tunnel structure in the dioctanoyl peroxide/urea inclusion compound have been investigated by incoherent quasielastic neutron scattering (IQNS) and solid state <sup>2</sup>H nuclear magnetic resonance (NMR) techniques. The IQNS investigations were carried out on samples of urea inclusion compounds containing perdeuterated urea to ensure that the incoherent scattering is dominated by the dioctanoyl peroxide guest molecules. Using semioriented polycrystalline samples, translational motions of the guest molecules along the tunnel were investigated separately from reorientational motions of the guest molecules about the tunnel axis. The <sup>2</sup>H NMR experiments used dioctanoyl peroxide deuterated selectively in both the  $\alpha$  CD<sub>2</sub> groups and urea with natural isotopic abundance. The dynamic models that have been found to describe the translational and reorientational motions of the guest molecules from the IQNS and <sup>2</sup>H NMR data are discussed in detail. The reorientational dynamics of the guest molecules about the tunnel axis can be described by a model of uniaxial rotational diffusion in a twofold potential, and the translations of the guest molecules along the tunnels can be interpreted by a model of translational jumps between sites with unequal probabilities of occupation. These models differ markedly from those found previously to describe the dynamic properties of alkane guest molecules within the urea tunnel structure. © 1998 American Institute of Physics. [S0021-9606(98)70332-0]

# I. INTRODUCTION

It is widely recognized that urea inclusion compounds are attractive systems for studying many of the fundamental physicochemical phenomena that underpin the properties of molecular solids, and as such they have been widely investigated for several years.<sup>1,2</sup> In these crystalline solids, the urea molecules form an extensively hydrogen-bonded

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"host" structure,<sup>3</sup> within which there are parallel onedimensional tunnels. In the "conventional" urea inclusion compounds, the host structure is hexagonal ( $P6_122$ ;  $a=b \approx 8.2$ ;  $c \approx 11.0$  Å) at ambient temperature, with the effective tunnel "diameter" ranging between about 5.5 and 5.8 Å. This host structure is stable only when the tunnels are packed densely with "guest" molecules. Because of the spatial constraints of the urea tunnel, only guest molecules based on sufficiently long alkane chains and with a limited degree of substitution are suitable for inclusion within the urea tunnel

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structure, and such guest molecules are constrained to adopt linear, extended conformations. In the present paper, we focus on the dynamic properties of dioctanoyl peroxide (OP) guest molecules within the urea tunnel structure. First, a brief overview of relevant background information is given.

For all "conventional" urea inclusion compounds, there is an incommensurate structural relationship<sup>4</sup> between the periodic repeat distance  $(c_h)$  of the host structure along the tunnel axis and the periodic repeat distance  $(c_g)$  of the guest molecules along the tunnel axis. While we focus here on these "conventional" urea inclusion compounds, we note that for certain guest molecules there is a commensurate relationship between the host and guest substructures<sup>5–9</sup>—in general, this is also associated with significant changes in the urea tunnel structure.

It has been shown<sup>10</sup> that the diffraction pattern of incommensurate urea inclusion compounds can be indexed in a four-dimensional superspace, and measurement of all aspects of the diffraction pattern (including satellite reflections) has been achieved recently.<sup>11,12</sup> Thus, the composite structure of the incommensurate urea inclusion compounds cannot be described using conventional three-dimensional space group formalism and a superspace group approach<sup>13</sup> is required. Clearly the physicochemical properties of urea inclusion compounds should depend markedly on the nature of the interactions between the host and guest substructures, and for the incommensurate materials many properties should therefore depend on the nature of the intermodulation function. A first attempt was made recently<sup>14</sup> to refine the structure of the heptadecane/urea inclusion compound in a four-dimensional superspace group, and to derive the intermodulation function. The intermodulation function is important not only with regard to the structural properties of the composite crystal, but also with regard to the dynamic<sup>15</sup> and conformational<sup>16</sup> properties of the guest molecules. For example, specific collective excitations-the so-called sliding modes of the host and guest substructures<sup>17</sup>—are expected for these quasiperiodic materials.

The prototypical family of "conventional" urea inclusion compounds is that with alkane guest molecules, and several detailed studies of fundamental structural and dynamic properties of these inclusion compounds have been reported. However, progress toward understanding fundamental properties of urea inclusion compounds also relies on understanding the behavior of systematic families of guest molecules containing well-defined functional groups. In alkane/urea inclusion compounds, diffraction studies<sup>18</sup> indicate that there is a one-dimensional periodic arrangement of the guest molecules along the tunnels, with only weak lateral correlation between guest molecules in adjacent tunnels. Urea inclusion compounds containing other families of guest molecules, however, exhibit markedly different behavior. For example, urea inclusion compounds containing diacyl peroxide [CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CO OO CO(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>] guest molecules exhibit a substantially ordered, three-dimensional periodic arrangement of the guest molecules.<sup>19</sup> These inclusion compounds have the "conventional" urea tunnel structure and it has been suggested<sup>19</sup> that there is an incommensurate relationship between the periodicities of the host and guest substructures along the tunnel. For all diacyl peroxide/urea inclusion compounds so far investigated (n = 6, 9, and 10), the offset (denoted  $\Delta_g$ ) along the tunnel axis between the positions of guest molecules in adjacent tunnels is  $\Delta_g \approx 4.6$  Å, at ambient temperature. These well-defined correlations between the positions of guest molecules in adjacent tunnels are presumably mediated by strong interactions between the host and guest substructures, and the intermodulation function for incommensurate inclusion compounds clearly plays a crucial role in this regard.

Many urea inclusion compounds undergo a phase transition (the temperature of which depends on the length and substitution pattern of the guest molecule) from a high temperature phase, in which the host structure is hexagonal, to a low temperature phase, in which the host structure is orthorhombic. For alkane/urea inclusion compounds, this behavior has been demonstrated directly by x-ray diffraction.<sup>20–22</sup> In contrast, for the lauroyl peroxide/urea inclusion compound, there is no evidence (from powder x-ray diffraction experiments<sup>23</sup> in the range 40–298 K and differential scanning calorimetry<sup>24</sup>) for the occurrence of a similar phase transition.

It has been shown<sup>25,26</sup> by incoherent quasielastic neutron scattering (IQNS) spectroscopy that, in the high temperature phase of the alkane/urea inclusion compounds, large amplitude translational and reorientational motions of the guest molecules occur on the picosecond time scale. <sup>2</sup>H NMR spectroscopy has also been used<sup>16,27–29</sup> to demonstrate that there is substantial motion of the guest molecules in the alkane/urea inclusion compounds. However, much less is known at present about the dynamic properties of functionalized alkane guest molecules within the urea tunnel structure.

We now extend this previous research to consider dynamic properties of diacyl peroxide guest molecules within the urea tunnel structure, selecting the dioctanoyl peroxide/ urea (OP/urea) inclusion compound for these studies. In view of the substantial contrasts between the structural properties of the diacyl peroxide/urea and the prototypical alkane/urea inclusion compounds, significant differences in the dynamic properties may be anticipated. As different aspects of the dynamic properties of the guest molecules may occur on different time scales, we exploit the specific advantages of a combined approach using IQNS spectroscopy and <sup>2</sup>H NMR spectroscopy.<sup>30–32</sup>

#### **II. EXPERIMENT**

#### A. Materials

Full details of the synthesis of the materials studied in this work are given in the Appendix. For the experiments described in this paper, inclusion compounds containing different levels of deuteration of OP and urea were used, with  $h_{30}$ -OP/ $d_4$ -urea used for IQNS studies and  $d_4$ -OP/ $h_4$ -urea used for <sup>2</sup>H NMR studies. The following abbreviations are used:  $d_4$ -urea denotes fully deuterated urea (in practice around 96% deuteration);  $d_4$ -OP denotes OP deuterated in all hydrogen positions within the  $\alpha$ -CH<sub>2</sub> groups [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CD<sub>2</sub>CO OO CO CD<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>]  $h_4$ -urea refers to urea with natural isotopic abundances;  $h_{30}$ -OP refers to OP with natural isotopic abundances. In all cases, powder x-ray diffraction confirmed that the crystals had the hexagonal tunnel structure of the conventional urea inclusion compounds at ambient temperature. Differential scanning calorigrams were recorded on a Perkin-Elmer Pyris I instrument. No phase transitions were observed for OP/urea between 108 and 353 K.

#### **B. IQNS experiments**

The use of the  $h_{30}$ -OP/ $d_4$ -urea inclusion compound for the IQNS experiments ensures that incoherent neutron scattering from the  $h_{30}$ -OP guest molecules represents more than ~98% of the total incoherent neutron scattering from the inclusion compound.

Typically,  $\approx 100$  single crystals of  $h_{30}$ -OP/ $d_4$ -urea were placed in grooved aluminium containers (slab type) such that the urea tunnel axes (long axis of the crystal morphology) of all crystals were parallel to each other. The orientations of the crystals with respect to rotation about this axis were random. The following experimental geometries were considered (Fig. 1), allowing translational motions of the guest molecules along the tunnel axis and reorientational motions of the guest molecules about the tunnel axis to be studied independently:

Neutron momentum transfer vector **Q** perpendicular (i) to the tunnel axis—denoted  $Q_{\perp}$  geometry. This geometry allows reorientational motions of the guest molecules about the tunnel axis to be studied. With the tunnel axes of all crystals perpendicular to the scattering plane, Q is perpendicular to the tunnel axis for all scattering angles  $2\theta_B$ . For the experiments performed on the IRIS and IN6 spectrometers (see below), the angle between the plane of the sample container and the incident neutron beam was 135°, allowing only scattering angles  $2\theta_B$  smaller than  $\sim 110^\circ$  to be investigated. In order to investigate  $Q_{\perp}$  spectra at larger  $2\theta_B$ , additional experiments were performed on the IN5 spectrometer (see below) with the angle between the plane of the sample container and the incident neutron beam equal to 45°-in this case, scattering angles  $2\theta_B$  between  $\sim 20$  and  $70^\circ$  could not be analyzed.



FIG. 1. Experimental geometries used for the IQNS experiments: (a)  $Q_{\perp}$  on IN6, (b)  $Q_{\perp}$  on IN5, (c)  $Q_{\parallel}$  geometry. In (a) and (b), the filled circles symbolize the tunnel axes perpendicular to the scattering plane, and in (c) the broken line symbolizes the tunnel axes parallel to the scattering plane.

(ii) Neutron momentum transfer vector  $\mathbf{Q}$  parallel to the tunnel axis—denoted  $Q_{\parallel}$  geometry. In this geometry, the tunnel axes of all the crystals lie in the scattering plane and motions of the guest molecules along the tunnel axis can be studied. With the tunnel axes aligned at an angle of 135° with respect to the incident neutron beam,  $\mathbf{Q}$  is strictly parallel to the tunnel axis only for the scattering angle  $2\theta_B = 90^\circ$ . For other scattering angles, the reorientational motions about the tunnel axis make a weak contribution to the scattering profile. This contribution is taken into account in the calculations discussed below.

IQNS spectra were measured in both  $Q_{\perp}$  and  $Q_{\parallel}$  geometries for semioriented polycrystalline samples of  $h_{30}$ -OP/ $d_4$ -urea using the time-of-flight spectrometers IN6 and IN5 at the Institut Laue-Langevin (Grenoble, France), at temperatures in the range 150–300 K. The instrumental resolutions were 130  $\mu$ eV (full width at half maximum height) for wavelength  $\lambda_0 = 4.6$  Å on IN6 and 80  $\mu$ eV for  $\lambda_0 = 5$  Å on IN5. The corresponding experimental energy windows used in our analysis were -2 meV $<\hbar\omega < 2$  meV.

Elastic scans in the  $Q_{\perp}$  geometry were performed using the backscattering spectrometer IRIS (instrumental resolution 15  $\mu$ eV) at the ISIS neutron spallation facility (Rutherford Appleton Laboratory, Didcot, UK), at temperatures in the range 50–270 K.

To determine the line shape of the instrumental resolution function  $R(\omega)$  as a function of  $2\theta_B$  for each spectrometer used, the IQNS spectrum of a vanadium standard (with the same dimensions as the sample of  $h_{30}$ -OP/ $d_4$ -urea) was recorded for both the  $Q_{\perp}$  and  $Q_{\parallel}$  geometries. The detectors were normalized using the spectra for vanadium, and other corrections were performed using conventional procedures.<sup>33</sup> For all data collections, the transmission was more than 90%, ensuring that the effects of multiple scattering can be neglected in the data analysis.

#### C. <sup>2</sup>H NMR experiments

<sup>2</sup>H NMR spectra for a polycrystalline sample of  $d_4$ -OP/ $h_4$ -urea were recorded at 46.1 MHz on a Bruker MSL300 spectrometer. A standard Bruker 5 mm high-power probe and a Bruker B-VT1000 temperature controller (stability and accuracy  $\sim \pm 1$  K) were used. The conventional quadrupole echo  $[(90^\circ)_{\phi} - \tau - (90^\circ)_{\phi \pm \pi/2} - \tau' - acquire - recycle]$  pulse sequence<sup>34</sup> was used, with 90° pulse duration 1.75  $\mu$ s and echo delay  $\tau = 15 \ \mu s$  ( $\tau' = 10 \ \mu s$ ). Quadrupole echo signals were left shifted prior to Fourier transformation and phase cycling was employed to eliminate quadrature phase errors. Other relevant experimental parameters are dwell time 1  $\mu$ s, number of acquisitions 1024, and acquisition time  $\approx 5$  ms.

### III. THEORETICAL BACKGROUND AND LINE SHAPE ANALYSIS

#### A. IQNS spectroscopy

In the quasielastic energy transfer window ( $\hbar \omega$  <3 meV), the incoherent neutron scattering law  $S(\mathbf{Q}, \omega)$  can be written<sup>35</sup> as

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$$S(\mathbf{Q},\omega) = e^{-2W(Q)} e^{-\hbar\omega/k_B T} S_d(\mathbf{Q},\omega) \otimes R(\omega) + B(Q),$$
(1)

where  $e^{-2W(Q)}$  is the Debye–Waller factor,  $e^{-\hbar\omega/k_BT}$  is introduced to fulfill the detailed balance condition,  $S_d(\mathbf{Q}, \omega)$  is the incoherent neutron scattering law due to diffusive motions of the <sup>1</sup>H nuclei,  $R(\omega)$  is the instrumental resolution function, B(Q) is an energy-independent background, and  $\otimes$ is the convolution operator. For restricted motions (i.e., reorientations and restricted translations), the scattering law  $S_d(\mathbf{Q}, \omega)$  takes the following form:

$$S_d(\mathbf{Q},\omega) = A_0(\mathbf{Q}).R(\omega) + \sum_{i=1}^{N-1} A_i(\mathbf{Q}).R(\omega) \otimes L_i(\Delta_i,\omega),$$
(2)

where  $A_0(\mathbf{Q})$  is the elastic incoherent structure factor (EISF) and represents the fraction of elastic intensity in the quasielastic profile, and  $L_i(\Delta_i, \omega)$  represent Lorentzian functions with half width at half maximum height (HWHM) given by  $\Delta_i$ . The formal expression of the above scattering function depends upon the experimental scattering geometry. For the semioriented samples of  $h_{30}$ -OP/ $d_4$ -urea used here, the scattering law  $S_d(\mathbf{Q}, \omega)$  takes the following form (after circular averaging over all orientations of the guest molecules in a plane perpendicular to the tunnel axis):

$$S_d(Q,\omega) = S_d^r(Qr_g \sin \alpha, \omega) \otimes S_d^t(Q \cos \alpha, \omega).$$
(3)

 $S_d^r(Qr_g \sin \alpha, \omega)$  is the quasielastic profile due to the uniaxial reorientational motions of the guest molecules about the tunnel axis (with gyration radius  $r_g$  for the <sup>1</sup>H nuclei),  $S_d^t(Q \cos \alpha, \omega)$  is the quasielastic profile due to translational motions of the guest molecules along the tunnel axis, and  $\alpha$  is the angle between the neutron momentum transfer vector **Q** and the tunnel axis at energy transfer  $\hbar\omega$ . Equation (3) assumes that there is no correlation between reorientational and translational motions of the guest molecules. This assumption has been shown<sup>36,37</sup> to be justified in the case of an incommensurate relationship between the host and guest substructures.

For  $Q_{\parallel}$  geometry, both reorientational and translational motions in Eqs. (1)–(3) are considered and the angle  $\alpha$  is given by

$$\alpha = \cos^{-1} \left( \frac{\lambda_0 Q}{4 \pi} - \frac{\pi}{\lambda_0 Q} \left( \frac{\hbar \omega}{E_0} \right) \right) - \frac{\pi}{4}, \tag{4}$$

where  $E_0$  is the incident neutron energy and Q is

$$Q = \sqrt{\frac{8\pi^2}{\lambda_0^2}} \left[ 1 + \frac{\hbar\omega}{2E_0} - \left( 1 + \frac{\hbar\omega}{E_0} \right)^{1/2} \cos(2\theta_B) \right].$$
(5)

In this geometry, the momentum transfer vector **Q** is strictly parallel to the tunnel axis ( $\alpha = 0^{\circ}$ ) for the scattering angle  $2\theta_B = 90^{\circ}$  and for  $\hbar \omega = 0$ . In the fitting procedure for  $Q_{\parallel}$ spectra, the Debye–Waller factor and the background B(Q)were fitted independently for each scattering angle, because for experiments on oriented single crystals the contribution of the internal and external vibrations to the intensity depends on the orientation of **Q** with respect to the tunnel axis.

For  $Q_{\perp}$  geometry,  $\alpha = 90^{\circ}$  for all values of scattering angle  $2\theta_B$  and energy transfer  $\hbar\omega$ , and only the reorientaarticle is copyrighted as indicated in the article. Reuse of AIP content is tional motions of the guest molecules about the tunnel axis contribute to the IQNS spectrum in  $Q_{\perp}$  geometry.

Finally, it has been shown previously<sup>38</sup> that within the time scale probed by IQNS spectroscopy, the urea molecules may be considered as "static." The theoretical spectra, as given by Eq. (1), were corrected by taking into account the additional elastic scattering due to the residual amount ( $\sim$ 4%) of <sup>1</sup>H nuclei in the  $d_4$ -urea.

Theoretical models were fitted to the experimental IQNS data through Eq. (1) [with Eqs. (2)-(5)] using standard methods.<sup>39</sup>

#### B. <sup>2</sup>H NMR spectroscopy

A nucleus with spin greater than 1/2 has an electric quadrupole moment which interacts with the electric field gradient at the nucleus. For <sup>2</sup>H nuclei in solids, this quadrupolar interaction is usually so large that other nuclear spin interactions are negligible in comparison with it. For a single crystal containing one type of <sup>2</sup>H nucleus, the <sup>2</sup>H NMR spectrum comprises a pair of peaks, the frequency separation of which depends on the orientation of the crystal with respect to the applied magnetic field. For a polycrystalline sample containing a random distribution of crystal orientations, superposition of such pairs of peaks for all crystal orientations gives a characteristic <sup>2</sup>H NMR "powder pattern." When the rate of molecular motion is intermediate on the <sup>2</sup>H NMR time scale (i.e., time scale between  $10^{-3}$  and  $10^{-8}$  s), the appearance of the <sup>2</sup>H NMR spectrum depends critically upon the exact rate and mechanism of the molecular motion. The effect of molecular motion on the <sup>2</sup>H NMR spectrum can be understood in terms of reorientation, with respect to the applied magnetic field, of the electric field gradient (EFG) tensor at the <sup>2</sup>H nucleus. In its principal axis system, the EFG tensor (denoted  $\mathbf{V}^{\text{PAS}}$ ) has principal components  $V_{xx}$ ,  $V_{yy}$ , and  $V_{zz}$ , with the axes assigned such that  $|V_{zz}| \ge |V_{xx}| \ge |V_{yy}|$ . The **V**<sup>PAS</sup> tensor is traceless, and it is convenient to characterize it in terms of the following two independent parameters: (a) the static quadrupole coupling constant  $\chi$ , defined as  $eQV_{zz}/h$ ; (b) the static asymmetry parameter  $\eta$ , defined as  $\eta = (|V_{xx}| - |V_{yy}|)/|V_{zz}|$  (note that  $0 \le \eta \le 1$ ). For the <sup>2</sup>H nuclei in  $d_4$ -OP, it is valid to assume that the z axis of  $\mathbf{V}^{\text{PAS}}$  lies along the direction of the C–D bond.

In general, <sup>2</sup>H NMR line shapes in the rapid motion regime (i.e., frequency of motion greater than ~ 10<sup>8</sup> s<sup>-1</sup>) can be simulated as though they are "static" spectra but using a motionally averaged ("effective") quadrupole coupling constant (denoted  $\chi^*$ ) and a motionally averaged ("effective") asymmetry parameter (denoted  $\eta^*$ ), which generally differ from the static quadrupole coupling constant ( $\chi$ ) and static asymmetry parameter ( $\eta$ ). Furthermore, in considering such spectra to be represented by an "effective" static deuteron with quadrupole interaction parameters  $\chi^*$  and  $\eta^*$ , the orientation of the principal axis system of the EFG tensor for this effective deuteron is generally different from the orientation of the principal axis system of the EFG tensor in the sites occupied by the true deuteron during the motion.

Simulations of quadrupole echo <sup>2</sup>H NMR spectra were obtained using the TURBOPOWDER program.<sup>40</sup> The line shape

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FIG. 2. Elastic intensity as a function of temperature for  $h_{30}$ -OP/ $d_4$ -urea (diamonds) and C<sub>19</sub>H<sub>40</sub>/ $d_4$ -urea (circles): the elastic intensity was normalized with respect to the spectra recorded at 50 K for  $h_{30}$ -OP/ $d_4$ -urea and 8 K for C<sub>19</sub>H<sub>40</sub>/ $d_4$ -urea.

simulations take into account distortions in the intensities of shoulders in the <sup>2</sup>H NMR spectrum arising from the finite pulse power. In these spectral simulations, the line broadening factor was 3 kHz, and typically 60 to 100 crystal orientations were considered in calculating the powder pattern. As discussed below, in order to obtain satisfactory agreement between experimental and simulated <sup>2</sup>H NMR spectra, it is necessary to optimize several parameters that define the dynamic process. <sup>2</sup>H NMR line shape analysis in the case of dynamic models with a large number of variables is potentially problematic, as the uniqueness of the fitting procedure is not necessarily straightforward to establish. In order to overcome this difficulty, the work reported here has combined the SIMPLEX optimization technique<sup>41</sup> with the programs for <sup>2</sup>H NMR line shape simulations (see Ref. 42 for further details). We emphasize that this approach provides an objective assessment of the level of agreement between experimental and simulated <sup>2</sup>H NMR spectra, and removes much of the subjectivity that is inherent in the traditional approach based on visual comparison of experimental and simulated <sup>2</sup>H NMR spectra.

#### **IV. RESULTS**

#### A. Qualitative assessment

First, we discuss qualitative aspects of the IQNS spectra recorded on the high-resolution IRIS spectrometer. The temperature dependence of the elastic peak intensity in  $Q_{\perp}$  geometry for  $h_{30}$ -OP/ $d_4$ -urea (at elastic momentum transfer  $Q = 1.3 \text{ Å}^{-1}$ ) is shown in Fig. 2. No discontinuity is observed in the temperature range investigated, suggesting that no structural phase transition occurs in this range. The temperature dependence of the elastic peak intensity for the  $h_{40}$ -nonadecane/ $d_4$ -urea  $(C_{19}H_{40}/d_4$ -urea) inclusion compound,<sup>25</sup> recorded under similar conditions [on the IN10 spectrometer at ILL (Grenoble)] is also shown in Fig. 2, illustrating the fundamentally different dynamic behavior of the guest molecules in the  $h_{40}$ -nonadecane/ $d_4$ -urea and  $h_{30}$ -OP/ $d_4$ -urea inclusion compounds. The variation of the elastic intensity with increasing temperature for  $h_{30}$ -OP/ $d_4$ -urea shown in Fig. 2 is due to fast reorientational



FIG. 3. IQNS spectrum recorded in  $Q_{\parallel}$  geometry  $(2\theta_B = 90^\circ)$  for  $h_{30}$ -OP/ $d_4$ -urea at 150 K. Note the scale expansion by the factor of 100.

and vibrational motions. As discussed below, fast reorientational motions of the guest molecules are detected in  $Q_{\perp}$ geometry in the temperature range 230–323 K on the timeof-flight spectrometers IN5 and IN6.

In  $Q_{\parallel}$  geometry, the quasielastic profiles indicate the existence of very weak inelastic modes at about 2.2 meV, shown in Fig. 3, which do not overlap with the quasielastic profile arising from diffusive translations of the guest molecules along the tunnel axis. These inelastic excitations have been assigned previously in alkane/urea inclusion compounds to the density of states of the sliding of the host and guest substructures relative to each other.<sup>43</sup> It is important to note that the maxima of the density of states for alkane/urea inclusion compounds have been observed previously<sup>44</sup> in the range 0.8–1.2 meV.

From the plot of the width (HWHM) of the quasielastic profiles in  $Q_{\perp}$  and  $Q_{\parallel}$  geometries shown in Fig. 4 [determined by fitting each scattering angle using Eq. (2) with N=2], it is clear that the translational and reorientational relaxation mechanisms are significantly different. For reorientational motions ( $Q_{\perp}$  geometry), the width of the quasielastic broadening increases continuously as the elastic momentum transfer Q increases, suggesting that the dynamic process is diffusive. For translational motions ( $Q_{\parallel}$  geometry), the width of the quasielastic broadening increases only smoothly as Q increases, suggesting that the dynamic model involves only two or perhaps three Lorentzian functions. In addition, the time scales of both motions are significantly different, with the broadening of the  $Q_{\perp}$  spectra more than two times larger than the broadening of the  $Q_{\parallel}$  spectra.



FIG. 4. Variation of the widths (HWHM), as a function of Q, of the quasielastic broadenings in the IQNS spectra recorded for  $h_{30}$ -OP/ $d_4$ -urea in  $Q_{\parallel}$ and  $Q_{\perp}$  geometries at 300 K.



FIG. 5. Experimental (left side) and simulated (right side) <sup>2</sup>H NMR spectra for  $d_4$ -OP/ $h_4$ -urea. The simulated spectra were calculated assuming a model of uniaxial rotational diffusion of the CD<sub>2</sub> groups in a twofold potential, as discussed in the text.

Clearly, the IQNS line shapes may be rationalized using models in which the reorientational and translational motions of the guest molecules are uncorrelated.

<sup>2</sup>H NMR spectra of  $d_4$ -OP/ $h_4$ -urea, recorded from 89 to 250 K, are shown in Fig. 5. The frequency separation between the perpendicular peaks  $(\Delta v_s \approx 122 \text{ kHz})$ ("horns") in the spectrum recorded at 89 K is characteristic of a static <sup>2</sup>H NMR powder pattern, and the best-fit simulation of this spectrum (Fig. 5) is obtained assuming no motion of the deuterons, with static quadrupole coupling constant  $\chi = 163$  kHz and static asymmetry parameter  $\eta = 0$ . These values are typical for deuterons of CD<sub>2</sub> groups in alkyl chains.<sup>45</sup> The changes in the <sup>2</sup>H NMR spectrum in the temperature range 110-250 K are characteristic of the deuterons passing through an intermediate motion regime. Within the constrained environment of the urea host structure, reorientation of the C–D bonds (of the  $CD_2$  groups) within the  $d_4$ -OP molecule is likely to take the form of reorientation about the tunnel axis. The angle between each C-D bond and the tunnel axis is  $\sim 90^{\circ}$ , and we therefore focus on models involving reorientation of the deuteron about an axis perpendicular to the C-D bond. From qualitative assessment of the <sup>2</sup>H NMR spectra in the range 110–250 K, it is immediately clear that the  $d_4$ -OP molecules do not undergo motions such as continuous rotation, three-site 120° jumps, or six-site 60° jumps about the tunnel axis, as the <sup>2</sup>H NMR spectrum in the upper intermediate motion regime and rapid motion regime for such motions would regain the axially symmetric  $(\eta^*=0)$  Pake powder pattern line shape, but with width scaled by a factor of 1/2 compared with the spectrum in the slow motion regime. Instead, the observed changes in the  ${}^{2}$ H NMR line shape for  $d_4$ -OP/urea resemble those for models involving two-site jumps of the deuteron. The observed changes in the <sup>2</sup>H NMR line shape are reproduced reasonably well by simulations based on a two-site jump model with  $2\varphi_0 = 113^\circ$ , where  $2\varphi_0$  denotes the angle between the



FIG. 6. Theoretical effective potential function  $V(\varphi)$  (calculated using  $\varphi_0 = 56.5^{\circ}$  and  $\gamma = 9$ ) for the model of uniaxial rotational diffusion. The potential barriers  $\Delta V_1$  and  $\Delta V_2$  are defined in the figure.

orientations of the C–D bond in the two sites. However, as discussed previously,<sup>46</sup> this two-site jump model can be ruled out, as it cannot fit the IQNS data in  $Q_{\perp}$  geometry.

#### B. Reorientational dynamics

From qualitative analysis of the IQNS and <sup>2</sup>H NMR spectra, we expect that a model of reorientational diffusion in a two-fold potential could fit both the IQNS spectra in  $Q_{\perp}$  geometry and the <sup>2</sup>H NMR spectra. Reorientational diffusion of the OP molecules in a twofold potential corresponding to the following orientational distribution function<sup>47</sup> has been considered,

$$P(\varphi) = F[e^{-\gamma \cos(\varphi + \varphi_0)} + e^{-\gamma \cos(\varphi - \varphi_0)}], \qquad (6)$$

where *F* is a normalization factor and  $\gamma$  is defined below [Eq. (10)]. The corresponding effective (mean force) potential for reorientations is,

$$\frac{V(\varphi)}{k_B T} = -\ln F + \gamma \cos(\varphi) \cos(\varphi_0) -\ln(2\cosh(\gamma \sin(\varphi)\sin(\varphi_0))).$$
(7)

The potential barrier  $\Delta V_1$  between the two minima, defined in Fig. 6, is given (for  $\gamma > 1$ ) by,

$$\frac{\Delta V_1}{k_B T} = -\ln 2 + \gamma (1 - \cos(\varphi_0)), \qquad (8)$$

and the potential barrier  $\Delta V_2$ , also defined in Fig. 6, is,

$$\frac{\Delta V_2}{k_B T} = -\ln 2 + \gamma (1 + \cos(\varphi_0)).$$
(9)

The relationship between  $\gamma$  and the activation energies  $\Delta V_1$ and  $\Delta V_2$  is,

$$\gamma = \frac{1}{1 - \cos(\varphi_0)} \left[ \ln(2) + \frac{\Delta V_1}{k_B T} \right]$$
$$= \frac{1}{1 + \cos(\varphi_0)} \left[ \ln(2) + \frac{\Delta V_2}{k_B T} \right]. \tag{10}$$

The rotational diffusion process that we have considered is defined by the orientational distribution function given in Eq. (6), and our approach has employed the finite difference approximation to the Smoluchowski equation for simulating both IQNS spectra<sup>48</sup> and <sup>2</sup>H NMR spectra.<sup>40</sup> The dimension

TABLE I. Final parameters obtained by fitting the model of uniaxial rotational diffusion in a twofold potential to the  $Q_{\perp}$  IQNS line shapes of  $h_{30}$ -OP/ $d_4$ -urea. The angle  $\varphi_0$  was fixed at 56.5°.

T/K	$D_r/\mathrm{ps}^{-1}$	γ
230	$4.90 \times 10^{-2}$	10.6
250	$7.10 \times 10^{-2}$	9.0
260	$1.15 \times 10^{-1}$	7.6
278	$1.37 \times 10^{-1}$	7.2
300	$1.67 \times 10^{-1}$	6.2

of the rate matrix was taken as N=24 (corresponding to a grid spacing  $\delta = 15^{\circ}$  on a circle). To obtain the final theoretical IQNS and <sup>2</sup>H NMR line shapes for this model of rotational diffusion, the master equation for the orientational distribution function has been considered with the following parameters varied in the fitting procedure:  $\gamma$ ,  $\varphi_0$ , and  $D_r$  (the rotational diffusion coefficient).

In fitting the IQNS data in  $Q_{\perp}$  geometry, the standard gyration radius for alkanes ( $r_g = 1.39$  Å) was taken. Thus, Eq. (1) was fitted to the experimental IQNS spectra in  $Q_{\perp}$ geometry using Eqs. (2)–(5) with  $\alpha = 90^{\circ}$ . In the preliminary stage of fitting, we found that the parameters  $\gamma$  and  $\varphi_0$  gave good results at 300 K with  $5 < \gamma < 6$  and  $40^{\circ} < \varphi_0 < 70^{\circ}$ . Because of the large uncertainty in the value of  $\varphi_0$ , this parameter was fixed at 56.5° (based on the value found from preliminary fits of the <sup>2</sup>H NMR data using a two-site jump model<sup>46</sup>) and the other parameters  $\gamma$  and  $D_r$  were refined simultaneously. The best agreement between the experimental and theoretical scattering functions was obtained with the parameters listed in Table I. To illustrate the quality of the fits, the experimental and theoretical EISFs are compared in Fig. 7 and the experimental and theoretical scattering profiles are compared in Fig. 8.

With regard to fitting this model to the experimental <sup>2</sup>H NMR spectra, it is anticipated that there may be a significant degree of correlation between different parameters defining the model (as for fitting to the IQNS data), and caution must therefore be observed. Preliminary simulations for this model suggested that the <sup>2</sup>H NMR line shape is particularly sensitive to the value of  $\varphi_0$ , and substantially less sensitive to the value of  $\gamma$  (in contrast to the case of fitting the IQNS data). For this reason, and in order to keep the number of fitted parameters as low as possible, approximate values of  $\gamma$  at the temperatures of the <sup>2</sup>H NMR experiments were ob-



FIG. 7. Comparison between the experimental and theoretical EISFs in  $Q_{\perp}$  geometry for  $h_{30}$ -OP/ $d_4$ -urea at 300 K. The theoretical curve (solid line) is for the model of uniaxial rotational diffusion discussed in the text.



FIG. 8. Comparison between the experimental and fitted IQNS spectra (IN5 spectrometer) for  $h_{30}$ -OP/ $d_4$ -urea in  $Q_{\perp}$  geometry. Left side: as a function of temperature for  $Q = 2.1 \text{ Å}^{-1}$ ; right side: as a function of Q at T = 300 K.

tained by extrapolating from the fitted values of  $\gamma$  from the IQNS data analysis at higher temperatures. In the temperature range 230–300 K probed by the IQNS experiments,  $\gamma$  is found to have an approximately linear dependence on temperature described by  $\gamma = 24.2 - 0.061 (T/K)$ . The starting value of  $\gamma$  at the temperature of each of the measured <sup>2</sup>H NMR spectra was then *estimated* by extrapolation from this linear relationship. Although this is an approximation, our earlier finding that the <sup>2</sup>H NMR spectra are rather insensitive to the value of  $\gamma$  lends justification to this approach. In fitting the <sup>2</sup>H NMR line shape at each temperature, the value of  $\gamma$ was initially fixed and the following parameters were optimized using the SIMPLEX algorithm:  $D_r$ ,  $\varphi_0$ , and  $\chi^*$  (the motionally averaged quadrupole coupling constant). Allowing  $\chi^*$  to vary with temperature effectively subsumes within the model the occurrence of small amplitude motions that are rapid on the <sup>2</sup>H NMR time scale but not straightforward to model explicitly. In the present case, these motions may comprise rapid small-amplitude "wobbling" of the  $d_4$ -OP molecule. The fact that  $\chi^*$  decreases as temperature increases is consistent with the amplitude of such motions increasing as temperature increases. As shown in Fig. 5, the rotational diffusion model gives a satisfactory fit to the experimental <sup>2</sup>H NMR spectra throughout the temperature range investigated (110-250 K). The optimum values of the parameters at each temperature are shown in Table II.

Comparison of Tables I and II shows that there is good agreement in fitting the same model of rotational diffusion in a twofold potential to both the IQNS and <sup>2</sup>H NMR data. The angle between the most probable orientations of the OP guest molecules (with respect to reorientation about the tunnel axis) is 116°, and the rotational diffusion coefficients  $D_r$  obtained from both techniques are of the same order of mag-

TABLE II. Final parameters obtained by fitting the model of uniaxial rotational diffusion in a twofold potential to the <sup>2</sup>H NMR line shape for  $d_4$ -OP/ $h_4$ -urea.

T/K	$D_r/\mathrm{ps}^{-1}$	γ	$arphi_0/^\circ$	$\chi^{*/\mathrm{kHz}}$
110	$6.90 \times 10^{-6}$	17.5	58	160
140	$1.97 \times 10^{-4}$	15.7	59	158
150	$2.06 \times 10^{-4}$	15.1	59	158
200	$1.50 \times 10^{-2}$	12.0	58	155
250	$4.60 \times 10^{-2}$	9.0	57	151

nitude in the 200–250 K temperature range, representing continuity in dynamic behavior between the temperature regions over which the two techniques are sensitive to the dynamic process. Furthermore, the fit of the experimental values of  $\gamma$  using Eq. (10) shown for example in Fig. 9(a), gives  $\Delta V_1 = 7.1 \pm 0.5$  and  $\Delta V_2 = 26.2 \pm 0.5$  kJ mol<sup>-1</sup> over the full experimental temperature range. As an illustration of the compatibility between the parameters obtained from fitting the IQNS and <sup>2</sup>H NMR results, the dependence of  $\ln(D_r)$  on  $T^{-1}$  is shown in Fig. 9(b). On the usual assumption of Arrhenius behavior  $[D_r = D_0 \exp(-E_a/k_BT)]$ , the activation energy is estimated to be  $E_a = 15$  kJ mol<sup>-1</sup> with  $D_0 = 102$  ps<sup>-1</sup>. We note that the activation energy obtained from the Arrhenius plot compares well with  $(\Delta V_1 + \Delta V_2)/2$ .

#### C. Translational dynamics

For  $Q_{\parallel}$  geometry, we have fitted the experimental spectra using Eq. (3) with the parameters describing the reorientational contribution, listed in Table I, kept fixed during the refinement. Initially, we considered a model of translational diffusion in a onefold potential as developed for alkane/urea inclusion compounds,<sup>26</sup> but the  $Q_{\parallel}$  spectra could be fitted using this model only for Q < 1.5 Å<sup>-1</sup>. In agreement with the qualitative analysis of the IQNS spectra reported in Sec. IV A, this model is unable to predict the fact that the width (HWHM) is nearly constant for  $Q > 1.5 \text{ Å}^{-1}$  (see Fig. 4). Clearly a model of translational diffusion in a more complex potential is required. With the information obtained from qualitative analysis of the data in  $Q_{\parallel}$  geometry [i.e., that it is sufficient to consider two or perhaps three Lorentzian functions (in addition to the weak contribution due to reorientational motions) to fit the quasielastic broadening, we must consider a model of translational diffusion in a potential with very large barriers (small barriers would involve too many Lorentzian functions for  $Q > 1.5 \text{ Å}^{-1}$ ). As a first approximation, we have considered a model of translational jumps over three equally spaced sites with *unequal* populations, as shown schematically in Fig. 10. For this model (with N=3), the structure factors determining the scattering law in Eq. (2) are,

$$A_{0}(Q) = (p_{1})^{2} + \frac{(1-p_{1})^{2}}{2} + 2p_{1}(1-p_{1})\cos(Qd) + \frac{(1-p_{1})^{2}}{2}\cos(2Qd), A_{1}(Q) = \frac{3p_{1}(1-p_{1})}{2} - 2p_{1}(1-p_{1})\cos(Qd) + \frac{p_{1}(1-p_{1})}{2}\cos(2Qd),$$
(11)  
$$A_{2}(Q) = \frac{(1-p_{1})}{2} - \frac{(1-p_{1})}{2}\cos(2Qd),$$

where  $p_1$  is the probability of occupation of site 1 and *d* is the distance between adjacent sites. The widths of the Lorentzian functions in Eq. (2) are,

$$\Delta_1 = \frac{2\tau^{-1}}{(1-p_1)}, \quad \Delta_2 = \frac{2p_1\tau^{-1}}{(1-p_1)}, \tag{12}$$

where  $\tau$  is the characteristic time of the motion and  $\tau^{-1}$  is the jump rate from site 1 to site 2 or site 3. The best agreement between the experimental and theoretical scattering functions was obtained with the parameters listed in Table III. Comparison of the experimental and theoretical EISFs (Fig. 11) and the experimental and theoretical scattering profiles (Fig. 12) demonstrates the good quality of the fits. We note that the jump distance found using this jump model is  $d\approx 1.8$  Å at all temperatures investigated by IQNS, i.e.,  $d\approx c_h/6$ . Assuming Arrhenius behavior  $[\tau^{-1} = \tau_0^{-1} \times \exp(-E_a/k_BT)]$ , the activation energy is found to be  $E_a$ = 13 kJ mol<sup>-1</sup> with  $\tau_0^{-1} = 0.2$  ps<sup>-1</sup>.

#### **V. DISCUSSION**

The results reported here for the reorientational and translational dynamics of OP guest molecules in the urea tunnel structure have important consequences that relate to our broader understanding of the structural and dynamic properties of urea inclusion compounds.



FIG. 9. (a): Temperature dependence of the parameter  $\gamma$ . The continuous line is the best fit of Eq. (10) to the data. (b): Plot of  $\ln(D_r)$  vs  $T^{-1}$  for the model of uniaxial rotational diffusion in a twofold potential. The symbols represent experimental values and the solid line represents the best fit of the Arrhenius equation to the data.

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TABLE III. Final parameters obtained by fitting the three-site jump model for translations to the  $Q_{\parallel}$  IQNS line shapes of  $h_{30}$ -OP/ $d_4$ -urea.

T/K	$ au^{-1}/\mathrm{ps}^{-1}$	$d/\text{\AA}$	<i>p</i> <sub>1</sub>
250	$0.7 \times 10^{-2}$	1.75	0.90
260	$1.3 \times 10^{-2}$	1.78	0.86
285	$1.9 \times 10^{-2}$	1.80	0.80
300	$2.3 \times 10^{-2}$	1.82	0.78

First, we believe that our strategy of combining <sup>2</sup>H NMR and IQNS techniques (and, in the case of IQNS, using two spectrometers with different instrumental resolutions) represents a comprehensive approach for establishing the reorientational dynamics of the guest molecules. In view of the hexagonal structure of the urea host tunnel, it is perhaps surprising that we have found a model of rotational diffusion of the guest molecules in a twofold potential with rather large barriers, and we may conclude that the hexagonal description of the urea tunnel structure is true only on an average basis. Indeed, as the basic guest structure in the OP/urea inclusion compound is known<sup>19</sup> to comprise six orientationally distinguishable monoclinic domains, it is not surprising that the local structure of the host should also be lower than hexagonal. From the temperature dependence of the rotational diffusion coefficient, there is no indication of any structural phase transition within the temperature range investigated. The reorientational behavior of the OP molecules is probably influenced largely by the C=O groups and their interaction with the urea tunnels (the C=O groups are oriented approximately perpendicular to the tunnel axis, directly toward urea molecules). These interactions are undoubtedly influential in dictating the nature of the intermodulation function.

Previous x-ray diffraction experiments<sup>19</sup> on OP/urea have shown that there is three-dimensional positional ordering of the guest molecules, with the basic guest structure having monoclinic space group symmetry C2/m or C2. The twofold axis (unique axis of the monoclinic system) is perpendicular to the tunnel axis of the host structure, and there are six equivalent, but orientationally distinguishable ways in which this basic guest structure can be oriented with respect to the host structure. In practice, a single crystal of the OP/ urea inclusion compound contains all six orientationally distinguishable domains of the basic guest structure, and (as discussed above) the average host structure (hexagonal) is an average over the local host structures (lower than hexagonal) in these six domains.



FIG. 10. Schematic representation of the model of translation jumps between three sites with unequal probability of occupation.



FIG. 11. Comparison between the experimental and theoretical EISFs in  $Q_{\parallel}$  geometry for  $h_{30}$ -OP/ $d_4$ -urea at 300 K. The theoretical curve (solid line) is for the dynamic model discussed in the text.

We now assess plausible structural interpretations of the reorientational dynamics of the OP guest molecules deduced from the IQNS and <sup>2</sup>H NMR data. The plausible conformation of the OP guest molecules within the urea tunnel is the conformation with point group  $C_2$ , in which the twofold axis passes through the center of the O-O bond and the dihedral angle C–O–O–C denoted  $\chi$ . This conformation with  $\chi$  $\approx 120^{\circ}$  is adopted in the pure crystalline phase of OP<sup>49</sup> and in the structures of other long chain diacyl peroxides.<sup>50</sup> The conformation with point group  $C_{2h}$ , in which all carbon atoms lie in the same plane and the dihedral angle C-O-O-C is  $\chi = 180^{\circ}$ , is considered unlikely. The OP molecule may fit within the urea tunnel only if the conformation of the alkyl chains is close to the "all-trans" conformation. Further, we assume that all OP guest molecules exist in the same conformational state within the urea inclusion compound. The dy-



FIG. 12. Comparison between the experimental and fitted IQNS spectra (IN5 spectrometer) for  $h_{30}$ -OP/ $d_4$ -urea in  $Q_{\parallel}$  geometry. Left side: as a function of temperature with  $Q = 2.2 \text{ Å}^{-1}$ ; right side: as a function of Q at T = 300 K.

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FIG. 13. Schematic representation of the orientations of the OP molecules in urea viewed along the tunnel axis: (a) and (b) assuming  $C_2$  conformation for OP reorienting as a whole; (c) and (d) assuming dynamic interconversion between  $-\chi$  and  $+\chi$  conformations ( $C_2$ ) of the OP molecules. The open circles represent the C=O group of the OP molecule closer to the viewer and the arrow represents the  $C_2$  symmetry axis.

namic model indicates that the CH<sub>2</sub> (CD<sub>2</sub>) groups of each OP molecule interconvert between two orientations (with  $2\varphi_o = 116^\circ$ ), and we now consider how this may be reconciled with knowledge of the molecular and crystal symmetry.

For OP molecules with the  $C_2$  conformation, a dynamic model involving reorientation of these molecules about the tunnel axis between two preferred orientations is consistent with the space group C2 for the average basic guest structure provided the two orientations are as shown in Figs. 13(a) or 13(b). In these cases, the C=O bonds point approximately toward the corners of the hexagonal urea tunnels (in projection). A second possible interpretation of the dynamics is that the OP molecules in the  $C_2$  conformation undergo dynamic interconversion between two mirror-image conformational states with  $\chi = 2 \varphi_o \approx 116^\circ$ . These enantiomeric conformations (denoted  $+\chi$  and  $-\chi$ ) are energetically equivalent for the isolated molecule, but within the chiral urea tunnel structure they give rise to different diastereoisomeric host/guest relationships, and are therefore not energetically equivalent. This second dynamic model is consistent with the average symmetry of the basic guest structure being described by space group C2, provided the two-fold axes of the molecule and the crystal are coincident [see Figs. 13(c)and 13(d)]. In support of this interpretation of the dynamics, molecular modeling suggests that a conformation of the OP molecule with  $\chi$  in the range 100 to 120° and with "alltrans" alkyl chains can be readily accommodated within the urea tunnel, and that interconversion between the  $+\chi$  and  $-\chi$  conformations is associated with little change in the overall shape and volume of the molecule. Furthermore, for this dynamic model involving interconversion between  $+\chi$ and  $-\chi$  conformations of the guest molecule, the two-fold symmetry axis is retained when the interconversion ceases at sufficiently low temperature; this may be consistent with the absence of evidence for a phase transition in OP/urea at low temperature.

ing interconversion between two conformations of the OP molecules is in better agreement with our experimental findings and our knowledge and intuitive understanding of the structural characteristics of the OP/urea inclusion compound. Currently, there is no experimental knowledge of the conformation adopted by the OP guest molecules inside the urea tunnel; such information may provide an independent assessment of the validity of the proposed relaxation mechanism. Further diffraction studies will significantly improve our understanding of this and many other aspects of the OP/urea inclusion compound. Such studies are planned in the near future.

For translational motions of the OP guest molecules along the tunnel axis, we have shown *first* that the amplitude of antitranslational vibrations of the two substructures is very small, and second that the maximum of their density of states is at about 2.2 meV. In addition, the translational diffusion mechanism of the guest molecules involves "jumps" (i.e., translational diffusion in a potential with large barriers) between specific positions along the tunnel axis separated by approximately  $c_h/6$ . These results suggest very strongly that there is "pinning" of the guest molecules at specific positions along the urea tunnels, although not necessarily commensurate with the host substructure. In agreement with this conclusion, no "sliding mode" with acoustic type behavior could be observed for OP/urea by Rayleigh-Brillouin scattering<sup>51</sup> because of the resulting "gap" in the dispersion branch. Despite the fact that the model used here to describe the translational dynamics of the OP guest molecules in a three-fold potential is to a large extent arbitrary, the jump distances deduced from IQNS (of the order of 1.8 Å) are clearly of significant magnitude. Recalling that the basic guest structure exhibits three-dimensional ordering, with a well-defined structural relationship between the positions of guest molecules in adjacent tunnels (with  $\Delta_{g} = 4.6$  Å), it is probable that the translations are strongly cooperative both for guest molecules within each tunnel and for guest molecules in adjacent tunnels.

## VI. CONCLUDING REMARKS

We have shown in this paper that a single model of uniaxial reorientational diffusion in a twofold potential provides a basis for interpretation of both <sup>2</sup>H NMR and IQNS spectra ( $Q_{\perp}$  geometry) for the OP/urea inclusion compound. The combination of these two techniques is a very powerful strategy for probing motions on very different characteristic time scales, and should be applied in future studies of the reorientational dynamics of other molecular solids over a wide range of temperatures.

We have shown that a model of uniaxial reorientational diffusion in a twofold potential is consistent with the hydrogens (deuterons) of the OP guest molecules occupying two preferred positions with respect to reorientation about the tunnel axis, with the angle between these positions differing by  $\sim 116^{\circ}$ , and a relaxation mechanism implying conformational interconversion of the OP molecules is proposed. Clearly, the orientational distribution function for the guest molecules in OP/urea is substantially more restricted than that for the guest molecules in alkane/urea inclusion com-

In summary, the proposed relaxation mechanism involv-

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pounds. Models used previously (in fitting IQNS data) to describe the reorientational motion of the guest molecules in alkane/urea inclusion compounds comprised reorientational diffusion in a onefold potential,<sup>26</sup> and further insights into the orientational characteristics of the guest molecules in nonadecane/urea have been established from computer simulation studies.<sup>37</sup>

For the translational component of the motion along the tunnel axis, the inelastic features ("side-peaks") observed in the IQNS spectra in  $Q_{\parallel}$  geometry occur at higher energy for OP/urea than for the alkane/urea inclusion compounds. This signifies a higher energy for the antitranslational vibrations of the host and guest subsystems in OP/urea, presumably on account of the additional interaction between the C=O groups of the OP guest molecules and the urea molecules that form the wall of the tunnel. In addition, unlike the situation for alkane/urea inclusion compounds, the translational diffusion of OP molecules along the urea tunnels is not "continuous," but can be interpreted in terms of jumps between specific sites. The combined knowledge of the translational dynamics is consistent with the possibility that local distortions of the tunnel wall may involve the establishment of C=O···H-N hydrogen bonds, similar to those observed recently<sup>6-8</sup> in commensurate urea inclusion compounds containing alkanedione guest molecules.

#### ACKNOWLEDGMENTS

We are grateful to ILL and EPSRC for generous allocations of neutron beam time which allowed the IQNS experiments described in this paper to be performed, and to University of London Intercollegiate Research Services and BP Research International for access to facilities for solid state NMR spectroscopy. The Nuffield Foundation, NATO, the British Council, the "Direction Générale de la Recherche et de la Technologie," and NSF (Grant No. CHE-9423726) are thanked for financial support. Professor R. G. Griffin is thanked for providing the TURBOPOWDER program.

#### APPENDIX: PREPARATION OF MATERIALS

Octanoic acid (99%), octanoyl chloride (99%),  $D_2SO_4$ (98%, 99.5+ atom % D), 20% DCl (99+ atom % D) and pentane (HPLC grade) were obtained from Aldrich Chemical Co. and used without further purification. Deuterium oxide (99.8%) and deuterium chloride (35% w/w in  $D_2O$ , 99 atom % D) were obtained from General Intermediates of Canada. Urea- $d_4$  (98+ atom % D) and MeOD (99.5 atom % D) were obtained from Sigma Chemical Co. and were used without further purification. Diethyl ether and THF were distilled from sodium benzophenone ketyl, and pyridine (Terochem) was distilled from CaH<sub>2</sub> before use. Thionyl chloride (BDH Chemicals) and H<sub>2</sub>O<sub>2</sub> (Fisher, 30%) were used as purchased. All glassware used for exchanges was dried before use.

## 1. Octanoic acid-2,2-d<sub>2</sub>

A mixture of octanoic acid (5.46 g, 37.9 mmol), DCl in  $D_2O$  (7.83 g, 8.0% DCl) and dry THF (22 mL) was stirred vigorously under  $N_2$  for 2.3 h before the layers were separated. This procedure was repeated with 7.86 g of 12.4% DCl

in  $D_2O$  (1 h) and 8.0 g of 13.8% DCl in  $D_2O$  (3 h in an ultrasonic bath). The mixture was extracted three times with a total of 37 mL of dry ether and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to give 4.675 g of a clear oil. The exchanged  $C_8H_{15}CO_2D$  was heated with 90%  $D_2SO_4$  in  $D_2O$  (38.7 g) for 60 h at 96 °C to form a black solution that was poured into cold H<sub>2</sub>O (100 mL) after cooling to room temperature. After extraction with three 50 mL portions of pentane, NaCl (3 g) was added to break up emulsions, and the aqueous layer was further extracted with a total of 200 mL of pentane. The combined pentane extracts were dried over anhydrous  $Na_2SO_4$  and condensed to give 4.67 g of a yellow oil. The partially deuterated decanoic acid was exchanged twice with DCl/D<sub>2</sub>O, extracted with pentane, and condensed to give 4.31 g of a yellow oil, which was heated to 90 °C under N<sub>2</sub> for 25 h with 90%  $D_2SO_4$  in  $D_2O$  (38.25 g). The black reaction mixture was poured into H<sub>2</sub>O (80 mL), NaCl (7.5 g) was added, and the labeled acid was extracted four times with a total of 375 mL of pentane. The organic layer was extracted three times with a total of 100 mL of 1 M aqueous KOH, then the aqueous layer was acidified (50 mL of 4.4 M HCl) and extracted with five 40 mL portions of CH<sub>2</sub>Cl<sub>2</sub> and one 40 mL portion of pentane. After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the yellow oil was distilled with a Kugelrohr (75 °C, 0.25 mm Hg) to give 2.74 g (50% overall) of the product as a clear oil. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): d 0.88 (t, 3H, J = 7 Hz), 1.29 (*m*, 8H), 1.62 (*t*, 2H, J = 7 Hz), 2.32 (*t*, 0.15*H*, J = 7 Hz) (93% atom% D by this method).

#### 2. Octanoyl chloride-2,2-d<sub>2</sub>

Octanoic acid-2,2- $d_2$  (1.23 g, 8.4 mmol) was stirred with SOCl<sub>2</sub> (1.80 g, 15.1 mmol) for 12 h at room temperature. The excess SOCl<sub>2</sub> was removed under vacuum and the product was distilled under vacuum (26 °C, 0.15 mm Hg) to yield 1.27 g (91.8%) of a clear oil. Mass spectral analysis (EI) of the methyl ester (formed by adding 5 mL of the acid chloride to 1 mL of MeOH) gave the following integrated intensities: m/e (relative intensity) 158 ( $M^+$  for  $d_0$ , 0.64), 159 ( $M^+$  for  $d_1$ , 16.84), 160 ( $M^+$  for  $d_2$ , 100). Comparison with unlabeled methyl octanoate (Eastman Kodak) (158 ( $M^+$ , 100), 159 ( $M^{+1}$ , 18.95), 160 ( $M^{+2}$ , 1.9) showed that the labeled ester contained 86.9% of  $\alpha$ - $d_2$  and 12.6% of  $\alpha$ - $d_1$  material (93.1% total <sup>2</sup>H incorporation).

#### 3. Dioctanoyl peroxide-2,2-2',2'-d<sub>4</sub>

To a stirred solution of octanoyl chloride-2,2- $d_2$  (0.91 g, 5.53 mmol) in ether (20 mL), hydrogen peroxide (30%, 0.48 g, 4.13 mmol) was added over 1 min at 1 °C. Pyridine (0.54 g, 6.8 mmol) in Et<sub>2</sub>O (10 mL) was added dropwise over 24 min while keeping the temperature below 3 °C. After warming over 10 min to 20 °C, the solution was stirred at 20 °C for 15 min before cold Et<sub>2</sub>O (10 mL), cold H<sub>2</sub>O (10 mL) and cold pentane (15 mL) were added, and the layers were separated. The organic layer was washed three times with a total of 25 mL of cold, 0.5 M HCl, twice with 10 mL portions of cold, 5% aqueous NaHCO<sub>3</sub>, once with 10 mL of cold, saturated, aqueous NaCl, dried over Na<sub>2</sub>SO<sub>4</sub> and then filtered through a glass frit to give a clear oil (0.75 g, 93.2%) after

evaporation of solvent. This clear oil was dissolved in MeOH (4.5 mL) and cooled to 5  $^{\circ}$ C to give a white powder (0.46 g), which was collected at 5  $^{\circ}$ C and used immediately for formation of urea inclusion compounds.

## 4. Dioctanoyl peroxide-2,2,2',2'- $d_4$ /urea

In a 50 mL Erlenmeyer flask, octanoyl peroxide-2,2,2',2'- $d_4$  (0.46 g) was dissolved in 10 mL of MeOH and then mixed with 25 mL of 1.8 M urea in MeOH. This solution was suspended in a 1 L Dewar flask containing H<sub>2</sub>O at room temperature and cooled over 12 h to 5 °C to form 1.0 g of hexagonal urea inclusion compound crystals.

#### 5. Dioctanoyl peroxide

To a stirred solution of octanoyl chloride (99%, 10.33 g, 63.5 mmol) in Et<sub>2</sub>O (60 mL) was added a cold solution of 30% aqueous H<sub>2</sub>O<sub>2</sub> (5.28 g, 46.5 mmol) at 4 °C over 1 min. Pyridine (5.91 g, 74.5 mmol) in Et<sub>2</sub>O (15 mL) was added dropwise over 1.5 h, keeping the temperature at 4–5 °C. After addition of 13 mL of cold Et<sub>2</sub>O and 33 mL of cold H<sub>2</sub>O, the layers were separated. The organic layer was washed three times with a total of 100 mL of cold 0.5 M aqueous HCl, 33 mL of cold 5% aqueous NaHCO<sub>3</sub>, and then with 25 mL of cold, saturated aqueous NaCl before drying over anhydrous Na<sub>2</sub>SO<sub>4</sub> and condensing to give 8.39 g (95.3%) of a clear oil. Crystallization from MeOH (50 mL) at -20 °C gave a first crop of a white powdery solid, which was collected at 5 °C.

#### 6. Dioctanoyl peroxide/urea-d<sub>4</sub>

Urea- $d_4$  (98+ atom % D, 1.95 g, 30.5 mmol), dioctanoyl peroxide (1.11 g, 3.88 mmol) and MeOD (99.5 atom % D, 23.7 mL) were added to a 50 mL Erlenmeyer flask, which was sealed and then suspended in an ultrasonic bath for 45 min (highest T=32 °C) to dissolve all solids. The flask was transferred to a Dewar flask containing H<sub>2</sub>O at 34 °C, which was placed in a cold room at 5 °C. After 30 h, 1.18 g of hexagonal needles were collected at 5 °C in a glove bag purged with N<sub>2</sub>.

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