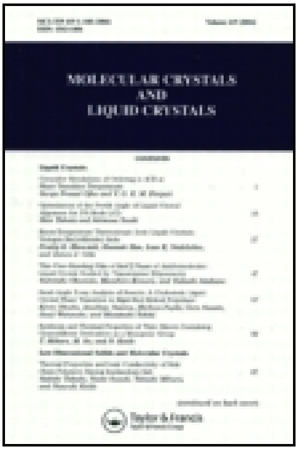

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In-situ Monitoring of Alkane-Alkane Guest Exchange in Urea Inclusion Compounds using Confocal Raman Microspectrometry

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The occurrence of alkane-alkane guest exchange within the one-dimensional channels of the urea host structure in alkane/urea inclusion compounds is demonstrated using confocal Raman microspectrometry. With appropriate deuteration of one of the alkane guest components, this technique represents a powerful strategy for in situ characterization of the alkane-alkane guest exchange process.

Keywords: confocal Raman microspectrometry; host-guest systems; molecular exchange; urea inclusion compounds

INTRODUCTION

There is currently much interest in the study of processes involving the transport of molecules or ions through channel systems, including those of biological [1,2] and industrial [3,4] importance, and including the transport of molecules within nanotubes and nanoporous materials [5–7]. Appropriate model systems, represented for example by

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crystalline channel systems of well-defined and regular structure, have an important role in developing an understanding of fundamental aspects of such processes. One such model system is based on conventional urea inclusion compounds [8–12], in which guest molecules are contained within one-dimensional channels (diameter *ca.* 5.5 Å) in a crystalline urea host structure [13,14] (Fig. 1). We have demonstrated previously [15] that transport of guest molecules in one direction along the urea channel system can occur by inserting new guest molecules at one end of the crystal (by putting it in contact with the liquid of another potential guest), with the original guest molecules expelled from the other end of the crystal. To understand details of the guest exchange process in this system, it is essential to understand the spatial distribution of the two types of guest molecule within the crystal and the variation of the spatial distribution of the two types of guest molecule as a function of time during the guest exchange process. To address these issues, we demonstrated recently [16] that confocal Raman microspectrometry can be used as an *in situ* probe of such guest exchange processes, yielding information on the spatial distribution of guest molecules and its time dependence. Our previous

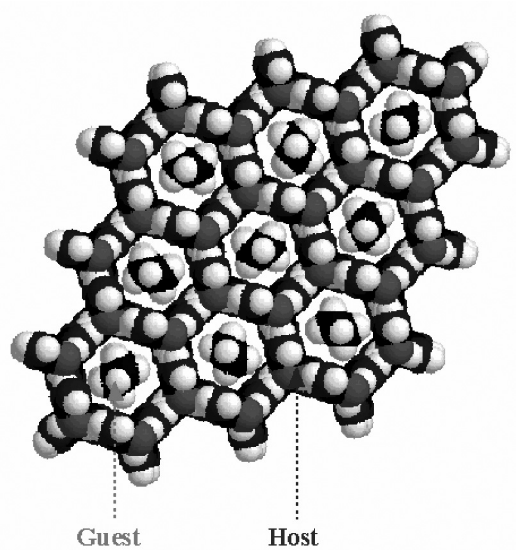


FIGURE 1 Structure of an alkane/urea inclusion compound showing nine complete channels filled with alkane guest molecules (the guest molecules are not actually located from X-ray diffraction data at ambient temperature, but have been inserted into the channels in the plot in a manner that illustrates orientational disorder).

work [15,16] was focused on the system in which the "original" and "new" guest molecules were 1,8-dibromooctane and pentadecane respectively. In the studies using confocal Raman microspectrometry, the C–Br stretching band was used to assess the relative amount of 1,8-dibromooctane guest molecules as a function of position and time within the material.

We have now extended our previous studies by focusing on the case in which the original and new guest molecules are members of the *same* homologous series, and differ only in chain length. In particular, we demonstrate in this paper the occurrence of alkane-alkane guest exchange within the urea channel structure, focusing on the urea inclusion compound containing dodecane [$CH_3(CH_2)_{10}CH_3$] as the original guest and pentadecane [$CH_3(CH_2)_{13}CH_3$] as the new guest. To monitor the guest exchange process by confocal Raman microspectrometry, fully deuterated pentadecane (pentadecane-d_{32}) was used in order to provide discrimination in the Raman spectrum between the regions of the crystal containing the original and new guest molecules. We note that, within the homologous series of alkane/urea inclusion compounds, the thermodynamic stability is greater the longer the guest molecule [17], and there is therefore a thermodynamic driving force for the pentadecane guest molecules to replace dodecane guest molecules within the urea channel system.

EXPERIMENTAL

Confocal Raman microspectrometry [18] was performed using a Labram II spectrometer (Jobin-Yvon), an Ar/Kr 2018 Spectra-Physics laser (514.5 nm) and a grating of 600 lines/mm (spectral resolution $\sim 6\,\mathrm{cm}^{-1}$). The laser was focused on the sample through a microscope with a 10 × Olympus objective of 0.25 numerical aperture and confocal pinhole diameter of 700 μm. The radial resolution was 50 μm.

Crystals of the dodecane/urea inclusion compound were prepared using standard procedures, as follows. An excess amount of the guest (excess with respect to the expected molar guest/host ratio in the inclusion compound) was added to a saturated solution of urea in methanol at 50°C. The solution was cooled to 20°C over a period of several days. Needle-shaped crystals with hexagonal cross-section were collected with diameter of *ca.* 1–2 mm and length of *ca.* 10–30 mm. The crystals were washed with 2,2,4-trimethylpentane prior each experiment to remove any guest molecules adhering to their external surfaces.

Raman spectra were also recorded for the pure liquid pentadecane-d_{32} (99% deuterated) sample used in this work, and showed that the intensity of the C–H stretching band is negligible for this material. Thus, as discussed below, we can confidently conclude that, for urea inclusion compounds containing both dodecane and pentadecane-d_{32} guest molecules during the guest exchange process, the pentadecane-d_{32} guest molecules will make no significant contribution to the observed C–H stretching band.

RESULTS AND DISCUSSION

The confocal Raman microspectrometry experiments used a single crystal (dimensions $1 \times 1 \times 16\,\text{mm}^3$) of dodecane/urea, which was attached (using Araldite as a sealing system) to a reservoir containing liquid pentadecane-d_{32} (Fig. 2). The single crystal and reservoir were mounted on the X,Y-motorized table of the confocal Raman microscope. The laboratory reference frame is defined in Figure 2, with the Z-axis collinear to the direction of the incident laser beam. The scattered light was collected in the same direction as the incident light (backscattering geometry). The long axis (channel direction) of the needle-shaped crystal was aligned parallel to the X-axis of the reference frame and polarized spectra were recorded [$(Z(XX)\overline{Z})$ and $(Z(XY)\overline{Z})$ in Porto notation; note that no polarizer was used for the backscattered light].

The analysis was performed at a depth $Z = 175\,\mu\text{m}$ beneath the upper surface of the crystal. The Raman spectra were collected in scans along the X-axis with a step size of $400\,\mu\text{m}$ and a total scan range of 14 mm; six separate scans of this type were carried out at Y-coordinates separated by $75\,\mu\text{m}$ (the "width" of each scan along Y, determined by the spatial resolution, was *ca.* $50\,\mu\text{m}$). The acquisition

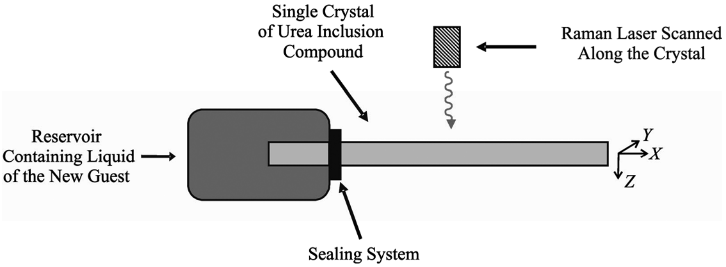


FIGURE 2 Schematic representation of the experimental assembly, comprising the single crystal of the urea inclusion compound (green), initially containing dodecane guest molecules, attached to a reservoir containing liquid pentadecane-d_{32}. The laboratory reference frame (X, Y, Z) is also defined.

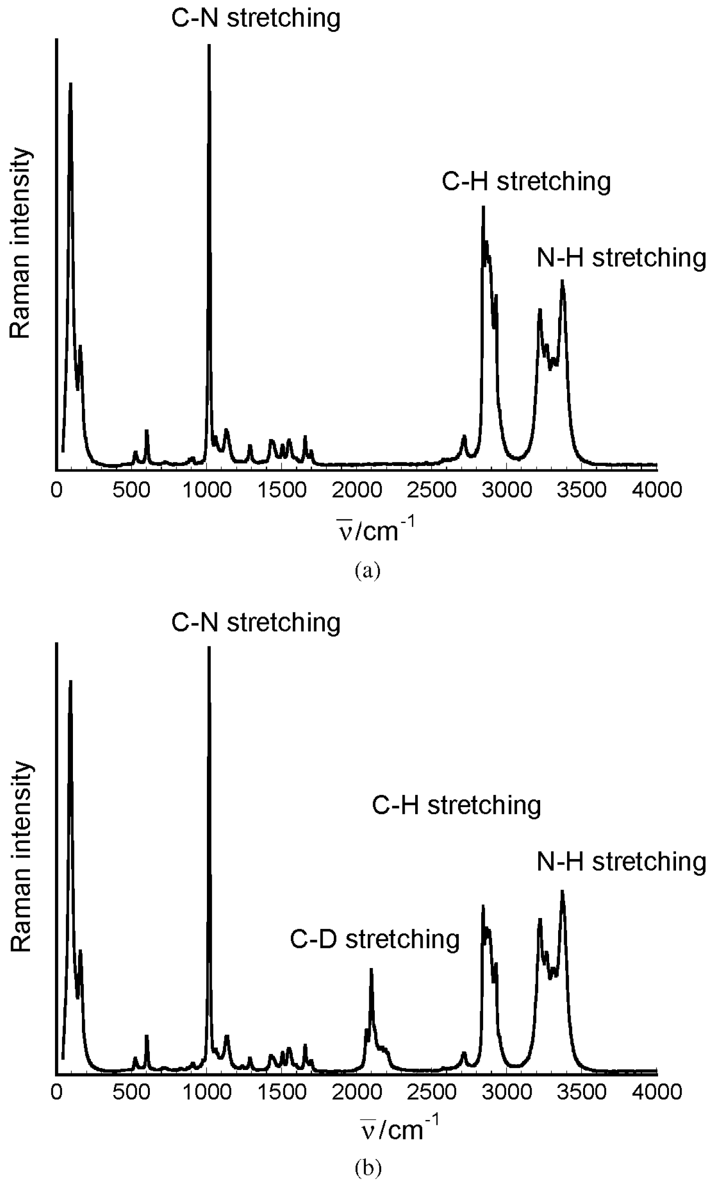
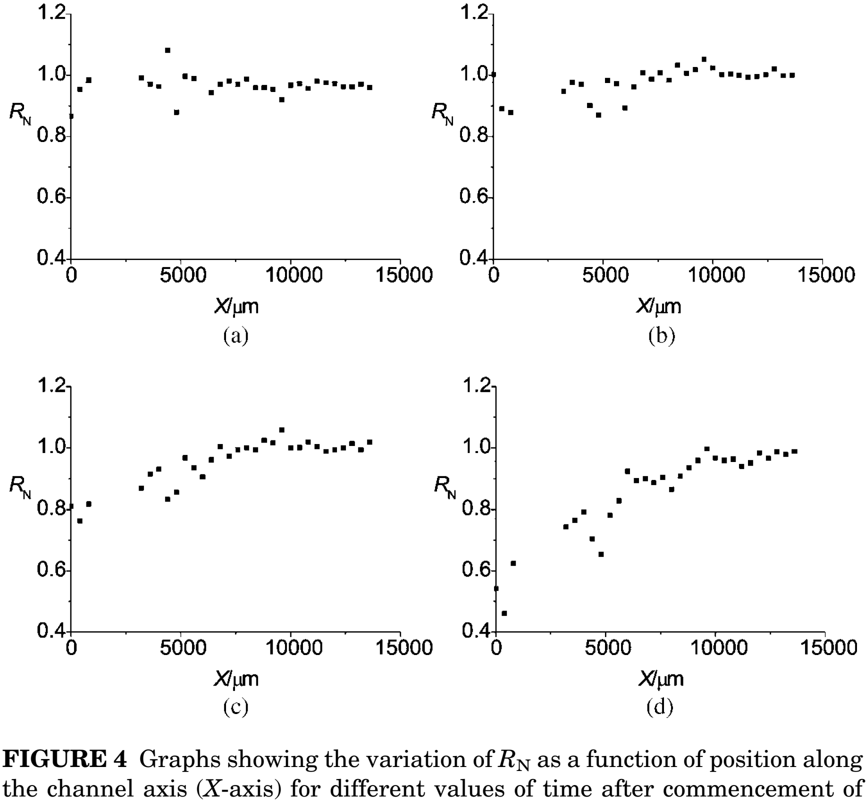


FIGURE 3 Raman spectra of (a) a crystal of the dodecane/urea inclusion compound (before guest exchange), and (b) the urea inclusion compound after partial exchange of the dodecane guest molecules by pentadecane-d_{32}.

time for each Raman spectrum was 2 s, and the time to record each scan was about 70 s. The time to record the complete Raman micrograph of the probed area was thus about 7 min, which is significantly shorter than the overall timescale of the guest exchange process.

To monitor the exchange of guest molecules, the C–H stretching band (*ca.* 2900 cm^{-1}) due to the dodecane guest molecules (as discussed above, the pentadecane-d_{32} guest molecules make a negligible contribution to the C–H stretching band) was compared to the N–H stretching band (*ca.* 3300 cm^{-1}) due to the urea molecules in the host structure (examples of Raman spectra are shown in Fig. 3). The ratio of integrated intensities [$R = I(C\text{–}H)/I(N\text{–}H)$] was measured and



(a) (b)

(c) (d)

FIGURE 4 Graphs showing the variation of R_N as a function of position along the channel axis (X-axis) for different values of time after commencement of the guest exchange process: (a) 0 hours, (b) 3.6 hours, (c) 10.4 hours, and (d) 19 hours. The crystal is in contact with liquid pentadecane-d_{32} at $X = 0$, and thus the transport of pentadecane-d_{32} guest molecules occurs from left-to-right in the graphs shown. Note that the region of the crystal between about $X = 1200$ μm and $X = 2800$ μm is "hidden" by the sealing system.

converted to the normalized ratio $R_N = R/R_o$, where R_o is the value of R (averaged over the probed area) for the original dodecane/urea crystal (before starting the guest exchange process). Thus, $R_N = 1$ if the crystal contains only dodecane guest molecules and $R_N = 0$ if the crystal contains only pentadecane-d_{32} guest molecules (i.e., complete exchange). The value of R_N allows an assessment of the relative amount of dodecane guest molecules as a function of position in the crystal and as a function of time.

In the results shown in Figure 4, it is clear that alkane-alkane guest exchange occurs in this system, with the proportion of the original guest molecules (dodecane) decreasing as a function of time and as a function of position in the crystal as the new guest molecules (pentadecane-d_{32}) enter the channels (from the left hand side in Fig. 4). Further work is in progress to assess in more detail the factors that dictate the rate of the guest exchange process in such materials, including systematic studies of the dependence on the chain lengths of the original and new guest molecules, and the dependence on the presence of particular functional groups in the guest molecules. A relevant aspect of such future studies is to recall that many urea inclusion compounds exhibit three-dimensional ordering of the guest molecules. The inter-channel ordering of guest molecules (characterized by the offset Δ_g shown in Fig. 5) depends on the functional groups present in the guest molecule, and different homologous families of guest molecules exhibit characteristic modes of inter-channel ordering. For example, at ambient temperature, $\Delta_g = 0$ Å for alkane/urea inclusion compounds, whereas for α,ω-dibromoalkane/urea inclusion

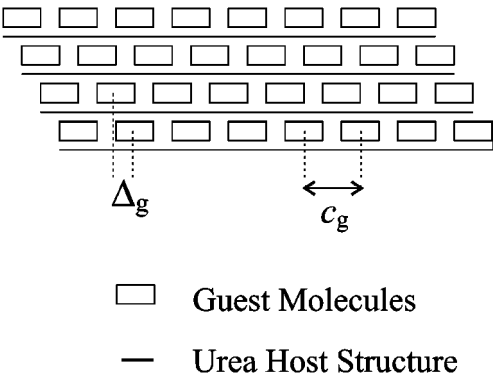


FIGURE 5 Schematic two-dimensional representation of a urea inclusion compound, viewed perpendicular to the channel axis, indicating the definitions of c_g and Δ_g.

compounds, Δ_g depends on the periodic repeat (c_g) of the guest molecules along the channel by the following relationship: $\Delta_g = c_g/3$ [10,11]. In our previous experiments [16] involving exchange of 1,8-dibromooctane guest molecules by pentadecane, there is a mismatch in the value of Δ_g between the original and new guest molecules, whereas for alkane-alkane exchange, the original and new guest molecules have the same value of Δ_g. This issue may have an important bearing on the local structure at the interface between the original and new guest molecules in the inclusion compound, and may therefore have important implications for several aspects of the guest exchange process. Systematic studies of this issue are also central to our on-going research in this field.

In summary, the preliminary results reported in this paper provide direct evidence for the occurrence of alkane-alkane guest exchange in urea inclusion compounds, with the alkane of longer chain length (in this case pentadecane) replacing the alkane of shorter chain length (in this case dodecane). The confocal Raman microspectrometry technique employed in this work, with appropriate deuteration of one of the alkane guest components, represents a viable strategy for *in situ* characterization of the guest exchange process.

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