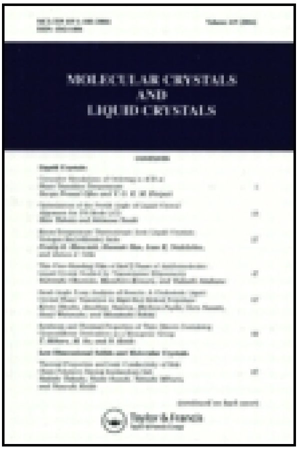

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Oriented n-Alkanes in urea-d_4 Inclusion Complexes for Inelastic Neutron Scattering Vibrational Studies

Bruce S. Hudson [a]

[a] Department of Chemistry, Syracuse University, Syracuse, NY, 13244-4100, USA

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Oriented n-Alkanes in urea-d_4 Inclusion Complexes for Inelastic Neutron Scattering Vibrational Studies

BRUCE S. HUDSON

Department of Chemistry, Syracuse University, Syracuse, NY 13244–4100 USA

Crystalline urea inclusion complexes (UIC) formed with urea-d4 and hexadecane are used to orient the n-alkane relative to a neutron beam for inelastic neutron scattering studies. Deuteration of the host lattice makes it nearly transparent for neutron studies. Comparison of the results for UIC orientation parallel and perpendicular to the neutron beam permits separation of the low frequency vibrational spectrum into those vibrations that are parallel to the alkane long axis and those perpendicular to the long axis.

Keywords: urea inclusion compounds; inelastic neutron scattering; vibrational spectroscopy

INTRODUCTION

The low frequency vibrational spectra of n-alkanes consist of bending motions and methyl torsions in which the atomic motions are transverse to the long molecular axis and longitudinal acoustic modes (LAMs) in which the atomic motions are directed along the molecular axis. In infrared and Raman spectra only a few of the LAM modes are active with most of the intensity being in the low order (long wavelength) motions. In neutron scattering spectra all vibrations, both LAM and out of plane motions are active. In the low frequency region these transitions overlap. In recent studies of the LAM vibrations of the n-alkanes[1,2] we were able to identify the higher frequency LAM modes between 200 and 525 cm^{-1} for a large number of n-alkanes. The LAM modes that are lower in frequency than 200 cm^{-1} could not be uniquely identified in the INS spectra due to this overlap.

Comparison of the INS spectral intensity with the results expected on the basis of DFT calculations results in generally good agreement and helps to assign the vibrations. However, it appears that, while the LAM modes are well represented by an isolated molecule calculation, the bending modes are shifted to higher frequency due to intermolecular interactions. The use of oriented samples provided by UIC structures avoids this difficulty since the two kinds of modes have different orientation properties. The UIC is an alternative environment for the n-alkane which may reduce the intermolecular interactions.

Figure 1 is an example of the analysis of an INS spectrum of an n-alkane, in this case n-hexadecane at 20 K. This data was obtained using the spectrometer TFXA [3]. The lighter line is a spectral calculation that is based on a density functional calculation using the B3LYP functional and the 6-31G** basis set. The intensity of a spectral feature is proportional to the sum of the squares of the hydrogen atom motions in each normal mode calculated for a single molecule. Details of the simulation method are given elsewhere [1,2].

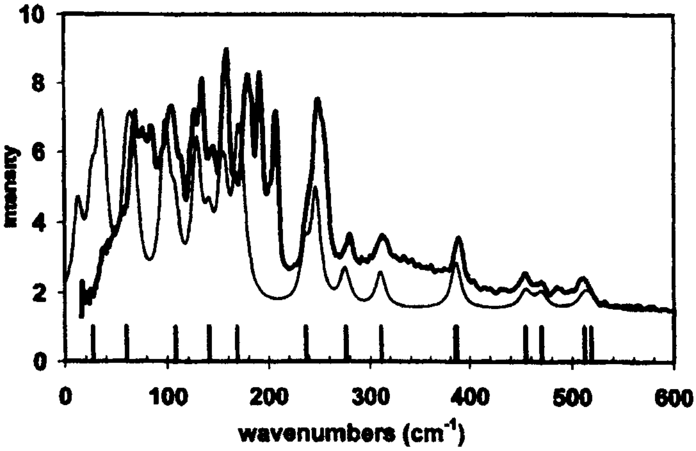

FIGURE 1 Observed (heavier line) and simulated (lighter line) INS spectra for n-hexadecane at 20K. The vertical lines indicate the calculated frequencies for the LAM modes.

The main features of such spectra are the LAM modes from 230 to 530 cm^{-1}, the overlapping LAM and bending modes below 200 cm^{-1}. The calculated LAM mode frequencies are indicated as vertical bars. The strong feature near 240 cm^{-1} includes both LAM contributions and the out-of-plane methyl rotation modes. The overtone of this strong peak is seen near 480 cm^{-1}. This feature is not included in the calculation.

UREA N-ALKANE INCLUSION CRYSTALS

Experiments with oriented samples can separate the longitudinal and transverse modes permitting assignment of overlapping transitions in the low frequency region and thus evaluation of the theoretical calculations in the very low frequency region. An easy way to orient long n-alkanes is by formation of hexagonal urea inclusion crystals.[4] These structures, shown in end and side view below, produce macroscopic hexagonal crystals that are easily oriented parallel and perpendicular to the incident neutron beam in TOSCA.[5] The urea used for these UIC crystals was highly deuterated so as to make this component nearly invisible in the INS spectrum.

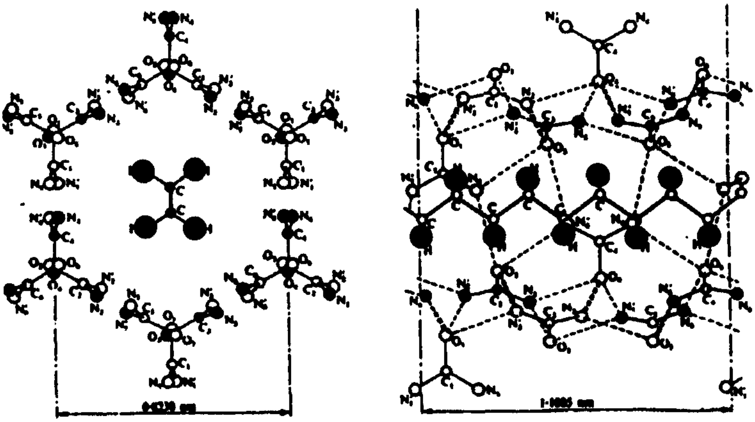

FIGURE 2 Structures of n-alkane/urea inclusion crystals.[4] The hydrogen atoms of the n-alkane have been shown extra large because they dominate the neutron scattering process.

The experimental samples of deuterated urea/n-hexadecane-h_{18} were crystals about 1 mm in diameter and about 4-8 mm in length. These crystals were placed flat in a shallow aluminium sample holder (for the perpendicular sample) and end-on in holes drilled in an aluminium plate (for the parallel sample). The urea and CH_3OD used for crystal growth were 99% deuterated.

INS DICHROISM

Figures 3 and 4 show the INS spectra in the 0-600 and 0-2000 cm^{-1} regions, respectively. In each case parallel and perpendicular spectra are superimposed at the bottom. The difference spectrum, parallel-perpendicular, is displayed shifted upward in the figure. The upward

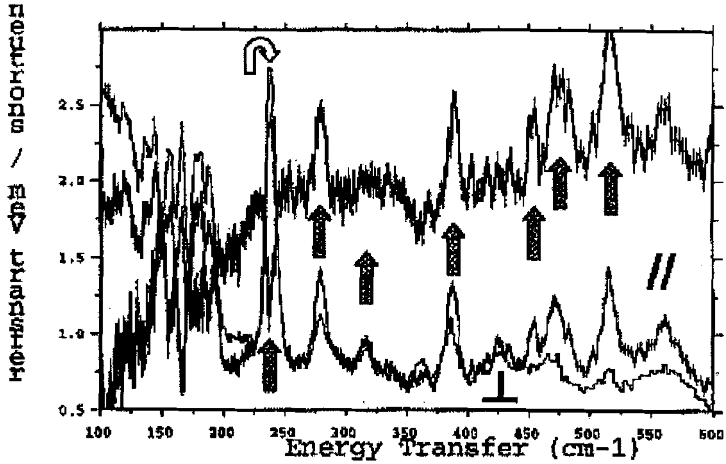

FIGURE 3 Dichroic INS spectra of urea-d4/n-hexadecane in the 100 - 600 cm^{-1} region. At the bottom are shown the spectra observed with the UIC crystals oriented parallel (//) and perpendicular (⊥) to the neutron beam. The difference (// - ⊥) is shown shifted vertically upward. The upward pointing grey arrows indicate the positions of LAM modes. The curved open arrow is at the position of the methyl rotation which overlaps a LAM mode.

pointing grey arrows indicate the positions of previously assigned LAM's with their longitudinal motion indicated by the greater intensity for the parallel orientation. The downward pointing empty arrows indicate the location of known transverse modes. At about 237 cm^{-1} a LAM mode and the transverse methyl rotation overlap. The methyl motion dominates the intensity and the net polarisation is transverse.

The extended frequency range of Figure 4 shows that TOSCA[5] becomes more sensitive to orientation at higher frequency where the momentum transfer vector is more nearly parallel to the incident neutron direction.[6] The strong band at 725 cm^{-1} indicated by an arrow is the CH_2 rocking twisting motion, transverse "polarized" as anticipated. The series of features extending from roughly 800 to 1500 cm^{-1} is due to CH_2 wagging motions that move the atoms parallel to the chain.

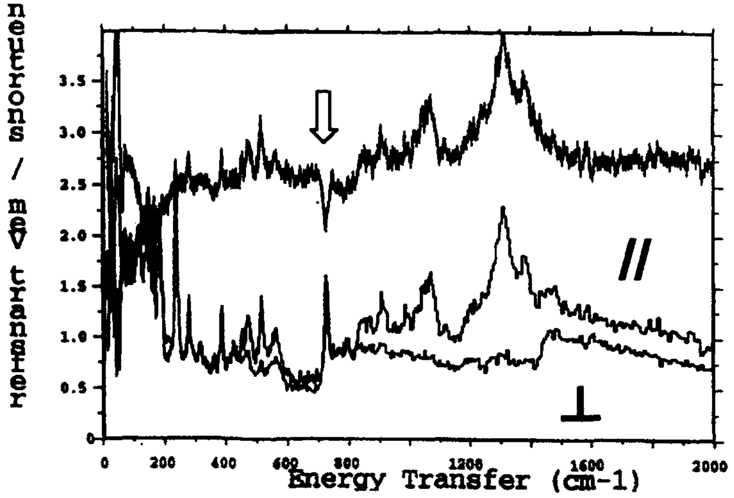

FIGURE 4 The dichroic INS spectra of urea-d4/hexadecane in the range from 0 to 2000 cm^{-1}. At the bottom are shown the spectra observed with the UIC crystals oriented parallel (//) and perpendicular (⊥) to the neutron beam. The difference spectrum (// - ⊥) is shown shifted vertically upward. The downward pointing arrow indicates the position of a transverse mode.

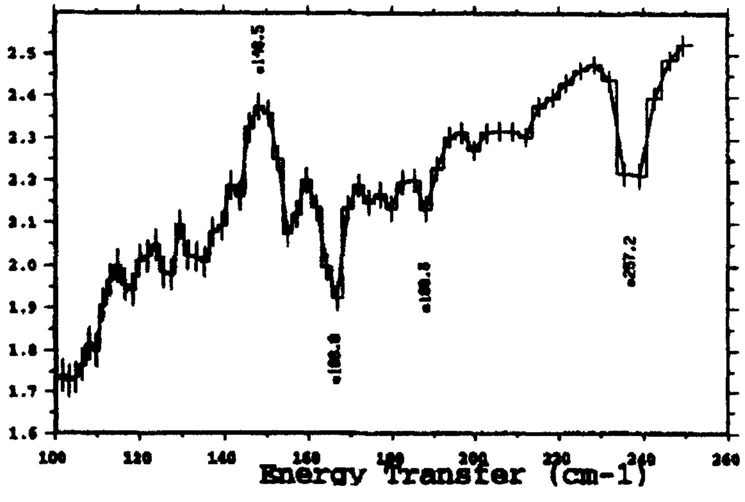

FIGURE 5 The urea-d4/$C_{16}H_{34}$ difference spectrum in the low frequency region. The LAM-1 mode is shown on the left and the overlapping LAM and methyl torsional modes on the right.

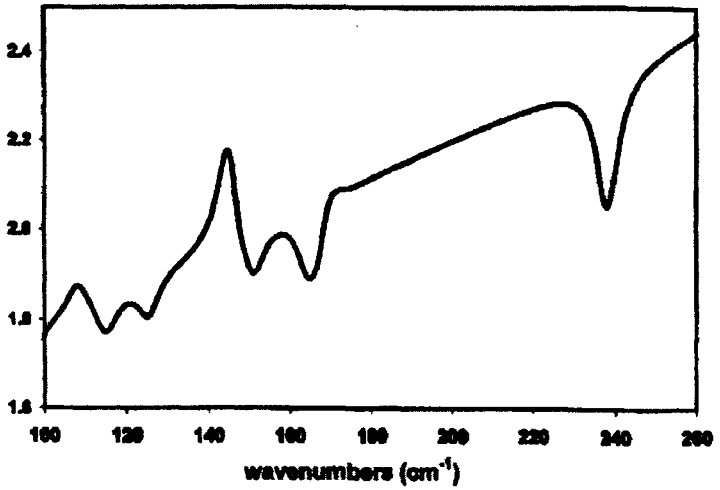

FIGURE 6 Simulation of the INS dichroism of Figure 5.

In the very low frequency range (see Figure 5) the positive (axial) feature near 149 cm^{-1} can be tentatively identified as the LAM-1 mode which has been seen for hexadecane in the Raman spectrum at 150 cm^{-1}. In this region of energy for this spectrometer design **Q** is no longer parallel to $-\mathbf{k}_0$ and the spectra are not very dichroic, as is expected. This variation, plus the overlapping nature of the vibrations in the low frequency region and the difficulty in determining the relative amount of material in the beam in the two different sample orientations conspire to make the interpretation of the data in the very low frequency region complex. However, these quantitative effects are well understood and, in conjuction with ab initio modeling of the INS intensities and their dichroism, it should be possible to sort out the spectra even below 200 cm^{-1}.

An attempt at analysis of the reslts of Figure 5 is shown in Figure 6. The results of the same DFT calculation used to construct the theoretical spectrum of Figure 1 were used as the basis for this dichroism spectrum. The intensity of a neutron scattering transition of a hydrogeneous substance depends on $(\mathbf{Q}\cdot\mathbf{C_H}^v)^2$, the dot product of the neutron moment transfer vector with the vector describing the motion of the H atoms of the molecule in the vth normal mode. The intensity of a given transition is then the sum of such terms over all H atoms in the molecule. For a randomly oriented sample this reduces to $\mathbf{Q}^2\Sigma(\mathbf{C_H}^v)^2$. For an oriented sample the corresponding expression is clearly $\mathbf{Q}^2\Sigma(\cos^2\theta)(\mathbf{C_H}^v)^2$. For perfect orientation this $\cos^2\theta$ factor is either 0 or 1 for a given orientation. For example, for axial orientation designated // in the above figures the angular factor is 1 for the LAM modes of A_g or B_u symmetry and 0 for the transverse (out-of-plane or in-plane transverse) modes of A_u and B_g symmetry. In ⊥ orientation these factors are reversed. In a difference spectrum I(//)-I(⊥) this has the effect of multiplying the A_g and B_u modes by +1 and the A_u and B_g modes by −1. Since the normal mode calculation has symmetry labels this assignment of sign is straightforward.

In constructing the curve of Figure 6 it was assumed that the variation of the intrinsic instrumental dichroism varied exponentially with distance approaching the ideal value in the limit of large inelasticity. A further modification of the calculated results was the multiplication of all of the frequencies of the *transverse* (negative intensity) modes by a scale factor of 0.96. This was chosen to match the negative feature at 237 cm^{-1}, due to overlap of the in-phase and out-of-phase methyl rotations with a LAM mode. The resulting simulated dichroism (Figure 6) is in qualitative agreement with that observed (Figure 5). It is clear, however, that quantitative simulation of the difference spectrum in this case requires having the proper line shape function. The present simulation uses lorentzian shapes. The true lineshape is sharper than lorentzian but not as sharply peaked as gaussian[2].

Comparison of Figures 5 and 6 reveals several small features in the experimental difference spectrum for which there are no counterparts in the simulation. One of these at 188.3 cm^{-1} is marked in Figure 5. There are no calculated fundamental vibrations in this frequency region. There are, however, transverse vibrations at 93 and 95 cm^{-1} as well as at 61 and 69 cm^{-1} whose overtones and combinations could give rise to the observed small features.

We turn now to a comparison of the longitudinal and transverse motions of n-hexadecane in the UIC crystals in comparison to the pure n-hexadecane crystal. Examination of Figure 1 shows that peaks just above and below 200 cm^{-1} are observed that are not reproduced by the isolated molecule simulation. There are no LAM modes in this spectral region so these are probably out-of-plane vibrations that are shifted to higher frequency in the solid. However, in order to reproduce the INS dichroism spectrum of Figure 5 it was necessary to shift the transverse modes *down* in frequency by 4% rather than up as would be implied by this assignment. Figure 7 shows the origin of this discrepancy. A comparison of the spectra for n-hexadecane with that for the (unoriented) UIC crystals shows that the LAM peaks at higher frequency are in the same location but the methyl rotation peaks near 250 cm^{-1} and the bending mode peaks near 200 cm^{-1} have moved down in frequency.

The general strategy of these experiments is to evaluate the effect and specificity intermolecular interactions of vibrational frequencies and amplitudes by comparison of two or more distinct solid environments. Those modes that shift in frequency are thus more sensitive than those that do not to these intermolecular interactions. In this particular case the bending modes shifts downward in frequency on going from the pure alkane to the inclusion crystal while the LAM modes do not. Simulations that include intermolecular interactions should be able to reproduce this specificity as well as the magnitude of the effect. For the n-alkanes it appears that the packing in the pure solid results in a much stronger effect of the bending modes than does the environment provided by the urea inclusion crystal.

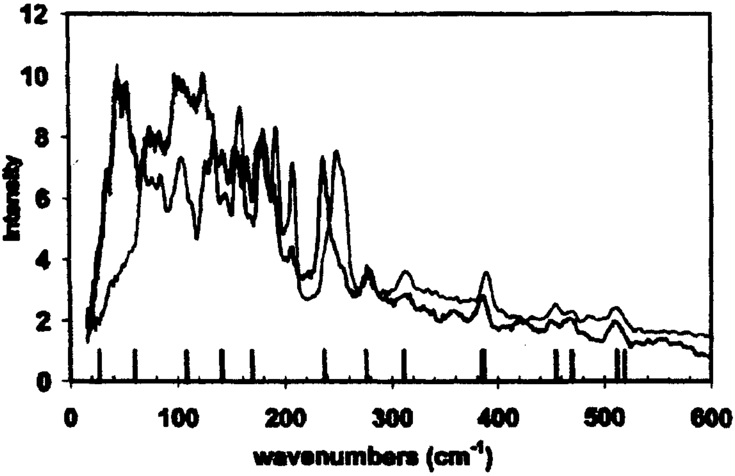

FIGURE 7 Comparison of the INS spectra for polycrystalline n-hexadecane and n-hexadecane in urea-d4 inclusion complex. The polycrystalline sample is the lighter line, uppermost at higher frequency. The LAM mode frequencies are indicated as in Figure 1.

CONCLUSIONS

These experiments have demonstrated the utility of deuterated urea inclusion complexes in providing orientational discrimination in inelastic neutron scattering experiments permitting the decomposition of complex spectra. Another potentially interesting class of guest molecules for such studies are linear conjugated polyenes which also form UIC structures. [7] The present study alos revealed that soe of the lack of agreement between isolated molecule calculations and experiment for pure n-alkanes is due to a differential shift of bending modes in the pure solid. The selective intermolecular interactions revealed by comparison of the UIC and neat solid spectra can be compared to future simulations that take the molecular surroundings into account.

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References

[1] S. F. Parker, D. A. Braden, J. Tomkinson and B. S. Hudson, *J. Phys. Chem.* **102,** 5955 (1998).
[2] D. A. Braden, S. F. Parker, J. Tomkinson and B. S. Hudson, *J. Chem. Phys.* **111**, 429 (1999).
[3] J. Tomkinson, *J. Serb. Chem. Soc.* **61,** 729 (1996).
[4] M. D. Hollingsworth and K. D. M. Harris, in *Comprehensive Supramolecular Chemistry*, J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, editors, **6,** 177 (1996).
[5] S. F. Parker, C. J. Carlile, T. Pike, J. Tomkinson, R. J. Newport, C. Andreani, F. P. Ricci, F. Sachetti, M. Zoppi, *Physica B* **241–243,** 154 (1998).
[6] S. F. Parker, *J. Chem. Soc., Faraday Trans.* **92,** 1941 (1998).
[7] Q.-Y. Shang, X. Dou, B. S. Hudson, *Nature* **352,** 703 (1991).