

Experimental test of the validity of the use of the *n*-alkanes as model compounds for polyethylene

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n-Alkanes are widely used as model compounds for the dynamics of the crystalline region of polyethylene; this use relies on the assumption of the transferability of the forcefield of the *n*-alkanes, a stringent test of this assumption is a comparison of the dispersion curves of the *n*-alkanes with those of polyethylene; the only direct measurements of the dispersion curves of polyethylene are for the ν_5 acoustic branch, the longitudinal acoustic mode (LAM), an in-plane skeletal mode of perdeuterated polyethylene; in the present work we have observed (by inelastic neutron scattering spectroscopy) and assigned (by the use of density functional theory calculations) the LAM modes of perdeuterated *n*-hexadecane in order to provide the first experimental test of the validity of the assumption.

Polyethylene is a major commodity polymer that is still the subject of active development.¹ Vibrational spectroscopy has played a key role in the characterisation of the material² and fundamental to the understanding of the dynamics of the polymer is a knowledge of the dispersion curves for the vibrational modes. The only direct method for the experimental determination of dispersion curves is by coherent inelastic neutron scattering (INS) spectroscopy. For hydrogenous polyethylene, this method fails because the background caused by the incoherent scattering from hydrogen completely swamps the coherent signal. This problem has been circumvented in two ways; the incoherent INS spectrum is related to the vibrational density-of-states which is in turn related to the dispersion curves. Comparison of the experimental spectrum³ with dispersion curves and the density-of-states derived theoretically allows the quality of the calculations to be assessed. The second method is the use of the *n*-alkanes as model compounds for polyethylene.^{4,5} This method relies on the assumption that the *n*-alkanes forcefield is directly transferable to polyethylene and that the end-effects caused by the finite length of the alkane chain can be neglected.

For perdeuterated polyethylene, the larger coherent and smaller incoherent cross-sections of deuterium⁶ (H: incoherent 79.7 barns, coherent 1.758, deuterium: incoherent 2.0 barns, coherent 5.597 barns, 1 barn = 1×10^{-28} m²) has allowed the ν_5 acoustic branch, the longitudinal acoustic mode (LAM), an in-plane skeletal mode, to be mapped by coherent INS.⁷⁻¹⁰ These results are the only *direct* experimental measurement of any of the dispersion curves of polyethylene. Thus any test of the validity of the assumption that the *n*-alkanes are good

models for polyethylene requires the determination of the LAM modes of a perdeuterated *n*-alkane. Unfortunately, while the LAM modes are formally IR and Raman active, their intensities are usually so small as to be unobservable for any but the first few modes (Raman) and the highest energy ones (IR).

We have recently shown that it is possible to both observe¹¹ and assign^{12,13} the LAM modes of the *n*-alkanes ($n = 5-25$) by a combination of incoherent INS spectroscopy and *ab initio* calculations. In the present report we have extended the method to perdeutero-*n*-hexadecane in order to compare the experimental data for perdeuterated polyethylene with the measured LAM frequencies of C₁₆D₃₄.

It is only with the development of pulsed neutron sources with their high flux of epithermal neutrons that it has been possible to record incoherent INS spectra of perdeuterated compounds. With the increase in detected flux resulting from the recent installation of TOSCA¹⁴ at ISIS (Rutherford Appleton Laboratory, Chilton, UK) it is now possible to routinely record spectra from such samples. Fig. 1 shows the incoherent INS spectrum of C₁₆D₃₄ in the region¹⁵ below 500 cm⁻¹. All of the modes between 200 and 400 cm⁻¹ are LAM modes, a further five modes occur below 200 cm⁻¹ where the out-of-plane transverse acoustic modes and the external

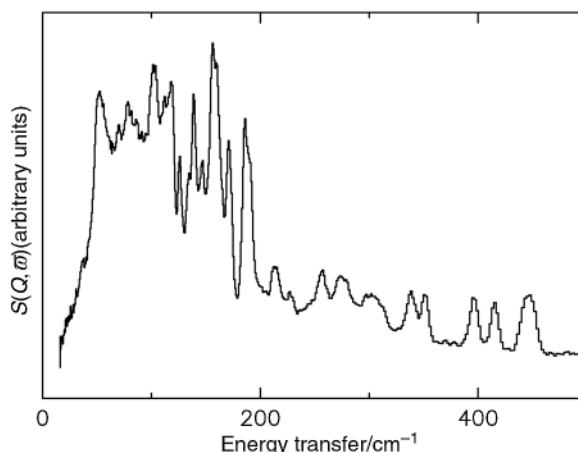


Fig. 1 Inelastic neutron scattering spectrum of C₁₆D₃₄ in the region 0–500 cm⁻¹ showing the longitudinal acoustic modes, transverse acoustic modes and the external modes.

Table 1 Observed and calculated (DFT) frequencies (cm⁻¹) for the longitudinal acoustic modes of C₁₆D₃₄

	κ													
	0.067	0.133	0.200	0.267	0.333	0.400	0.467	0.533	0.600	0.667	0.734	0.800	0.867	0.934
Obs.	(159)	257	353	416	449	449	399	339	277	213	(127)	(102)	(54)	(25)
DFT	152	253	350	416	454	447	398	339	275	211	131	98	54	24
Symmetry	A _g	B _u	A _g	B _u	A _g	B _u	A _g	B _u	A _g	B _u	A _g	B _u	A _g	B _u

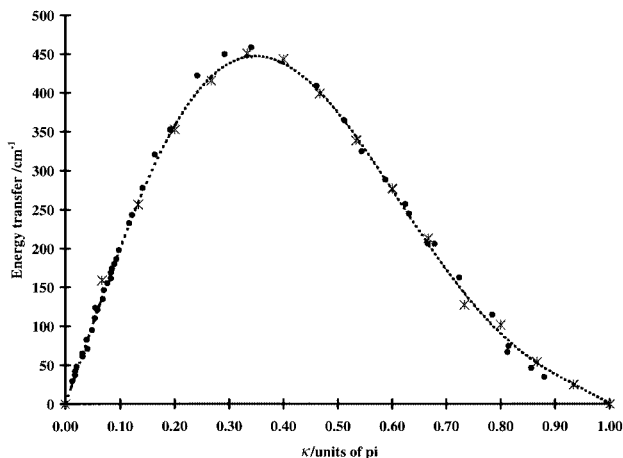


Fig. 2 Comparison of experimental data for the ν_5 mode of deuterated polyethylene (●) and the experimental LAM frequencies of $C_{16}D_{34}$ (*). The dashed line is a quintic least squares fit to the DFT data for perdeuterated n -hexadecane.

modes also occur. The density functional theory (DFT) calculations were performed using the GAUSSIAN-94¹⁶ program in the B3LYP density functional approximation. The basis set used was 6-31-G**. The DFT results allow the modes to be assigned to a specific phase angle, κ . The results are shown in Table 1. The experimental frequencies below 200 cm^{-1} are given in parentheses since the DFT calculations show that out-of-plane modes lie close-by, thus there is some uncertainty (a few wavenumbers) in the exact value of the frequency.

Fig. 2 shows a comparison of experimental data for the ν_5 mode of perdeuterated polyethylene, the experimental frequencies and the frequencies calculated by DFT. The solid line is a quintic least squares fit to the DFT results for perdeuterated n -hexadecane as a guide to the eye. It can be seen that there is excellent agreement between all three sets of data. This provides the *first* experimental validation of the assumption that the forcefields derived from the n -alkanes are transferable to polyethylene.

This work is noteworthy for two other reasons: first that it is now possible to routinely obtain high quality incoherent inelastic neutron scattering spectra of perdeuterated samples and second the demonstration of the success of DFT calculations for the analysis of inelastic neutron scattering spectra provides a benchmark against which other methods can be tested.

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