

Full Longitudinal Acoustic Mode (LAM) Spectrum of an *N*-Alkane: Comparison of Observed and Computed Incoherent Inelastic Neutron Scattering Spectrum of *N*-Octadecane

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The incoherent inelastic neutron scattering spectrum of solid *n*-octadecane below 600 cm⁻¹ is presented and compared with the results of a scaled HF ab initio calculation. Ten vibrations in the 300–550 cm⁻¹ region, eight of which have not been previously observed, are easily assigned as longitudinal acoustic modes (LAMs). On the basis of the good agreement between calculated and observed modes in this region, the location of the lower frequency LAMs is postulated.

This Letter presents the incoherent, inelastic neutron scattering spectrum of polycrystalline *n*-octadecane and compares this spectrum with that calculated by an ab initio method. This comparison permits the first determination of the full longitudinal acoustic mode (LAM) spectrum of an *n*-alkane. The *n*-alkanes are the prototypical “homologous series” with polyethylene as the asymptotic member. The problem of the nature of the low-frequency vibrations of *n*-alkanes and polyethylene has a long and interesting history.⁵ The vibrations of these molecules were among the first to be treated using an extensive transferable force field⁶ and are still being used to test ab initio methods for potential function development.⁷ The modes of greatest interest for this series of molecules are probably the LAMs. These in-plane deformations of the C–C–C bond angles and C–C bond stretches have alternating a_g and b_u symmetry in the C_{2h} point group of the planar extended chain. The LAM-1 or “accordion” mode has atomic displacement vectors along the chain axis with opposite signs for the left- and right-hand sides of the molecule with a node in the middle. Increasing the number of nodes in the pattern of displacement vectors causes the frequency to first increase and then decrease. The odd-numbered LAMs are Raman active with decreasing intensity.

There have been many experimental and normal mode studies of the vibrations of *n*-octadecane.^{5,6,8} There are 33 internal modes below 600 cm⁻¹, of which 16 are the LAMs. These modes are insensitive to intermolecular interactions and can be treated using an isolated molecule model. The other 17 low-frequency internal modes consist of torsional and out-of plane bending skeletal motions of a_u and b_g symmetry. There are, in addition, lattice modes, the number of which depends on the crystal type. These nonlongitudinal acoustic modes are sensitive to the crystal packing and so depend on morphology. The simplest treatment of the LAMs⁸ that contains all of the important features treats the CH₂ groups as point masses and involves five parameters (CC stretch, CCC angle bend, and neighboring CC/CCC, CCC/CCC, and CC/CC interaction). The

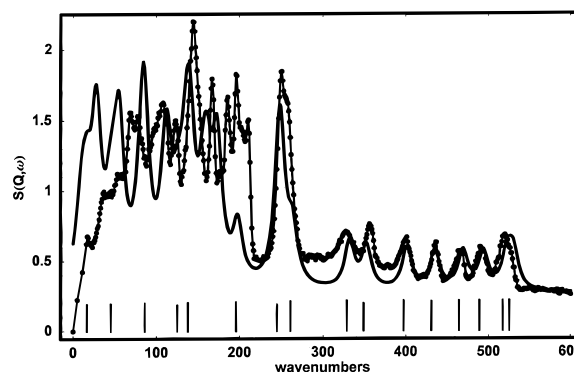


Figure 1. Observed (line with dots) and calculated (smooth line) inelastic neutron scattering spectrum of *n*-octadecane. The calculated LAM frequencies and intensities are shown on the bottom.

parameters are adjusted to fit 12 LAM-1 and LAM-3 mode frequencies for short *n*-alkanes ($n = 5–17$), LAM-1, -3, and -5 for octadecane and LAM-1, 3, 5, 7, and 9 for C₃₆H₇₄. The 16 calculated LAM frequencies for octadecane start with LAM-1 at 129 cm⁻¹ (observed at 133 cm⁻¹ in Raman spectra at room temperature), increase to a maximum value of 568 cm⁻¹ for LAM-6, and then decrease to 12 cm⁻¹ for LAM-16. Besides LAM-1, the only other observed modes of this series for *n*-octadecane are LAM-3 (355 cm⁻¹ obs; 358 cm⁻¹ calcd) and LAM-5 (493 cm⁻¹ obs; 524 cm⁻¹ calcd). LAM-1 is found to be 58% C–C stretch and 42% CCC bend, while LAM-16 is 100% CCC bend.

The incoherent inelastic neutron scattering spectrum below 600 cm⁻¹ of polycrystalline *n*-octadecane at ca. 20 K is shown in Figure 1. This spectrum was obtained with the TFXA spectrometer⁹ at the ISIS pulsed neutron facility of the Rutherford Appleton Laboratory. This spectrum reflects the superior resolution of this spectrometer in comparison with the devices used in previous neutron scattering studies of *n*-alkanes.¹⁰

The solid line shown in Figure 1 is the IINS spectrum calculated on the basis of an ab initio normal mode calculation for *n*-octadecane. This calculation used the Gaussian-94¹¹ program with the 6-31G** basis in the Hartree–Fock ap-

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TABLE 1: LAM Frequencies from Scaled HF 6-31G Calculation**

LAM no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
cm ⁻¹	138	245	349	431	489	525	517	464	397	329	261	196	125	86	45	17

proximation. The IINS spectrum is calculated as the summation of peaks with amplitudes corresponding to the mean square amplitude of motion of the hydrogen atoms at frequencies equal to 0.945 times the calculated HF values. This value was chosen to give the best overall fit in the region from 220 to 540 cm⁻¹. This scaling factor is slightly higher than the value recently recommended for this basis set and gas-phase frequencies of 0.91.¹² A width corresponding to the spectrometer resolution has been included for each line. The Debye–Waller factor appropriate to external motional contributions is treated empirically by a multiplicative factor $\exp(-GQ^2)$ where G is adjustable. For the TFXA spectrometer configuration, Q increases with energy transfer. An arbitrary baseline offset has also been added.

All of the transitions in the 300–550 cm⁻¹ region are LAMs (LAM-3–10). The highest frequency band is an overlapped combination of LAM-6 and LAM-7. Six of these eight LAM transitions are reported here for the first time. LAM-3 and LAM-5 have been previously reported from the Raman spectrum. The pattern of these modes calculated by the simple empirical model of Shimanouchi and Tasumi is correct, and the two lowest frequency peaks in this region (LAM-10 and LAM-3 near 330 and 360 cm⁻¹) are correctly placed but all higher frequencies are calculated too high by up to 40 cm⁻¹ (for LAM-6 and LAM-7). The strong peak near 255 cm⁻¹ has contributions from LAM-2 and LAM-11 as well as the two out-of-plane modes that include methyl hydrogen motions. The spectrum below 220 cm⁻¹ has contributions from the six remaining LAMs and 15 out-of-plane skeletal modes. The ab initio calculation shows that all 21 of these vibrations contribute roughly equally to the spectral intensity. It is clear that many of the observed peaks are composite in nature. The deviation between the computed and observed spectral intensity distribution is due to the lack of inclusion of phonons in the calculation and shifts (to higher frequency, apparently) of the crystal vibrations relative to those of the isolated molecule owing to intermolecular interactions. These factors can, in principle, be taken into account by use of a lattice model in the calculation. The librational phonon modes of triclinic ($Z = 1$) *n*-octadecane have been reported to occur at 30, 32,^{13,14} and 65¹⁵ cm⁻¹ from Raman studies.

The good agreement observed between the scaled HF/6-31G** results and the eight highest frequency LAMs indicates that similar agreement would be observed for the lower frequency modes if they were not obscured by overlap with non-longitudinal acoustic modes and phonons. This argument is substantiated by the fact that the LAM-1 mode calculated to be 138 cm⁻¹ is observed in the Raman spectrum of the room-temperature solid at 133 cm⁻¹. The (scaled) LAM frequencies are shown as vertical lines in the bottom of Figure 1. The length of the lines is proportional to the calculated intensity. The values of the frequencies are shown in Table 1.

The HF calculation presented here serves to confirm the assignment of these new spectral bands and demonstrates that this simple method provides usefully accurate eigenvectors as reflected in the intensities. A study of *n*-octane and comparison of the IINS spectrum with the results of a DFT calculation (B3LYP/6-31G**) show that no scaling is needed to match these higher frequency LAMs. This eliminates the need to introduce a scaling factor as is required when using HF methods. The

reliability of such a simple procedure in this extreme low-frequency region is not established. Using DFT or other more advanced methodology for the normal mode calculation permits concentration on the intermolecular interactions that are important for the low-frequency modes. This can be done using either cluster¹⁶ or Car-Parrinello¹⁷ methods.

Previous treatments of the LAM vibrations of finite *n*-alkanes have relied on scaling arguments that lead to the conclusion that the LAM frequency should depend uniquely on the ratio m/n , where m is the order of the LAM and n is the *n*-alkane chain length. According to a simple elastic rod model $\nu = a(m/n)$, where the proportionality constant a depends on the ratio of the elastic (Young's) modulus to the density. This behavior is observed for small (m/n). As (m/n) exceeds 0.1, the deviations from linearity exceed experimental uncertainty; for (m/n) = (5/18) (i.e., LAM-5 for *n*-octadecane), the data falls below this linear relation by almost 200 cm⁻¹. More fundamental, however, is the idea that the determining factor is simply m/n , i.e., that the form of the mode and the value of the frequency for, say LAM-1 of *n*-octane and LAM-3 of *n*-C₂₄H₅₀, should be the same. In fact these two vibrations differ in frequency by only about 5 cm⁻¹ out of about 280 cm⁻¹ so this is, perhaps, a reasonable approximation. The present work shows that the full set of LAMs can be determined from IINS data for comparison with normal mode calculations without the need to make assumptions about transferability of the form of the normal mode from one chain length to another.

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References and Notes

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- (5) Schaufele, R. F.; Shimanouchi, T. *J. Chem. Phys.* **1967**, *47*, 3605–3610 and references therein.
- (6) Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *19*, 117–168.
- (7) Palmö, K.; Mirkin, N. G.; Pietilä, L.-O.; Krimm, S. *Macromolecules* **1993**, *26*, 6831–6840.
- (8) Shimanouchi, T.; Tasumi, M. *Ind. J. Pure Appl. Phys.* **1971**, *9*, 958–961.
- (9) Tomkinson, J. *J. Serb. Chem. Soc.* **1996**, *61*, 729–743. Parker, S. E. *Spectrosc. Eur.* **1994**, *6*, 14–20.
- (10) Nelligan, W. B.; LePoire, D. J.; Brun, T. O.; Kleb, R. *J. Chem. Phys.* **1987**, *87*, 2447–2456. Logan, K. W.; Danner, H. R.; Gault, J. D.; Kim, H. *J. Chem. Phys.* **1973**, *59*, 2305–2308.
- (11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.
- (12) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.
- (13) Olf, H. G.; Fanconi, B. *J. Chem. Phys.* **1973**, *59*, 534–544.
- (14) Takeuchi, H.; Shimanouchi, T.; Tasumi, M.; Vergoten, G.; Fleury, G. *Chem. Phys. Lett.* **1974**, *28*, 449–453.
- (15) Kobayashi, M.; Kobayashi, T.; Uesaka, T.; Tadokoro, H. *Spectrochim. Acta* **1979**, *35A*, 1277–1282.
- (16) Tam, C. N.; Bour, P.; Eckert, J.; Trouw, F. R. *J. Phys. Chem. A* **1997**, *101*, 5877–5884.
- (17) Remler, D. K.; Madden, P. A. *Mol. Phys.* **1990**, *70*, 921–966.