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Intensities of longitudinal acoustic modes and their structural implications

It is now commonly known that an intense longitudinal acoustic mode (*LAM*) can be observed in the low frequency Raman spectra of linear paraffins and polyethylene. However, the higher orders of the *LAM* in polyethylene are relatively weaker than for paraffins. Whereas up to 31 orders have been reported for n-tetranonacontane[1] only the 3rd order has been detected for polyethylene[2]. It has been suggested that the relative weakness of the *LAM* in polyethylene arises because of perturbations brought about by the fold surface[3], although this has been challenged on the basis of degradation studies[4]. In this Letter it will be shown that a further consideration of the factors controlling intensity as a function of wavenumber calls for a reappraisal of conclusions based on intensity measurements.

Schaufele and Shimanouchi[1] used a form of the theoretical Raman intensity in which for a given length of paraffin chain the *LAM* intensity depends upon $1/\bar{\nu}_m$ where $\bar{\nu}_m$ is the wavenumber shift of the *LAM* in the *m*th order. Because $\bar{\nu}_m$ is directly proportional to *m* through the *LAM* equation

$$\bar{\nu}_m = \frac{m}{2Lc}\left(\frac{E}{\rho}\right)^{1/2}$$

it was suggested that the *LAM* intensity should depend upon $1/m$. Here E is Youngs Modulus, ρ is density, L is length of paraffin chain and c is the speed of light. However, multiplication of the observed intensities of the higher orders in n-hexatriacontane by *m* did not reveal this dependence. *Table 1* shows these results and others from this laboratory.

A full treatment of Raman intensities as given in standard texts[5,6] shows that the intensity depends not only upon $1/\bar{\nu}$ but also upon the scattering efficiency of the radiation and upon the population of vibrational energy levels, which give rise respectively to terms in $(\bar{\nu}_0 - \bar{\nu})^4$ and $[1 - \exp(-h\bar{\nu}c/kT)]^{-1}$. Here $\bar{\nu}_0$ is the absolute wavenumber of the exciting radiation, h is Planck's constant, and T is absolute temperature. The term in $[1 - \exp(-h\bar{\nu}c/kT)]$ results from summing the population of vibrational energy levels. Assuming that the potential is harmonic, these levels are equally spaced and transitions between them give rise to Raman lines at the same wavenumber. Since kT/hc has a value of 200 cm^{-1} at room temperature the *LAM*s fall in the range where this term has a significant effect on their relative intensities. Although the dependence upon 4th power of absolute wavenumber is important when comparing intensities obtained using different exciting lines, it has a small effect, of the order of 10%, for a given exciting line over the range out to 500 cm^{-1}. Consequently, this

Table 1 *LAM* data for n-hexatriacontane (n-$C_{36}H_{74}$) and n-tetranonacontane (n-$C_{94}H_{190}$). *n*, number of carbon atoms; *m*, *LAM* mode order; $\bar{\nu}_m$, wavenumber shift of *m*th order *LAM*; *I*, integrated intensity. Intensities are normalized to that of the first order throughout. The data for n-$C_{36}H_{74}$ are those of Schaufele and Shimanouchi in ref 1. The data for n-$C_{94}H_{190}$ were obtained in this laboratory

n	*m*	$\bar{\nu}_m$	*I*	*I.m*	$[1 - \exp(h\bar{\nu}c/kT)]$	*I.m.* $[1 - \exp(h\bar{\nu}c/kT)]$
	1	65.9	1.0	1.00	0.28	1.00
	3	189	1.7×10^{-1}	0.51	0.61	1.11
36	5	306	9.2×10^{-2}	0.46	0.78	1.28
	7	403	4.8×10^{-2}	0.34	0.87	1.06
	9	473	2.8×10^{-2}	0.25	0.91	0.81
	1	27.9	1.0	1.00	0.13	1.00
94	3	74.5	1.6×10^{-1}	0.48	0.31	1.15
	5	122.2	5.2×10^{-2}	0.26	0.46	0.92

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Table 2 *LAM* data for four different samples of high density polyethylene (Rigidex 50) crystallized from the melt. The column headings have the *same meanings as* in *Table 1* with the exception of *I* which is peak height

m	$\tilde{\nu}_m$	I	Im	$[1 - \exp(h\tilde{\nu}c/kT)]$	$I.m.[1 - \exp(h\tilde{\nu}c/kT)]$
1	15.0	1.0	1.00	7.2×10^{-2}	1.00
3	46.0	1.4×10^{-1}	0.42	2.1×10^{-1}	1.23
1	13.0	1.0	1.00	6.3×10^{-2}	1.00
3	35.0	1.3×10^{-1}	0.39	1.6×10^{-1}	0.99
1	10.0	1.0	1.00	4.9×10^{-2}	1.00
3	29.0	1.0×10^{-1}	0.30	1.3×10^{-1}	0.79
1	7.0	1.0	1.00	3.4×10^{-2}	1.00
3	20.0	1.1×10^{-1}	0.33	9.5×10^{-2}	0.92

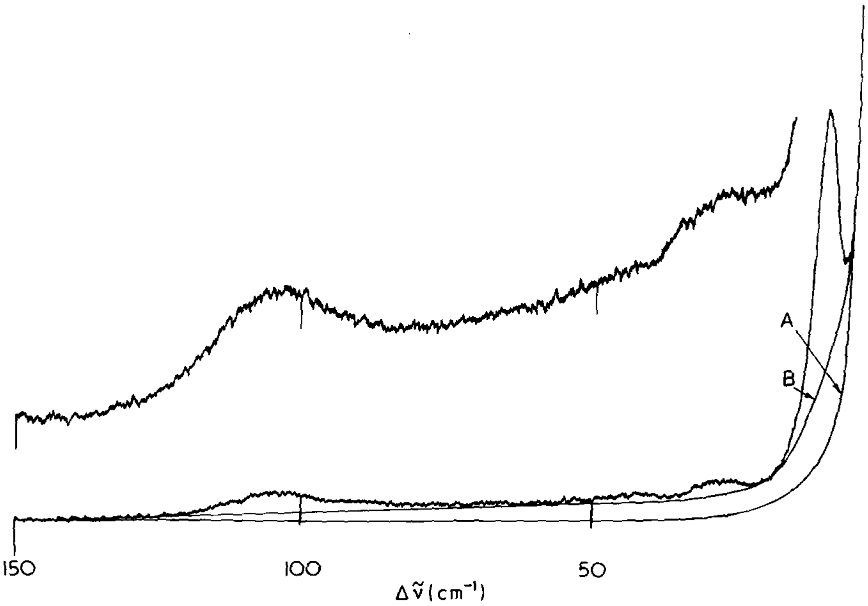

Figure 1 Raman spectrum in the range below 200 cm^{-1} of a sample of melt crystallized polyethylene (recorded using 100 mW of excitation at 530.9 nm and a Coderg T800 spectrometer operating at 0.75 cm^{-1} spectral bandwidth). It has been observed that the general intensity of the trace below 100 cm^{-1} decreases with decreasing temperatures[8] and thus it does not arise solely from stray light. Consequently, a baseline of the type A is thought to represent the stray light better than type B and was used in this work

term will not be considered.

As shown in *Table 1*, after multiplication of the observed intensities by $[1 - \exp(-h\tilde{\nu}c/kT)]$ the *LAM* intensities of the paraffins do, indeed, show a closer dependence upon $1/m$.

Table 2 shows the results of a similar survey of the relative intensities of the first and third order *LAM*s in melt crystallized polyethylene available in this laboratory. So far, no data on the higher orders of polyethylene crystallized from solution have been reported. The results demonstrate the principle that correction for the positions of the *LAM*s restores the apparently low intensity for $m = 3$ in polyethylene.

The first order *LAM* in melt crystallized polyethylene is generally at a much lower wavenumber than in paraffin spectra and this is a key factor when comparing the observed intensities as a function of mode order. In the range 500–30 cm^{-1} (n-paraffin spectra) the term $[1 - \exp(-h\tilde{\nu}c/kT)]^{-1}$ increases by about 7 times whereas in the relatively narrow range 30–1 cm^{-1} (polyethylene spectra) it increases by nearly 30 times. The *LAM*s in melt crystallized material generally occur below 15 cm^{-1} and, therefore, are in the range where the first order *LAM* is greatly enhanced relative to the higher orders by the operation of this effect.

The data do not permit a closer examination of the dependence of intensity upon mode order since the correct form of baseline is not known. The factors which make the baseline more difficult to determine for polyethylene than for paraffins[7] are (a) the closeness of the first order to the exciting line in polyethylene and hence the instrumental straylight influences its intensity; (b) the broad envelope of rotational lattice modes[8] near 100 cm^{-1} which tend to swamp the third order and (c) the roots of the first and third orders overlap. Under these circumstances a spread of relative intensities can be accommodated within the range of plausible baselines. A representative Raman spectrum of the range below 200 cm^{-1} is shown in *Figure 1.*

To summarize, therefore, the dependence of Raman intensity upon wavenumber is a significant effect in the range where *LAM*s are observed. Within the present limitations on resolution the observed intensities of the first and third order *LAM*s in n-paraffins and in polyethylene can be accounted for without invoking fold surface effects peculiar to polyethylene. Although it is still expected that fine differences in structural order should be revealed by *LAM* intensities 'spectroscopic effects' must be eliminated before 'structural effects' can be investigated.

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