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On the longitudinal acoustic mode in branched and unsaturated polyethylenes

Hans Lewandowski, Robert J.Meier*

Institute Agrosphere, ICG-IV, Forschungszentrum Jülich GmbH, D-52425 Julich, (GERMANY)

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ABSTRACT

The Raman vibrational spectra of branched alkanes and alkenes were studied by quantum calculations in order to investigate the effect of branching and unsaturation on the main chain LAM mode in polyethylenes. It was found that alkyl side chains have a minor effect on the main chain LAM mode. On the contrary, non-terminal unsaturations within the main chain do have a significant effect on the LAM-1 mode. It is shown that former interpretation of the spectra of LAM bands in non-terminally unsaturated $C_{18}H_{26}$ requires a different, renewed, description.

INTRODUCTION

The Longitudinal Acoustic or Accordion Mode (LAM) is a well-known characteristic vibrational mode in polymer systems having linear extended chain segments[1]. It is a vibrational mode that involves atomic displacements resembling accordion like mode, viz. figure 1. In general, for long chain length, the frequency ν_m (in cm^{-1}) is inversely proportional to this chain length (L):

$$\nu_m = \frac{m}{2cL}\sqrt{\frac{E_c}{\rho}}$$

with m the mode order (m = 1, 2, 3, c the speed of light, E_c the elastic (Young's) modulus, and ρ the density. The LAM-1 is, also because the intensity drops quickly with increasing order, the mostly studied mode.

Unfortunately, the LAM mode is not studied very often these days although it is one of the prominent possibilities to study morphology of the polymer by Raman spectroscopy. In the more distant past quite a few publications on the LAM mode in polymers appeared as it provides additional information on the structure of polymeric materials. Whereas X-ray diffraction enables the determination of the thickness of the crystalline lamellae, the LAM mode frequency provides along with this information from X-ray diffraction whether the chains are oriented perpendicular or under an angle with respect to the lamellae. The overwhelming majority of publications involving the LAM mode has been on alkanes and polyethylenes. For these, also effects of chain defects[2], unsaturations[3], and intermolecular chain interactions[4] have been reported.

Polyolefins normally have side groups along the main

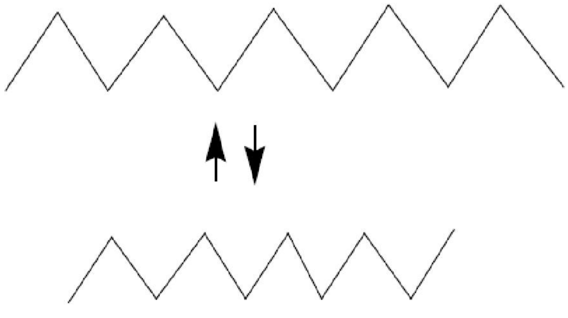

Figure 1 : Illustration of longitudinal acoustic (or accordion) mode type (LAM)

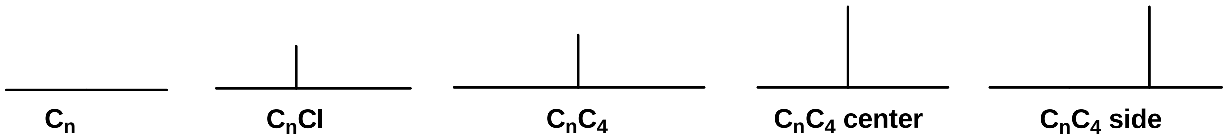

Figure 2 : Schematic illustration of typical alkane structures simulated in this study

chain. Sometimes these are unwanted effects in the polymerisation, sometimes these are on purpose when we are talking about co-polymerisation or long-chain branching. As far as we know there is published study into the effects of such branching on the LAM mode. Whereas one may argue there will be no vibrational mixing between the main chain LAM vibration and side chains vibrations, which is definitely true, the weight of the side group could have a non-negligible effect on the main chain LAM vibration. When the effects are non-negligible, this means on the one hand that we can not interpret the LAM mode in the traditional straightforward way, but on the other hand it may yield us additional information on the polymer chain. Therefore this paper reports on the LAM mode in branched alkanes by taking alkanes ($C_{16}H_{34}$-$C_{32}H_{66}$) as model systems. Similarly, unsaturations are present in many polyolefin chains, and only an incidental report on the LAM mode in such a system seems available from the past[3].

Our analysis for the branched systems is a theoretical one, as we can not make a sample with one particular type of branching for experimental validation. It has been shown that current quantum calculations are an independent and proven way of accessing vibrational frequencies and intensities for alkanes and polyethylenes[5-9]. In former days, i.e. the 1950's through the 1980's, the state of the art was to invoke force fields to evaluate vibrational frequencies and dot products of the eigenvectors to obtain relative intensities. Many interpretations of vibrational spectra were actually based on such analyses. However, the outcome from such a study might be biased, as the force fields were usually constructed starting from experimentally available vibrational frequencies. In addition, in particular the intensity calculation is prone to errors, as many more modes might show interference in the frequency range of the LAM when comparing to experiment. Thus, we here report full quantum mechanical calculations that have previously been shown to be capable of capturing details of LAM mode frequencies contrary to more simple models[6].

Computational details

It has been shows before that the semi-empirical AM1 method is an adequate method for the calculation of semi-quantitative trends in LAM mode frequencies[5,6]. For instance[5], the semi-empirical AM1 method well represents the LAM frequencies for alkanes with a constant offset of about 10%.

As it could also occur that certain effects would not be observable in experiment due to changing intensities, we should also investigate whether the intensities of the Raman active LAM are not changing significantly upon branching. We report selected Hartree-Fock level (HF/6-31G*) level calculations aiming for Raman intensities. Although this is a low level of calculation, previous studies have shows that variations in Raman intensities for alkanes are well reproduced at this level[5-9].

In this paper we will occasionally use a short-hand notation for the alkanes: C_nH_{2n+2} is simply written as C_n. For branched alkanes, a C_nH_{2n+2} chain with a C_8H_{17} side chain is represented by C_nC_8.

RESULTS

For the straight chain model systems studied, we calculated the LAM mode for $C_{16}H_{34}$ as 164cm^{-1} to be compared to the experimental value of 150cm^{-1}[10]. For $C_{20}H_{42}$ the values are 131cm^{-1} (AM1) and 114cm^{-1} (experimental), respectively, whereas for $C_{24}H_{50}$ the calculated value of 111cm^{-1} should be compared to the experimental value of 98cm^{-1} (experimental values from Ref.[11]). Calculated values are thus about 10% higher than experimental values as previously found[5].

In general, the normal alkane LAM modes have the character like illustrated in figure 1. We note that from our analysis it turned out that branched structures exhibit LAM modes that have some other character mixed in. So in branched systems we often can not speak of a pure accordion type motion as illustrated by figure 1, which is due to the fact that the side chain actually distorts the linear character of the main chain.

TABLE 1 : AM1 calculated LAM frequencies for various alkanes, with and without side chains. Please note that C_nH2_{n+2} is simply written as C_n. An alkane chain with a C_8H_{17} side chain is represented by C_nC_8

Alkane	LAM
C_{16}	164
$C_{16}C_1$ center	171
$C_{16}C_4$ center	163
$C_{16}C_4$ side	155
$C_{16}C_8$ center	159
C_{20}	131
$C_{20}C_1$ center	142
$C_{20}C_4$ center	136
$C_{20}C_4$ side	136
$C_{20}C_8$ side	140
C_{24}	111
$C_{24}C_1$ center	122
$C_{24}C_4$ center	112
$C_{24}C_8$ side	114
C_{32}	83
$C_{32}C_1$ center	89
$C_{32}C_4$ center	89
$C_{32}C_4$ side	83

Therefore, next to the identification of LAM modes in the branched systems by visual inspection of the atomic displacement, it is important to obtain information on vibrational intensities in order to validate that there is still Raman intensity related to the mode of interest.

LAM frequencies of branched alkanes

Relevant short chains in polyolefins include methyl up to hexyl branches, which are deliberately or undeliberately appearing in copolymers of ethylene and higher alkenes. We have studied the vibrational spectra for the structures displayed schematically in figure 2. The calculated LAM frequencies are collected in TABLE 1. It is interesting to note that apparently a single side chain carbon (methyl branch) leads to a significant perturbation of around 10cm^{-1} in the frequency of the LAM, whereas longer branches have a smaller effect. With increasing length of the main chain the effect of the side chain becomes smaller. This suggests that for polyethylenes the effect of the side chain is small to negligible. It should be noted, however, that the character of the LAM vibration, i.e. the atomic displacement as illustrated in figure 1, is seriously affected by the introduction of side chains. Therefore it is absolutely relevant to check Raman intensities before making any definite conclusions.

TABLE 2 : AM1 calculated LAM frequencies for C_{16} alkane and mono-brominated C_{16} alkane, with the bromine at the chain end (C_{16}Br), at the carbon 8-position (C_{16}-8-Br), or at the carbon 5-position

Species	LAM (cm^{-1})
C_{16}	164
C_{16}Br	125
C_{16}-8-Br	168
C_{16}-5-Br	160

We additionally verified this observation of a small effect of a long side chain by attaching a much heavier atom onto the chain rather than an alkyl side chain. Taking the bromo-alkanes we previously studied[6], we observe a significant downward shift when we attach the Br at the chain end, but attached along the chain the calculated effect is at most a few wavenumbers, viz. TABLE 2.

Thus, in conclusion, no significant effects of a side chain on the LAM frequency of a long alkane are expected. The results for the long alkanes suggest that for a polyethylene chain, and even more so while LAM bands for real polyethylenes are usually not very narrow, there will in practice no experimentally discernable effect. Obviously, we now have to check whether any major changes occur with respect to Raman intensities.

LAM intensities in branched alkanes

The HF/6-31G(d) calculated frequencies and intensities for selected branched alkanes are shown in TABLE 3. Due to the introduction of the branch, the character of the LAM does not display exactly the atomic displacement shown in figure 1 for a pure linear alkane. In addition, Raman intensity due to other vibrational modes might show up at or very near to the LAM frequency. Obviously, from the experimental spectrum one can not discriminate between LAM and non-LAM intensities. Therefore, in TABLE 3, we have also presented the summed intensities in the frequency region of the LAM.

From the intensities in TABLE 3 it can be concluded that with increasing chain length ($C_{16} \rightarrow C_{20}$) there is only a limited decrease in intensity of the Raman intensity in the LAM spectral range. For the interpreta-

TABLE 3 : Calculated LAM(-like) frequencies and Raman intensities for two (branched) alkanes

Alkane	HF frequency (exp. freq.) cm^{-1}	HF intensity (a.u.)	Summed intensity (a.u.)
C_{16}	150	5.9	5.9
$C_{16}C_4$	151 (150)	4.55	
	156	0.54	5.1
C_{20}	119 (114)	2.56	
	123	2.56	5.1
$C_{20}C_4$	122	4.3	
	124	0.18	
	129	0.40	4.9

tion of experimental spectra this will not have noteworthy consequences.

The LAM in trans-alkenes

Next to branching, a common feature in polyethylenes is an unsaturation. In a polyethylene a terminal (vinyl) or a vinylidene type unsaturation ($-CR = CH_2$) does not have a significant effect on the LAM-1, as we indeed observed from AM1 calculations ($C_{16}H_{34}$: 164cm^{-1}, $C_{14}H_{31}$-CH = CH_2: 168cm^{-1}, C_8H_{17}-CH(= CH) C_8H_{17}: 167cm^{-1}). However, a double bond *within* the main chain might have a more noticeable effect.

Rabolt et al. reported the influence of unsaturations in the alkane on the LAM[3]. According to their data the effects should not be that large, as can be seen from their data collected in TABLE 4 of the present paper. We particularly note that the former work suggested that LAM bands are still in the 120-130cm^{-1} spectral range for 6-$C_{18}H_{36}$ and 9-$C_{18}H_{36}$, with the total intensity not changing significantly (according to so-called 'dot-product' calculations[3]). When looking at the experimental spectrum in figure 1 of Ref. 3, however, it is observed that upon placing the unsaturation within the chain, i.e. the 6 or 9 position in this case, the spectral range 100-200cm^{-1} does not exhibit just the LAM mode like for $C_{18}H_{38}$ and 1- $C_{18}H_{36}$, but a range of bands. Furthermore, for the 6-$C_{18}H_{36}$ and 9-$C_{18}H_{36}$ structures a calculated LAM frequency was reported but no LAM band was experimentally observed, despite the comparatively small change in calculated intensity compared to the saturated alkane.

TABLE 4 : Calculated and experimental LAM mode frequencies according to Rabolt c.s.[3] and the calculated low-frequency Raman active modes according to the present work. oop reads out-of-plane

Alkene	Calc. freq. (cm^{-1})[3]	Exp.freq. (cm^{-1})[3]	Calc. freq. (cm^{-1}) Present work	Calc.Int. (a.u.) Present work	Character of vibration
n-$C_{18}H_{38}$	126	133	134	5.3	LAM-1
	358	356	373	2.4	LAM-3
1- $C_{18}H_{36}$	128	136	136	2.9	LAM-1
			141	1.5	
			362	1.3	
	371	369	387	2.2	LAM-3
6- $C_{18}H_{36}$	121	not. obs.	----		
			116	0.5	
			119	1.0	
			159	1.1	
		~200	191	3.6	HC = CH oop
			212	0.7	
			280	1.7	
	363	357	379	3.1	LAM-3
9- $C_{18}H_{36}$	130	not obs.	---		
			109	0.7	
	118		118	0.5	
			158	0.6	
			166	0.8	
			172	0.6	
		~200	211	6.1	HC = CH oop
			305	0.9	
	385	355	375	3.4	LAM-3

Our HF/6-31G(d) quantum calculations reveal precisely that what is observed in the experimental spectra[3]. The LAM-1 and LAM-3, both reported experimentally[3], are well recovered from our AM1 calculations (TABLE 4) for both $C_{18}H_{38}$ and 1-$C_{18}H_{36}$. The calculations reveal that the intensity lowers upon introduction of the terminal unsaturation, which seems in agreement with experimental data, although we should notice that no intensity reference was used in the experimental work[3]. However, for 6-$C_{18}H_{36}$ and 9-$C_{18}H_{36}$ the stronger band at the position of the LAM in $C_{18}H_{38}$ vanished, a series of lower intensity bands pops up in the range up till 200cm^{-1}, whereas a stronger band shows up near 200cm^{-1}. The character of this latter band is out-of-plane CH motion of the unsaturation. This is, at least qualitatively, in agreement with the experimental spectra. Interestingly, although the LAM-1 vanished, the LAM-3 is retained as corroborated from experimental data and confirmed by our calculations.

SUMMARY

The effect of side chain on the Longitudinal Acoustic Mode in polyethylenes was studied by simulations on alkanes using quantum chemical methods. The effects turned out minimal, both in frequency and intensity, and thus LAM modes in branched polyethylene samples can be interpreted without the need to consider possibly effects of branching.

We then concluded the same holds for unsaturations at the end of the polymer chain or as a side chain. We rationalized the effect of an unsaturation within the main chain, in agreement with experimental observations[3]. More explicitly, for several $C_{18}H_{36}$ alkenes analysis from the past was actually not in agreement with full experimental observations[3], whereas our calculations clearly revealed the experimental facts. The calculations show once more that relatively simple HF/6-31G(d) quantum calculations are well capable of rationalizing and forecasting effects in the Raman spectra of alkanes and polyethylenes.

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