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The influence of double bonds on the Raman active longitudinal acoustical model (LAM) in *trans*-alkenes

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Raman measurements on a series of *trans*-alkenes having the double bond at various locations along the backbone have been obtained. Compared to the *n*-alkanes, a dramatic decrease in the intensity of LAM-1 has been observed, while that of LAM-3 and LAM-5 remains relatively unchanged. Normal coordinate calculations indicate that in the *trans* alkenes there is a significant long-range coupling between longitudinal and transverse motion in LAM-1 due to the presence of the double bond which effectively diminishes its intensity. In LAM-3 and LAM-5 the longitudinal/transverse coupling is less, and much more localized about the double bond, preserving both the longitudinal character and intensity of these modes. Raman intensity variations in the $-CH_2-$ bending region have been utilized to study the lateral packing of methylene groups in the crystalline subcell, and the *trans*-alkenes have been found to crystallize in structures analogous to their polyalkenamer counterparts.

INTRODUCTION

The low frequency Raman active longitudinal acoustical mode (LAM) has proven useful in the study of polymer structure,[1,2] morphology,[3-14] and dynamics.[15] The use of LAM to characterize ordered chain sequences in isostructural oligomers indicated that its frequency varied inversely with chain length, and hence a calibration curve could be established.[16] The observation of LAM in the corresponding polymer could then be used to determine a measure of the stem length in the folded chain lamella.[1] Depending on the thermal and mechanical processing history, it was possible, in many cases, to get a reasonable agreement between this value and that obtained from small angle x-ray scattering. However, this was often not the case because of the various perturbing influences (forces and masses)[17-20] which could affect the frequency of the LAM. The effect of methyl groups,[21] polymorphism,[22] and hydrogen bonds[23] has been assessed experimentally and found to cause predictable shifts in frequency. In a recent study,[23] it was reported that strong intermolecular forces also appear to affect the intensity of LAM.

A problem of considerable interest, which has received very little attention, is the effect of a double bond on both the frequency and intensity of LAM. This is particularly important for the study of unsaturated alkane chains which are the primary components of certain membranes and cholesteric liquid crystals. In addition, an understanding of the effect of unsaturation on LAM should extend the applicaton of LAM to a whole class of polymers containing double bonds within the skeletal backbone.

In order to investigate the double bond effect on LAM a series of *trans*-alkenes have been investigated experimentally. Normal coordinate calculations in the isolated chain approximation have also been used to elucidate the influence of a double bond on the atomic displacements parallel to the molecular axis which are characteristic of the LAM.

EXPERIMENTAL

Spectroscopy

All Raman data were recorded with the 4880 Å line of a Spectra Physics 165-08 Ar ion laser. The spectra were obtained at $-100 \pm 3\,^{\circ}C$ using a vertical Harney-Miller cell in which the samples were held in sealed melting capillaries. The scattered light was collected at 90° and focused onto the entrance slit of a Jobin-Yvon HG-2S double monochromator containing concave holographic gratings. Data were collected and processed using a Nicolet 1180 minicomputer interfaced to standard photon counting electronics. Spectra were generally recorded in the 15–1700 cm^{-1} region with the coaddition of 10 scans at a rate of 240 cm^{-1}/min. Unless otherwise stated, no digital smoothing was applied to the recorded data.

The n-$C_{14}H_{30}$, n-$C_{18}H_{38}$, n-$C_{19}H_{40}$, 1-$C_{18}H_{36}$, and *trans*-9-$C_{19}H_{38}$ were all obtained from commercial sources.

The *trans*-7-tetradecene was prepared by a modification of Campbell and Eby's general method[1] involving the stereospecific dissolving metal reduction of 7-tetradecyne (Farchan Chemical Co.).

Sample preparation

Trans-7-tetradecene (Ref. 24)

Liquid ammonia (450 ml) was distilled from sodium into a dry three-neck 1ℓ round bottom flask equipped with stirbar, addition funnel, dry ice condenser, and nitrogen bubbler. A solution of 7-tetradecyne (9.70 g, 50 mmol) and anhydrous *t*-butanol (14.8 g, 200 mmol) in anhydrous ether (125 ml) was added to the ammonia and sodium metal (3.10 g, 135 mmol) was added in small portions over the next three hours at such a rate to just maintain the blue color. The reaction was terminated by the addition of piperylene and the ammonia was allowed to evaporate overnight. The next day hexane (250 ml) and water (250 ml) were added and the solution trans-

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ferred to a separatory funnel. The phases were separated and the organic phase washed with brine (200 ml), dried ($MgSO_4$), filtered through a pad of silica gel, and concentrated by rotary evaporation to a colorless oil (10.0 g). The olefin was further purified by distillation through a 15 cm vigreaux column and a center cut (bp 70°, 0.27 mm) was used for Raman studies; ^1H NMR ($CDCl_3$) δ 0.90 (crude t, 6H), 1.30 (broad s, 16H), 1.8–2.3 (m, 4H) 5.25–5.45 (m, 2H); IR(neat) 970 cm^{-1} (*trans* olefin C–H bend); Raman (neat) 1673 cm^{-1} (*trans* olefin C=C stretch); mass spectrum (70 eV) m/e 196 (M^+).

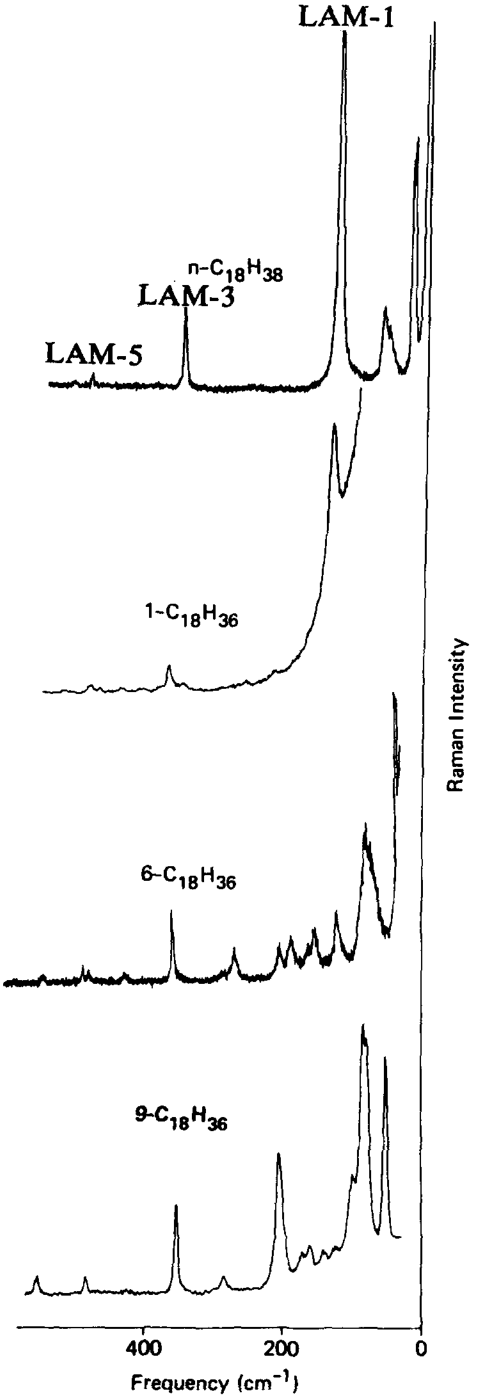

FIG. 1. Low frequency Raman spectra of n-octadecane and a series of *trans*-alkenes recorded at −100 °C (bandpass = 1 cm^{-1}).

RESULTS AND DISCUSSION

Low frequency Raman spectra of *trans*-alkenes

Earlier studies[25] of the effect of unsaturation on the LAM in long chain fatty acids indicated that the C=C bond essentially decoupled the molecular vibrations along the chain axis giving rise to a LAM characteristic of each of the two isolated all-*trans* chain segments. More recent work has shown that the effect of end group masses[21,26] and hydrogen bonds[23,27] on the frequency and intensity of LAM may be substantial and, hence, this earlier conclusion should be re-examined. The use of *trans*-alkenes in this study was chosen in order to minimize the perturbation of LAM by forces and masses and, hence, a more accurate assessment of the influence of *trans*-double bonds on the vibrational spectrum can be made.

In Fig. 1 the low frequency Raman spectrum (at ~100 °C) of n-$C_{18}H_{38}$ is compared to that of a series of *trans*-alkenes. As can be seen the position of LAM-1 in 1-octadecene is very similar to that of the n-alkane, however, in *trans*-6-octadecene and *trans*-9-octadecene the location of LAM-1 is no longer apparent. However, LAM-3 and LAM-5 do not appear to be appreciably changed (see Table II) in position or intensity (except 1-octadecene) from that of their n-alkane counterpart.

Initially it was noted that the LAM-1 region in both the *trans*-6- and 9-octadecene contained significantly more intense bands than the n-octadecane possibly attributable to lattice vibrations due to a change in crystal structure (to be discussed in a later section) or perhaps resulting from certain skeletal vibrations which have gained intensity due to the removal of the molecular symmetry by the incorporation of the double bond into the backbone. A reasonable explanation of this inability to locate LAM-1 in these *trans*-alkenes could be given if some type of Fermi resonance[28] had occurred between LAM-1 and some other vibrational band(s) which exhibited the appropriate symmetry in this extremely rich spectral region. Both intensity borrowing and frequency shifts can be associated with Fermi resonance and, hence, could explain this observation.

Since an inverse relationship between the frequency of LAM and the chain length has been established, a shorter *trans*-alkene was investigated since LAM-1 would occur at a higher frequency removing it from the complex low frequency region. In Fig. 2, the low temperature Raman spectrum (uncorrected for temperature and frequency) of n-tetradecane is compared to that of *trans*-7-tetradecene. The band at 1673 cm^{-1} in the latter compound is indicative of the *trans*-double bond.[25] No *cis* double bond content can be detected within the experimental limits (1%–2%) of the Raman technique. Interestingly enough, there again appears to be no band in the *trans*-alkene which corresponds to the intense LAM-1 in the n-alkane. In addition, the narrow LAM-3 band is present in both spectra and its position appears to be unchanged. Hence, the lack of intensity of LAM-1 in these two different chain length *trans*-alkenes precludes any significant intensity borrowing due to Fermi resonance.

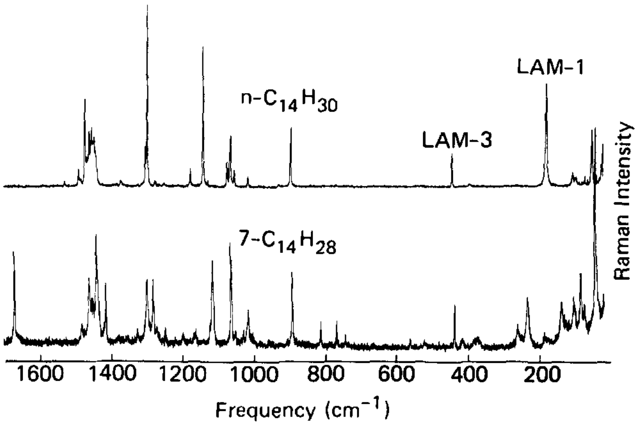

FIG. 2. Raman spectra of *n*-tetradecane and *trans*-7-tetradecene recorded at − 100 °C (bandpass = 1 cm^{-1}).

In order to rule out any odd–even effects, known to influence lattice packing in the *n*-alkanes,[29] a sample of *trans*-9-nonadecene was also investigated. Its Raman spectrum is compared to that of *n*-nonadecane in Fig. 3. The band at 1673 cm^{-1} can once again be attributed to the *trans*-double bond stretch but in this case a small amount of *cis* content is present as evidenced by the weak band at 1655 cm^{-1} characteristic of the *cis* double bond stretch.[25] However, a LAM-1 band is again not observed in the *trans*-alkene, although that assigned to LAM-3 and LAM-5 are observed in both the *n*-alkane and the predominantly *trans*-alkene. It therefore appears that the lack of observation of LAM-1 does not result from an odd–even effect and, as discussed previously, its lack of intensity cannot be attributed to an intensity exchange mechanism resulting from Fermi resonance.

Normal coordinate calculations

In order to assess the effect of the double bond on both the intensity and frequency of LAM, the normal modes of *n*-$C_{18}H_{38}$ and three additional *trans*-alkenes containing a single double bond in an 18 carbon backbone were calculated. In all cases an isolated chain in the skeletal approximation was used containing the reduced masses of the CH, CH_2, and CH_3 groups. A nontetrahedral geometry[30] with $< CCC = 112°$ and C-C = 1.54 Å was used for the paraffinic molecules, while a staggered configuration about the *trans*-double bond in the alkenes was adopted since x-ray studies[31] of *trans*-polyalkenamers indicated that this was the most probable structure. A top view of the structure used for *trans*-9-octadecene is shown in Fig. 4.

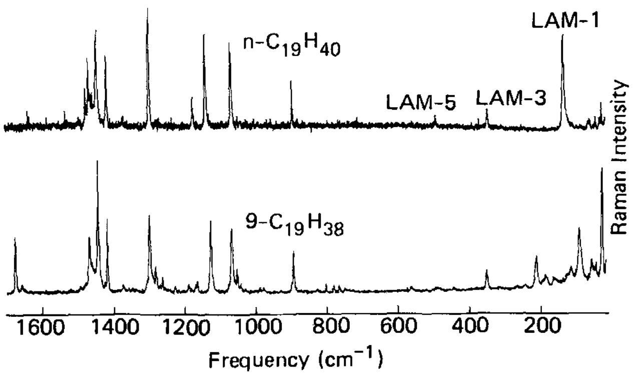

FIG. 3. Raman spectra of *n*-nonadecane and *trans*-9-nondecene recorded at − 100 °C (bandpass = 1 cm^{-1}).

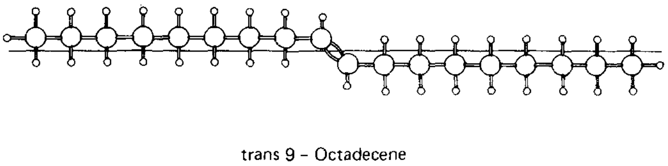

FIG. 4. Top view of *trans*-9-octadecene structure used for normal coordinate calculations.

A valence force field taken from Shimanouchi and Tasumi[30] was combined with that taken from *trans*-1,4-polybutadiene[32] for the region around the double bond and used in the normal coordinate calculations. In all cases LAM-1 and other multinodal vibrations (LAM-3 and LAM-5) were identified by the significant atomic displacements parallel to the molecular axis which they exhibit. In order to quantify the amount of longitudinal character present during the LAM vibration in the various molecular structures studied, the criteria of Reneker and Fanconi[33] was adopted. Since in the LAM of *n*-octadecane the atomic displacements are extensively along the chain axis direction, an 18 component vector was constructed from the normalized atomic displacements in the chain axis (*z* axis) direction. A dot product was then formed between this vector and a similar vector constructed from these same atomic displacements parallel to the chain axis for each of the structures containing a single double bond at different locations in the backbone. In the simple case this dot product has a magnitude of 1.0 and the mode will have a similar intensity to that of LAM in the *n*-octadecane. This presented a very convenient method of characterizing longitudinal character in the *trans*-*n*-alkenes and has been shown to be valid[34] provided that the structure plane of the zig–zag on both sides of the double bond remains parallel to the chain axis.

It is often instructive to plot the longitudinal Cartesian displacements corresponding to LAM vibrations since

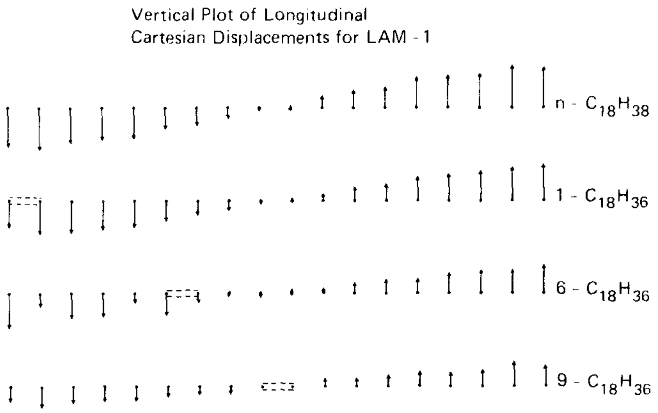

FIG. 5. Vertical plot of the longitudinal Cartesian displacements for LAM-1 in the *trans*-alkenes and *n*-octadecane.

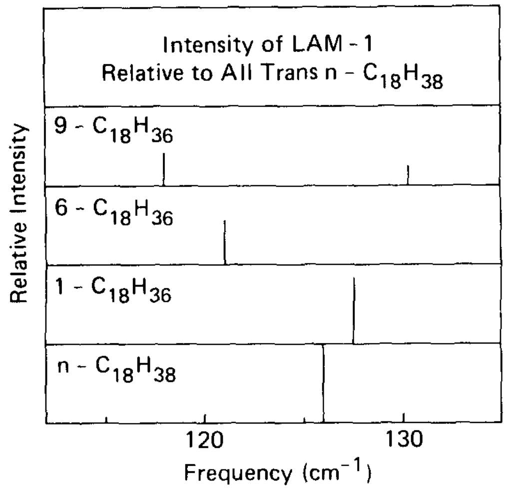

FIG. 6. Dot product intensities of *trans*-alkenes relative to *n*-octadecane.

the effect of a perturbation can easily be assessed by studying the atomic motions. This is shown in Fig. 5, where the LAM-1 Cartesian displacements parallel to the chain axis are plotted vertically for *n*-octadecane and the *trans*-octadecenes investigated experimentally. The position of the double bond is indicated by the dashed line. As can be seen, the magnitude of the atomic displacements parallel to the chain axis continue to decrease as the double bond approaches the central position of the molecule. If, as mentioned previously, the Raman intensity is assumed to be proportional to the dot product between eigenvectors of the *trans*-alkenes and the single nodal LAM-1 of the *n*-alkane then it becomes apparent that the intensity of LAM-1 in the *trans*-alkenes will be diminished. This is graphically illustrated in Fig. 6 where these dot products (normalized to that of the *n*-octadecane) have been plotted versus frequency. In addition to shifts in frequency, it is apparent that the intensity of the LAM-1 has undergone a considerable decrease in both *trans*-6-octadecene and *trans*-9-octadecene. In fact, in the latter there are actually two weak bands in the LAM-1 region which have longitudinal character.

An insight into the diminishing intensity of LAM-1 can be obtained by considering both in and out-of-plane displacements as shown in Fig. 7. In this case, the longitudinal Cartesian displacements (z axis) are now plotted horizontally while the transverse Cartesian displacements are plotted vertically (y axis). In the *n*-octadecane, the Cartesian displacements are exclusively longitudinal in character. However, upon introduction of the *trans*-double bond in a staggered configuration considerable out-of-plane (transverse to the chain axis) motion is introduced. In fact, the coupling between longitudinal and transverse motion is the greatest in the *trans*-9-octadecene. Thus, the overall change in polarizability associated with LAM-1, and therefore the Raman intensity will be the least when the double bond is positioned at the center of the hydrocarbon chain.

In contrast, an investigation of the same longitudinal Cartesian displacements for LAM-3, shown in Fig. 8, indicates that there is very little effect on the amplitude of the longitudinal displacements upon introduction of the *trans*-double bond. This is further verified upon examination of Fig. 9, where both the longitudinal and transverse Cartesian displacements are plotted for LAM-3. Although there is a slight coupling of longitudinal and transverse motion in the vicinity of the double bond in *trans*-alkenes, there is a predominant longitudinal character in LAM-3 independent of the location of the double bond. Hence, the change in polarizability, and therefore the Raman intensity, should remain qualitatively similar to that of the *n*-octadecane. This is shown in Table I where the dot products obtained for both LAM-3 and LAM-5 (normalized to the *n*-alkane intensity) are listed with those of LAM-1. It is interesting to note that the contents of Table I predict qualitatively and semiquantitatively that which is observed experimentally. The intensity of LAM-1 is considerably reduced compared to its *n*-alkane counterpart when a *trans*-double bond is in-

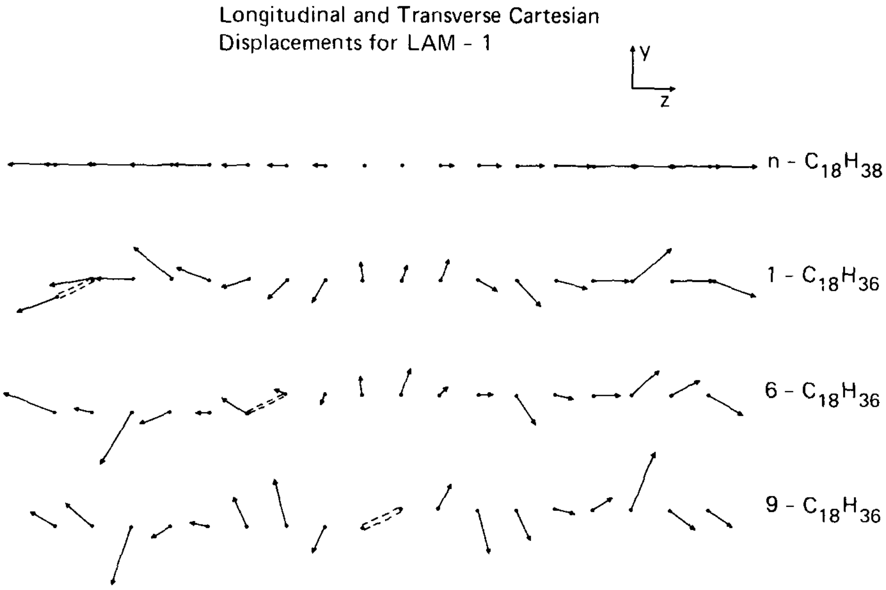

FIG. 7. Longitudinal (z) and transverse (y) Cartesian displacements for LAM-1 in the *trans*-alkenes and *n*-octadecane.

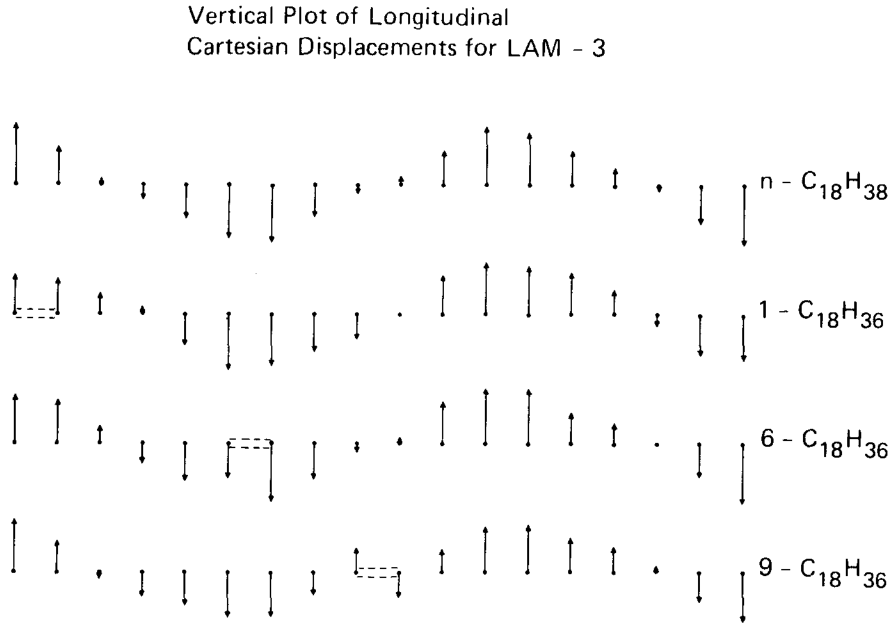

FIG. 8. Vertical plot of the longitudinal Cartesian displacements for LAM-3 in the *trans*-alkenes and *n*-octadecane.

troduced into the interior of a hydrocarbon chain. This is due to a considerable loss of longitudinal character resulting from coupling through the double bond with atomic motions transverse to the chain axis. However, the intensity of LAM-3 and LAM-5 is preserved independent of the position of the double bond since no significant coupling of longitudinal and transverse motion occurs.

An insight into this result is provided by a calculation of LAM in *n*-alkanes by Shimanouchi and Tasumi.[30] They have shown that the potential energy distribution of the LAM changes from a combination of CC stretch (58%) and CCC bend (42%) in LAM-1 to predominantly CCC bend (80%) in LAM-5. Since the CCC bending force constants in the planar zig–zag chain and those which are adjacent to the double bond are approximately equal, it will be the large C=C stretching force constant which will have the greatest effect on LAM-1 with diminishing effects on the higher multinodal vibrations.

The calculated and observed values of LAM for the series of *trans*-alkenes and *n*-octadecane are shown in Table II. Although the calculated values are in general agreement the differences result, in part, from the skeletal approximation. In particular, a comparison of the calculated and observed LAM-5 value indicates that the use of a force field composed only of diagonal elements is inadequate to predict the curvature of the longitudinal dispersion curve (ν_9)[35] of the infinite polyethylene chain.

Structure of the crystalline subcell in *trans*-alkenes

Intensity variations of bands in the methylene bending region (1400–1500 cm^{-1}) have been shown[36] to reflect the lateral packing of $-CH_2-$ groups in a subcell of the crystal

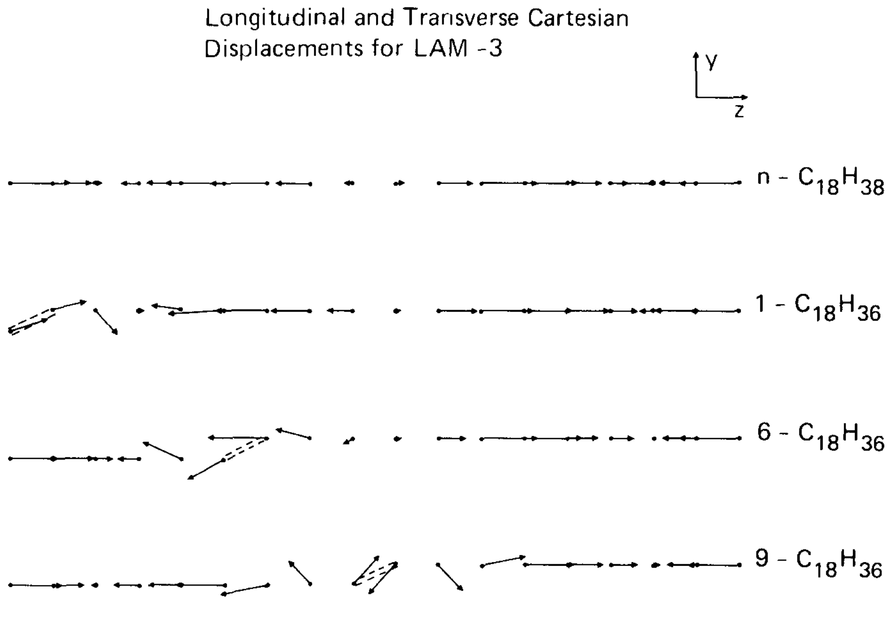

FIG. 9. Longitudinal (*z*) and transverse (*y*) Cartesian displacements for LAM-3 in the *trans*-alkenes and *n*-octadecane.

TABLE I. Intensity of LAM vibrations predicted by dot product method.[a]

	n-$C_{18}H_{38}$	1-$C_{18}H_{36}$	6-$C_{18}H_{36}$	9-$C_{18}H_{36}$
LAM-1	1.0[b]	0.858	0.616	{0.432 {0.252
LAM-3	1.0	0.990	0.985	0.867
LAM-5	1.0	0.953	0.843	0.978

[a] Reference 33.

[b] Intensities of LAM in n-alkane normalized to 1.0.

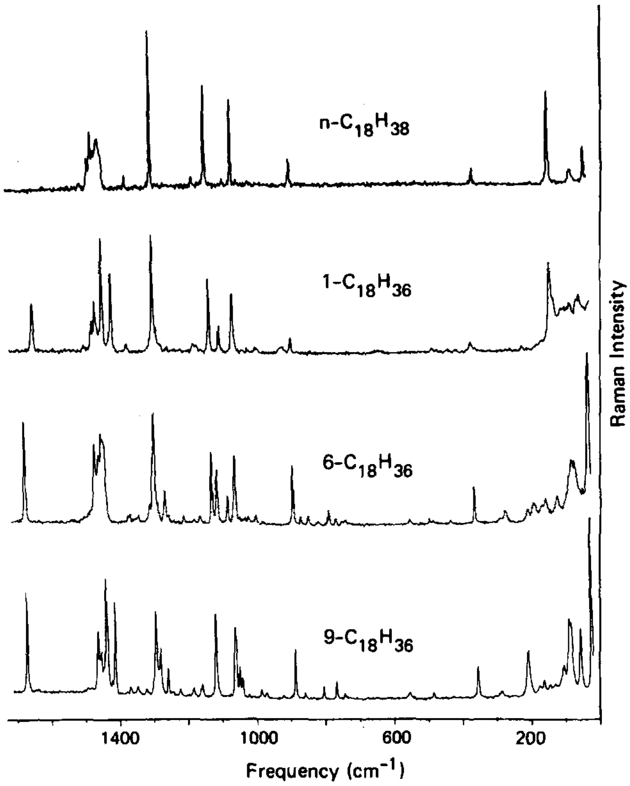

FIG. 10. Raman spectra of a series of *trans*-alkenes and n-octadecane recorded at $-100\,^{\circ}C$ (bandpass = 1 cm^{-1}).

lattice. This can be seen by comparing this region in the low temperature spectra of n-octadecane (Fig. 10) and n-tetradecane (Fig. 2) with that of n-nonadecane in Fig. 3. The former crystallize with triclinic subcell packing while the latter packing is orthorhombic.[29] Since the origin of this region is believed to arise from Fermi resonance of a $-CH_2-$ bending mode (Raman active) with overtones and possibly a combination of $-CH_2-$ rocking modes (IR active), a difference in both the number of bands and their relative intensities will arise depending on whether there are one or two molecules in the unit cell. In the latter case splitting of both the IR and Raman bands by the crystal field makes this region more complex.

Although it is tempting to classify the crystal structures of the *trans*-alkenes, since no x-ray data has appeared in the literature, it should be pointed out that n-alkenes which exhibit either the orthorhombic or monoclinic crystal structure have orthorhombic subcell packing of methylene groups, and will thus have identical Raman intensity patterns in the $-CH_2-$bending region.[29,36]

By comparing the 1400–1500 cm^{-1} region in the Raman spectra of the *trans*-alkenes in Figs. 2, 3, and 10 it becomes apparent that all except *trans*-6-octadecene show evidence for orthorhombic subcell packing. The *trans*-6-octadecene, on the other hand, exhibits a Raman intensity pattern characteristic of the triclinic subcell packing of methylene groups identical to that of n-tetradecane in Fig. 2.

It is of interest to compare the crystal structures of these *trans*-alkenes with that of the polyalkenamers reported by Natta *et al.*[31] in an x-ray diffraction study. It was found that when the chemical repeat unit contains an odd number of carbon atoms before the double bond, the polymer crystallizes in an orthorhombic crystal modification. However, the "even" polyalkenamers crystallize in either monoclinic or triclinic crystal structures. In this classification the *trans*-1-octadecene, *trans*-9-octadecene, and *trans*-7-tetradecene are considered short chain "odd" polyalkenamers and, hence, should crystallize in the orthorhombic crystal modification. As seen by the intensity pattern in the $-CH_2-$ bending region these three *trans*-alkenes do exhibit orthorhombic subcell packing but as mentioned previously the unit cell may be either orthorhombic or monoclinic. Likewise the *trans*-6-octadecene being a short chain even polyalkenamer would be expected to be triclinic which is what is observed experimentally. The *trans*-9-nonadecene is a strange case in point since it has an odd number of carbon atoms on one side of the double bond and an even number of carbon atoms on the other. The

TABLE II. Longitudinal acoustical mode frequencies.

	Calculated			Observed		
	LAM-1	LAM-3	LAM-5	LAM-1	LAM-3	LAM-5
n-$C_{18}H_{38}$	126	358	526	133	356	490
1-$C_{18}H_{36}$	128	371	533	136[a]	369	484
6-$C_{18}H_{36}$	121	363	525	···	357	489
9-$C_{18}H_{36}$	130 118	385	531	···	355	485

[a] Frequency uncorrected for instrumental background (see Fig. 1).

Raman measurements in this case indicate orthorhombic subcell packing as mentioned previously. Thus, with this one exception, the *trans*-alkenes appear to crystallize in structures analogous to their polyalkenamer counterparts.

Skeletal optical region (1000-1150 cm^{-1}) in *trans*-alkenes

The region encompassing 1000–1150 cm^{-1} in the Raman spectrum of n-alkanes includes two intense bands assignable to asymmetric (1065 cm^{-1}) and symmetric (1130 cm^{-1}) CC stretching vibrations of a planar zig–zag structure. In addition, a number of weak-medium bands[36] occur in this region which are a function of all *trans*-chain length reflecting phonon dispersion in the ν_4 branch of the infinite polyethylene chain. The position and intensity of these nonzone center modes has been shown to be perturbed by strong hydrogen bonding.[23] By comparing this skeletal stretching region in the *trans*-alkenes (Figs. 2, 3, and 10) it is also clear that the introduction of a *trans*-double bond into the n-alkane backbone does cause significant complexity in this spectral region. Intensity variations in this skeletal optical region usually accompany differences in subcell packing,[36] but the increase in number of bands most probably originates from a change in the shape of the CC stretch dispersion curve (ν_4)[35] brought about by the inclusion of the double bond. Regions which were previously flat now contain curvature with the net effect that nonzone center modes, previously degenerate, now are observed as discrete bands adding to the complexity of this region. In any case, the presence of the 1065 and 1130 cm^{-1} bands in all the *trans*-alkene spectra indicate that the paraffinic sequences joined together by the double bond exist in the planar zig–zag conformation.

CONCLUSIONS

Raman measurements on a series of odd and even *trans*-alkenes indicate that although the intensity and position of LAM-3 and LAM-5 are not significantly perturbed, a band assignable to LAM-1 is not observed. Normal coordinate calculations in conjunction with the dot product method for intensity determination verify that the effect of the incorporation of a *trans*-double bond into a hydrocarbon backbone is to severely decrease the intensity of LAM-1 while leaving that of LAM-3 and LAM-5 relatively unperturbed. An investigation of the Cartesian displacement coordinates for LAM-1 in the *trans*-alkenes indicates that significant long-range coupling between transverse and longitudinal motion occurs due to the *trans*-double bond while this same coupling is considerably diminished and very localized in LAM-3 and LAM-5, thus preserving the predominant longitudinal character and, hence their intensity.

Recent studies by Fraser *et al.*[37] on a series of folded chain lamella of *trans*-polyalkenamers found that no intense band characteristic of the lamella stem length could be assigned to LAM-1. A weaker band was observed at higher frequency and attributed to the LAM of the planar zig–zag segments contained between double bonds since it shifted to higher frequency with decreasing length of the segment. In light of the present study it is reasonable to conclude that the absence of LAM-1 in the low frequency Raman spectrum (< 50 cm^{-1}) of the *trans*-polyalkenamers is due to its lack of intensity. On the other hand, LAM-3 should be present but may be very broad since, like LAM-1, its bandwidth reflects[8] the distribution of stem lengths within a lamella and/or a distribution of crystallite thicknesses within the scattering volume and, hence will be very dependent on previous thermal history. In addition, it has been shown[8] that unless adequate spectral correction for instrumental background, frequency, and temperature effects are made, the observation of LAM-3 in polymers is difficult.

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