

Force Constant Calculations of the LAM-1 Modes of *n*-Alkanes and Their Substituted α -Monohalo- and α,ω -Dihalo- Species in Their Extended Zig-zag Planar Configurations as Found in Urea Inclusion Compounds

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Abstract. Force constants were determined for the C_8 , C_{10} , C_{12} and C_{14} series of *n*-alkanes C_nH_{2n+2} using an approximate SVFF calculation and observed LAM = 1 wavenumbers. In this calculation the hydrogen atoms were neglected and only the carbon backbone chain and terminal atoms were considered; this was valid since only low-frequency vibrations were under consideration. Using force constant transfer, the wavenumbers of the LAM = 1 accordion modes for the analogous α - $C_nH_{2n+1}X$ and α,ω - $C_nH_{2n}X_2$ species, where X = Cl, Br or I were calculated. For α -chloroalkanes and α,ω -dichloroalkanes, the $m = 1$ accordion modes are calculated to be in the 220–130 cm^{-1} and 200–120 cm^{-1} regions, respectively. For the bromo- and iodo-analogues the $m = 1$ accordion modes are calculated to be in the 200–100 cm^{-1} , 150–90 cm^{-1} and in the 170–100, 135–80 cm^{-1} regions, respectively.

Key words. Force constant calculations; *n*-alkanes; mono-halo and di-halo alkanes; urea inclusion compounds; LAM-1 modes; accordion vibrational modes.

1. Introduction

A vibrational analysis of Raman spectroscopic data from *n*-alkanes isolated in specific molecular configurations in urea inclusion compounds was first carried out by Fawcett and Long [1]. Long chain *n*-alkanes with even numbers of carbon atoms extended in a planar zig-zag skeletal arrangement as found in the urea inclusion compound belong to the molecular point group C_{2h} . Previous force constant calculations [2, 3] and vibrational analyses [4–7] have been carried out for extended chain *n*-paraffins and polymers with a zig-zag carbon chain backbone, such as polyethylene [8, 9] and polypropylene [10–13].

In this present work, approximate SVFF calculations on the C_8 , C_{10} , C_{12} and C_{14} *n*-alkanes and their α -substituted monohalo- and α,ω -substituted dihalo-analogues have been carried out to determine the assignments of the longitudinal acoustic modes (LAM) for $m = 1$, also known as the 'accordion modes' of the zig-zag carbon skeletal chain. In this approximation, in order to simplify the calculations, the hydrogen atoms have been neglected and only the carbon atoms in the backbone of the alkane and the terminal halogen substituents have been considered.

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Since, in these calculations, we are only considering the low frequency vibrations, the approximation is valid as the CH vibrations play little part in the molecular motion in this wavenumber range. It is the intention of this work to investigate the effect on the LAM-mode wavenumbers of substituting the end-groups with heavy atoms, such as halogens. In this way, the assignment of the low frequency vibrational spectra of alkanes and substituted alkanes as inclusion compounds in their extended zig-zag planar configuration would be made possible.

We shall develop the intramolecular force-field and investigate the transferability of the force-constants from the alkanes to the α mono- and α,ω dihalo-alkane species. Thereby, the relationship between the LAM ($m = 1$) mode vibrational wavenumbers, the chain length and the mass of the halo-substituents will be established for the assignment of the vibrational spectra of alkane inclusion compounds.

2. Theory and Force Constant Calculations

2.1. ACCORDION MODES IN n -ALKANES

Vibrational spectroscopic information on oriented single crystals of unsubstituted n -paraffin/urea inclusion compounds of the species and type studied here has already been reported [1]. The n -paraffin molecules are trapped in *one* configuration in the hexagonal urea lattice [1, 14], in which there are long channels whose cross-sectional dimensions are sufficient to accommodate the n -paraffin chain in an extended planar zig-zag configuration with small lattice-paraffin and paraffin-paraffin interactions. For n even, the n -paraffin has the molecular point group C_{2h} and the Raman-active vibrations belong to the symmetry classes A_g and B_g . A single molecule of n -decane, for example, will have 90 internal vibrations of which 45 (26 A_g and 19 B_g) will be Raman-active; these 45 vibrational modes reduce to only twelve observed bands when intensity factors are considered [1].

For an n even n -alkane, the normal mode with the lowest wavenumber corresponds to a one-mode wave of expansion or contraction of the whole skeletal zig-zag chain and is symmetric with respect to the centre of the molecule. This is the accordion mode of LAM ($m = 1$) mode, and is Raman-active. Through the application of the semi-empirical formula derived by Schaufele and Shimanouchi [15], which assumes that the skeletal backbone acts as a spring which vibrates longitudinally, the wavenumbers of the LAM modes can be calculated:

$$\tilde{\nu} = A(m/n) + B(m/n)^2 + C(m/n)^3 + \dots + F(m/n)^6 \quad (1)$$

where $\tilde{\nu}$ is the wavenumber (cm^{-1}), $A = 2495$, $10^3B = -5.867$, $10^5C = 6.253$, $10^5D = 3.485$, $10^5E = 7.329$, $10^5F = -4.724$ and m is the order of the mode, n is the number of C atoms in the skeletal chain of the paraffin.

The observed and calculated $\tilde{\nu}$ values for the $m = 1$ modes of n even n -alkanes are given in Table I. There is a good agreement between the observed and calculated $m = 1$ mode wavenumbers. The purpose of our calculation in this work was to set up an approximate SVFF force field and to demonstrate its applicability of transfer to substituted n -alkanes.

Table I. Wavenumbers of the accordion mode LAM ($m = 1$) for the *n*-alkanes.

<i>n</i> -Alkane	Accordion mode		
	Calculated [15]	Observed [1]	This work
C ₈ H ₁₈	277.8	284	289.4
C ₁₀ H ₂₂	225.4	234	235.4
C ₁₂ H ₂₆	189.3	198	193.0
C ₁₄ H ₃₀	163.4	174	169.2

2.2. FORCE CONSTANT CALCULATIONS

The force constant calculations were undertaken using a modified form of the original programme of Snyder and Schachtschneider [2] with changes in formatting data input suggested by Fuhrer *et al.* [16] and adapted further by ourselves for running on a Cyber 180-830 Computer. The calculations used the Wilson FG-Matrix method and a simple valence force field with interaction constants. Input data consisted of molecular parameters, symmetry elements, the number of atoms in the molecule, the molecular stereochemistry and the molecular vibrations. The setting-up of the routines, the operation of the programme and the stages involved in the refinements of the calculated and observed wavenumbers to a 'best-fit' situation have been described previously [17].

In the constructions of the G-matrices the following molecular bond lengths and bond angles and relative atomic masses were used:

$$m_{\text{C}} = 12.011 \text{ a.m.u.} \quad m_{\text{H}} = 1.008 \text{ a.m.u.}$$

$$m_{\text{H}} = 1.008 \text{ a.m.u.}$$

$$m_{\text{Cl}} = 35.453 \text{ a.m.u.}$$

$$m_{\text{Br}} = 79.904 \text{ a.m.u.}$$

$$r(\text{CC}) = 1.540 \text{ \AA}; \quad r(\text{CH}) = 0.770 \text{ \AA}; \quad r(\text{CCl}) = 1.767 \text{ \AA};$$

$$r(\text{CI}) = 2.135 \text{ \AA}; \quad r(\text{CBr}) = 1.937 \text{ \AA}; \quad \text{H}\hat{\text{C}}\text{H} = \text{C}\hat{\text{C}}\text{C} = 109.47^\circ.$$

Initial values of the primary force constants were taken from the literature for similar species [18]; interaction constants were added progressively as refinement proceeded.

Sets of wavenumbers were calculated for the C₈ to C₁₄ species using the same skeletal force-constant sets for each molecule. Although the refinements were carried out using all the available vibrational spectroscopic data only the LAM ($m = 1$) modes will be considered here; since the LAM ($m = 1$) mode in each *n*-alkane and substituted alkane species is *gerade* in symmetry it can be identified clearly from inspection of the eigenvalues in the *F*-matrix. As will be seen later, the percentage contributions of skeletal stretching and bending force constants to the LAM vibration are very similar to each other and this also assists in identification of the accordion modes.

2.2.1. *Unsubstituted n-Alkanes*

The wavenumbers of the LAM ($m = 1$) mode for the C_8 to C_{14} *n*-alkanes are given in Table I; the agreement between observed and calculated values is good to about 0.5–2.5%, the worst case being $C_{12}H_{26}$, for which case the difference $|\Delta\tilde{\nu}_{\text{calc}} - \tilde{\nu}_{\text{obs}}| \cong 5 \text{ cm}^{-1}$. These results confirm that the approximate SVFF force field is a good model and that the transferability of the force constants in the *n*-alkane series is acceptable.

As a prelude to a consideration of the substituted *n*-alkanes, it was now possible to transfer the force constants and force field model for unsubstituted *n*-alkanes and to examine the effect on the LAM ($m = 1$) mode wavenumbers of an increase in mass of the terminal groups on the CC skeleton. Table II gives the calculated wavenumber positions of the LAM ($m = 1$) modes for octane, decane, dodecane and tetradecane for stepwise increases in the atomic masses of the terminal C atoms of the skeletal chain from 10 to 100 a.m.u. The wavenumbers of the LAM ($m = 1$) modes for all terminal substituents decrease as the number of carbon atoms in the CC skeletal backbone increases and for any particular C_n substituted alkane the LAM ($m = 1$) wavenumber decreases with increase in mass of the terminal substituents. This is demonstrated graphically in Figure 1. The case of octane, however, requires further discussion. At C_8H_{18} , octane is the lightest *n*-alkane considered here; the stepwise increase in terminal masses not only has a proportionately larger effect on the molecular mass as a whole but around a terminal mass of 60 (which represents a terminal substituent cumulative mass of 120 a.m.u. *cf.* a backbone mass of 96 a.m.u.) the force constant calculations and potential energy distributions

Table II. Calculated wavenumbers for LAM ($m = 1$) modes in *n*-alkanes.

Terminal atom atomic mass	Octane*		Decane	Dodecane	Tetradecane
	(C_8H_{18}) $\Delta\tilde{\nu}(\text{cm}^{-1})$ (1) (2)		$(C_{10}H_{22})$ $\Delta\tilde{\nu}(\text{cm}^{-1})$	$(C_{12}H_{26})$ $\Delta\tilde{\nu}(\text{cm}^{-1})$	$(C_{14}H_{30})$ $\Delta\tilde{\nu}(\text{cm}^{-1})$
10	314.5	212.3	250.0	208.5	178.1
20	270.6	186.9	218.5	184.2	159.0
30	244.6	172.8	196.5	166.5	144.8
40	228.5	162.0	181.0	153.4	133.8
50	218.2	152.6	169.5	143.2	125.1
60	221.2	144.6	161.4	135.2	118.1
70	206.4	137.4	154.1	128.6	112.2
80	202.8	131.0	148.3	123.2	107.3
90	200.2	125.4	144.6	119.2	103.1
100	198.1	120.3	141.0	114.9	99.4
110	196.4	115.8	138.3	111.7	96.0
120	195.1	111.7	135.9	108.9	93.4
130	193.9	108.0	134.0	106.5	90.7
140	193.0	104.7	132.3	104.3	88.7

* Italic numbers in *n*-octane columns indicate non-unique assignments of LAM ($m = 1$) modes for terminal atomic masses > 50 a.m.u. (1) and (2) refer to two internally-consistent frequency sets.

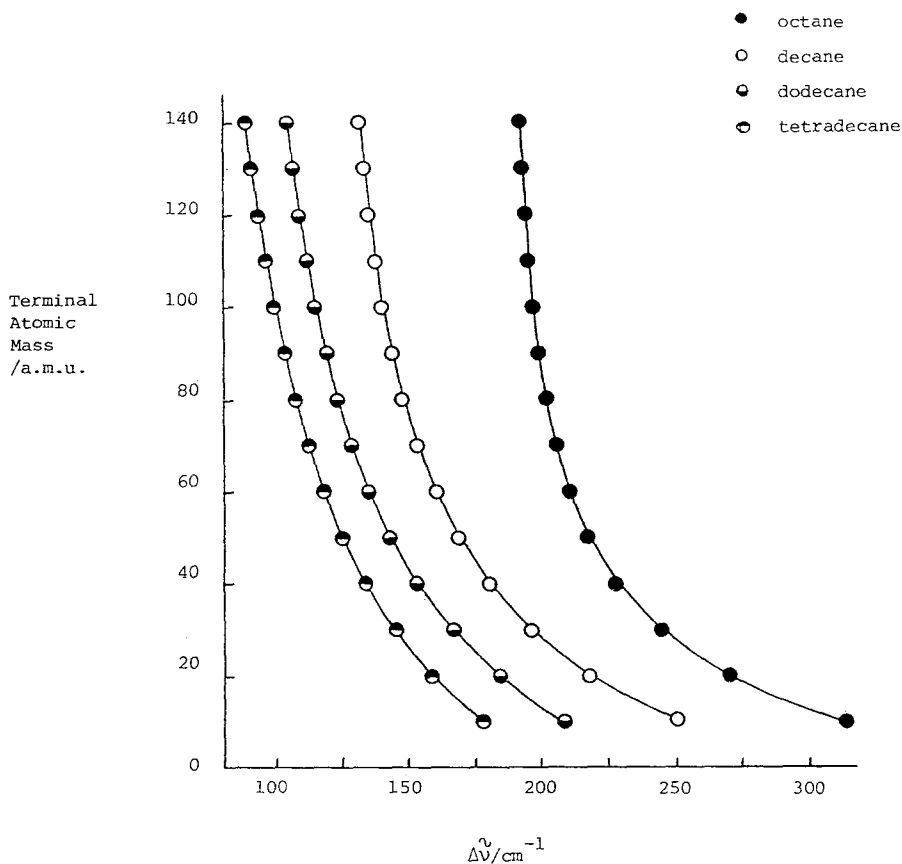


Fig. 1. Mass of end-group substituent plotted against the wavenumber shifts of LAM ($m = 1$) modes for unsubstituted *n*-alkanes.

indicate that the discrete LAM ($m = 1$) mode disappears. The normal modes of the octane backbone with its substituents are grossly distorted by the substituents with mass around 60 a.m.u. Hence, the $\Delta\bar{\nu}$ values of the LAM ($m = 1$) mode for octane with terminal substituents in the range 50–70 a.m.u., instead of decreasing with increase in terminal mass actually increase from 50–60 a.m.u. and then decrease rapidly to 70 a.m.u. and thereafter decrease more slowly to 140 a.m.u. The explanation of this phenomenon cannot merely be dependent on the mass ratios of terminal substituents and carbon chain because, in that case, we might expect that the decane, dodecane and tetradecane systems would demonstrate similar effects near terminal atom masses of 70, 80 and 90, respectively. The calculations do not support this hypothesis.

2.2.2. Monosubstituted *n*-Alkanes

To investigate the effect of end-group substitution on the LAM ($m = 1$) mode vibration in paraffins, the mass of the terminal atom was increased and the atomic mass of the substituent plotted against the wavenumber shift, $\Delta\bar{\nu}$. The results are

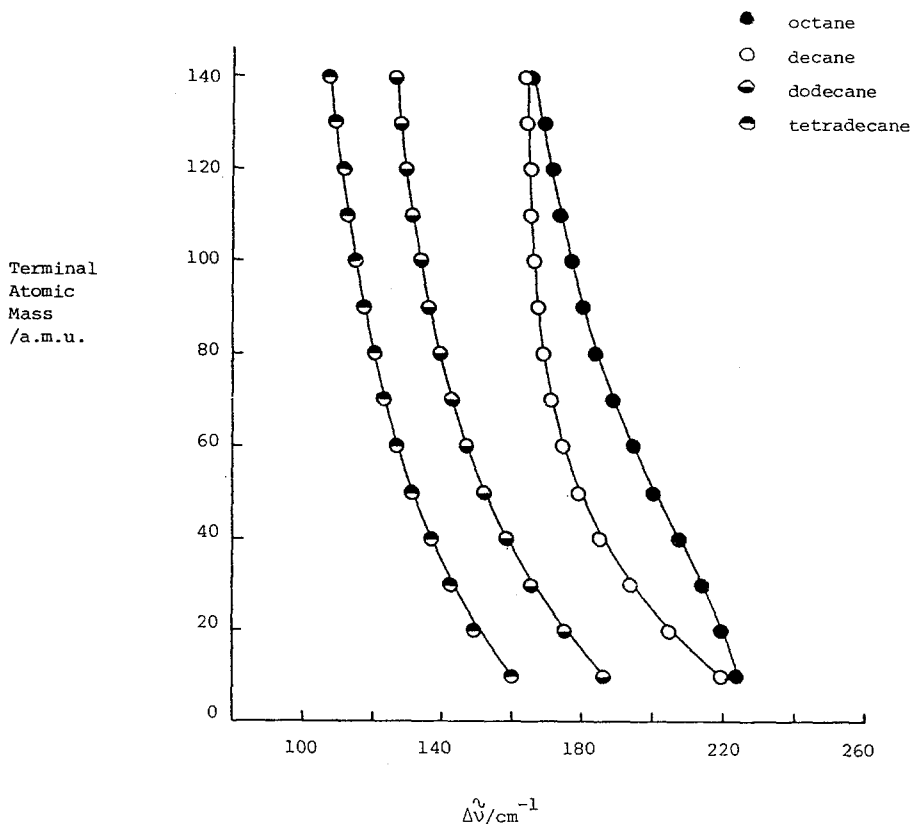


Fig. 2. Mass of end-group substituent plotted against the wavenumber shifts of LAM ($m = 1$) modes for monosubstituted n -alkanes.

shown in Figure 2 for octane, decane, dodecane and tetradecane molecules with end-group substituents of atomic mass between 10 and 140 relative a.m.u. The general trend is as anticipated in that the LAM ($m = 1$) wavenumber decreases as the end-group atomic mass increases. Also, the effect is most marked for tetradecane, which has the lowest wavenumber accordion mode of the molecules studied here.

Examination of the F -matrix eigenvectors for the mono-substituted n -decane model indicates an abnormality in the normal modes; between substituent masses of 50 and 110 a.m.u. the analysis shows that the assigned LAM ($m = 1$) mode has become an asymmetric vibration. At a relative atomic mass of 110 a.m.u. the LAM ($m = 1$) mode again appears but shifted to a low wavenumber curve (Figure 3); the extrapolations of both upper and lower wavenumber curves for monosubstituted n -decane gives a LAM ($m = 1$) limit of 162 cm^{-1} .

It is also instructive to consider the breakdown of the LAM ($m = 1$) mode vibrations into stretching and bending components, each expressed as a percentage contribution to the whole vibrational mode. Graphical plots of stretching and bending contributions to the LAM ($m = 1$) modes against the substituent masses

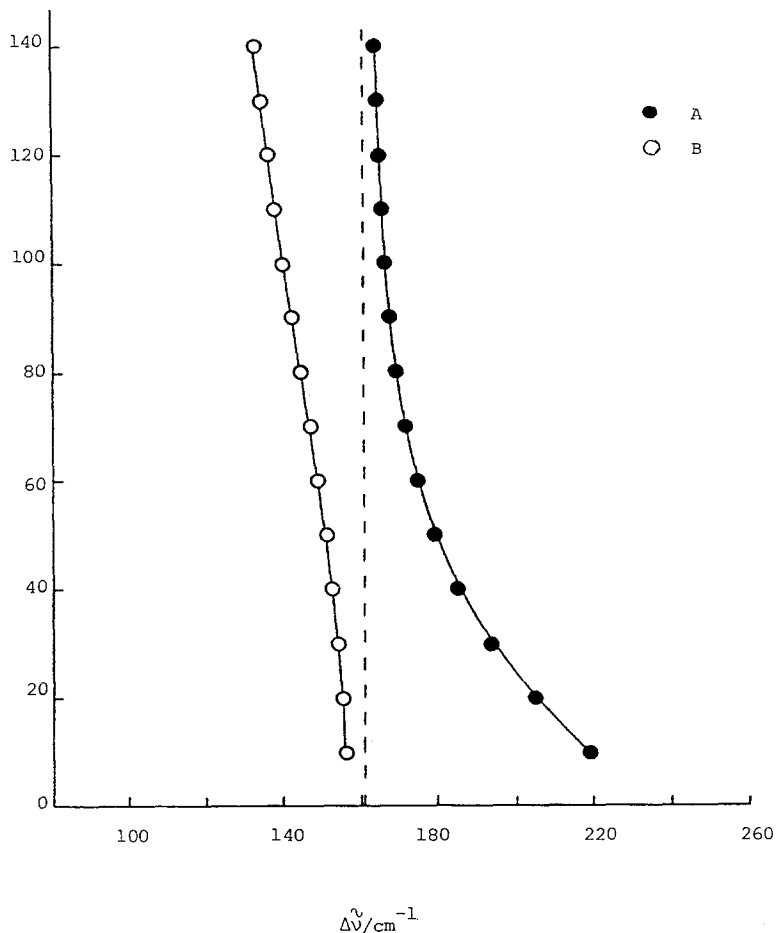


Fig. 3. Mass of end-group substituent plotted against the wavenumber shifts of LAM ($m = 1$) modes for monosubstituted *n*-decane.

for monosubstituted *n*-decane are shown in Figure 4. For low mass substituents a *gerade* type of vibration occurs at higher wavenumbers and stretching and bending motions are evenly distributed along the skeletal backbone. For high mass substituents, however, the LAM ($m = 1$) mode occurs at lower wavenumbers and the vibration becomes *ungerade* in form. When the substituent mass has reached that of the skeletal backbone, a new type of vibrational motion is created and this is again *gerade* in form. An example of the distribution of potential energy between stretching and bending vibrations in the LAM ($m = 1$) mode is shown in Table III for chlorodecane. In Table III, two situations, defined as set A and set B are presented; in both cases the calculated wavenumber of the LAM ($m = 1$) mode decreases as the end-group substituent mass increases but the effect is achieved in two ways. In set A, the percentage contribution of the backbone stretching modes decreases from 23.3 to 12.2% and the bending contribution increases from 39.2 to 94.8% over the mass range 10–140 a.m.u.. However, in set B, the stretching

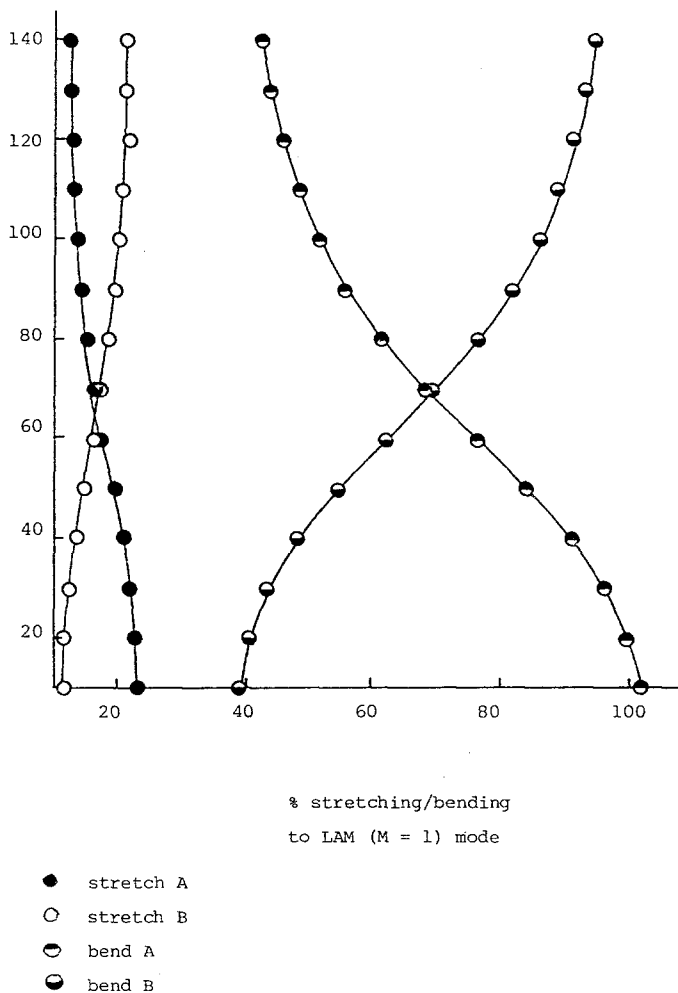


Fig. 4. Percentage contribution of stretching and bending vibrational mode for monosubstituted *n*-decane as a function of the terminal group mass.

contribution increases with mass increase from 11.6 to 21.5% and the bending contribution decreases from 102.1 to 42.7% over the same mass range.

When the stretching force constants for halogen substituents, for example, Cl, Br and I, are now considered along with the existing skeletal force constant analyses described above, it is possible to compare the new, predicted LAM ($m = 1$) wavenumbers for mass substituted alkanes with the experimentally observed wavenumbers (Table IV).

2.2.3. Disubstituted *n*-Alkanes

The next stage of the calculations took the α,ω -distributed *n*-alkanes as models, in which the substitution was effected at both ends of the carbon skeleton. A plot of

Table III. Potential energy distribution between bending and stretching in the LAM ($m = 1$) modes of chlorodecane as function of end-group substituent mass.

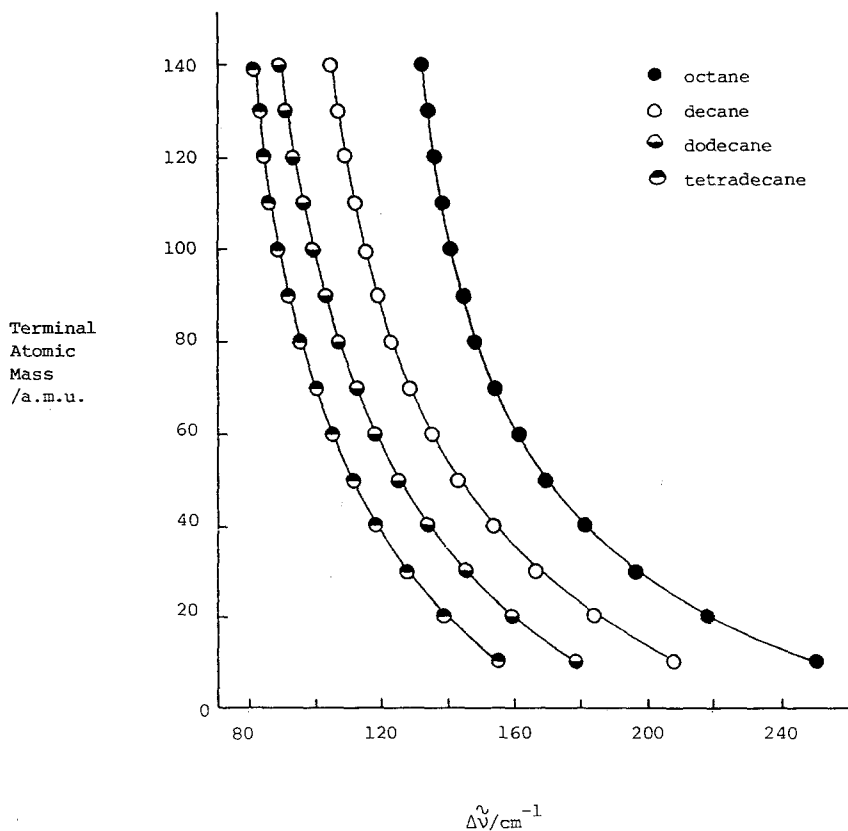
Atomic mass	Wavenumbers $\Delta\bar{\nu}(\text{cm}^{-1})$		Potential Energy Matrix			
	(A)	(B)	Stretch (%)		Bend (%)	
			(A)	(B)	(A)	(B)
10	219.2	156.4	23.3	11.6	39.2	102.1
20	205.0	155.5	22.9	12.0	40.9	100.0
30	193.8	154.4	22.1	12.7	43.8	96.5
40	185.3	152.8	21.0	13.7	48.5	91.3
50	179.1	151.2	19.6	15.0	54.9	84.3
60	174.6	149.3	18.0	16.4	62.5	76.4
70	171.5	147.1	16.6	17.1	70.0	68.5
80	169.3	144.8	15.4	18.8	76.6	61.7
90	167.7	142.6	14.4	19.6	81.9	56.1
100	166.6	140.4	13.7	20.3	86.0	51.9
110	165.8	138.4	13.2	20.7	89.1	48.6
120	165.1	136.6	12.8	21.6	91.5	46.2
130	164.6	134.9	12.5	21.3	93.4	44.2
140	164.2	133.3	12.2	21.5	94.8	42.7

Table IV. Observed [19] and calculated wavenumber shifts (cm^{-1}) for monosubstituted *n*-alkanes with LAM ($m = 1$).

Halogen	Difference $\Delta\bar{\nu}(\text{cm}^{-1})$	Calculated wavenumber (cm^{-1})	Observed wavenumber (cm^{-1})
Chloroparaffin Stretch force constant = 3.420 N m^{-1}			
$\text{C}_8\text{H}_{18}\text{Cl}$	+0.7	221.2	210.5
$\text{C}_{10}\text{H}_{22}\text{Cl}$	+0.4	188.9	188.5
$\text{C}_{12}\text{H}_{26}\text{Cl}$	+1.1	162.4	161.3
$\text{C}_{14}\text{H}_{30}\text{Cl}$	+1.0	140.0	139.0
Bromoparaffin Stretch force constant = 2.90 N m^{-1}			
$\text{C}_8\text{H}_{18}\text{Br}$	+1.0	184.9	183.9
$\text{C}_{10}\text{H}_{22}\text{Br}$	+0.5	168.2	167.7
$\text{C}_{12}\text{H}_{26}\text{Br}$	-0.1	138.9	139.0
$\text{C}_{14}\text{H}_{30}\text{Br}$	-0.6	119.7	120.3
Iodoparaffin Stretch force constant = 2.340 N m^{-1}			
$\text{C}_8\text{H}_{18}\text{I}$	-2.0	167.6	169.6
$\text{C}_{10}\text{H}_{22}\text{I}$	+1.2	153.8	152.6
$\text{C}_{12}\text{H}_{26}\text{I}$	-2.1	126.4	128.5
$\text{C}_{14}\text{H}_{30}\text{I}$	+2.0	107.6	109.6

Table V. Calculated wavenumber shifts for disubstituted *n*-alkanes with LAM ($m = 1$) modes.

Terminal atom atomic mass	Octane	Decane	Dodecane	Tetradecane
	(C ₈ H ₁₈) $\Delta\tilde{\nu}(\text{cm}^{-1})$	(C ₁₀ H ₂₂) $\Delta\tilde{\nu}(\text{cm}^{-1})$	(C ₁₂ H ₂₆) $\Delta\tilde{\nu}(\text{cm}^{-1})$	(C ₁₄ H ₃₀) $\Delta\tilde{\nu}(\text{cm}^{-1})$
10	250.0	208.5	178.1	154.9
20	218.5	184.2	159.0	139.0
30	196.5	166.5	144.8	127.5
40	181.0	153.4	133.8	118.5
50	169.5	143.2	125.1	111.3
60	161.4	135.2	118.1	105.2
70	154.1	128.6	112.2	100.2
80	148.3	123.2	107.3	95.6
90	144.6	119.2	103.1	92.0
100	141.0	114.9	99.4	88.7
110	138.3	111.7	96.0	85.7
120	135.9	108.9	93.4	84.0
130	134.0	106.5	90.7	83.1
140	132.3	104.3	88.7	80.5

Fig. 5. Mass of end-group substituent against wavenumber shifts of LAM ($m = 1$) modes for distributed *n*-alkanes.

the calculated wavenumber shifts for the LAM ($m = 1$) mode against the relative atomic mass of the substituent is shown in Table V and in Figure 5. The LAM ($m = 1$) mode shifts to lower wavenumber with increase in mass of the substituents in a trend which is similar to that observed for the monosubstituted alkanes, except that the effect is greater. However, the wavenumber and substituent mass relationship observed for the disubstituted series is free of the anomalies found for the monosubstituted series.

In a more detailed vibrational analysis of the disubstituted *n*-alkanes the stretching force constants adopted from the monosubstituted series are transferred to the disubstituted models. The differences between observed and calculated wavenumbers for the LAM ($m = 1$) modes are small and indicate that the transferability of force constants and the models chosen are applicable (Table VI). As for the monosubstituted series, the LAM ($m = 1$) wavenumbers increased as the carbon chain length decreased.

The graph shown in Figure 6 of LAM ($m = 1$) mode wavenumbers versus the number of carbon atoms in the skeletal backbone for chloro-, bromo- and iodoalkanes and for the disubstituted analysis provide assistance in the identification of these modes in the Raman spectra [19] of these species and enable unambiguous assignments to be made for these modes for the first time.

Table VI. Observed [19] and calculated wavenumber shifts (cm^{-1}) for disubstituted *n*-alkanes with LAM ($m = 1$) modes.

Dihalogen <i>n</i> -alkanes	Difference $\Delta\bar{\nu}(\text{cm}^{-1})$	Calculated wavenumber (cm^{-1})	Observed wavenumber (cm^{-1})
Dichloroparaffin Stretch force constant = 3.420 N m^{-1}			
Cl C ₈ H ₁₈ Cl	+0.5	187.5	187.0
Cl C ₁₀ H ₂₂ Cl	+1.4	159.8	157.5
Cl C ₁₂ H ₂₆ Cl	+0.8	138.5	137.7
Cl C ₁₄ H ₃₀ Cl	+0.4	122.4	122.0
Dibromoparaffin Stretch force constant = 2.90 N m^{-1}			
Br C ₈ H ₁₈ Br	-0.4	148.6	149.0
Br C ₁₀ H ₂₂ Br	+0.7	124.5	123.8
Br C ₁₂ H ₂₆ Br	-1.2	106.8	108.0
Br C ₁₄ H ₃₀ Br	-0.5	90.5	96.0
Diiodoparaffin Stretch force constant = 2.340 N m^{-1}			
I C ₈ H ₁₈ I	-0.8	133.2	134.0
I C ₁₀ H ₂₂ I	-1.5	107.3	108.8
I C ₁₂ H ₂₆ I	-1.3	90.2	91.5
I C ₁₄ H ₃₀ I	-2.5	80.4	82.5

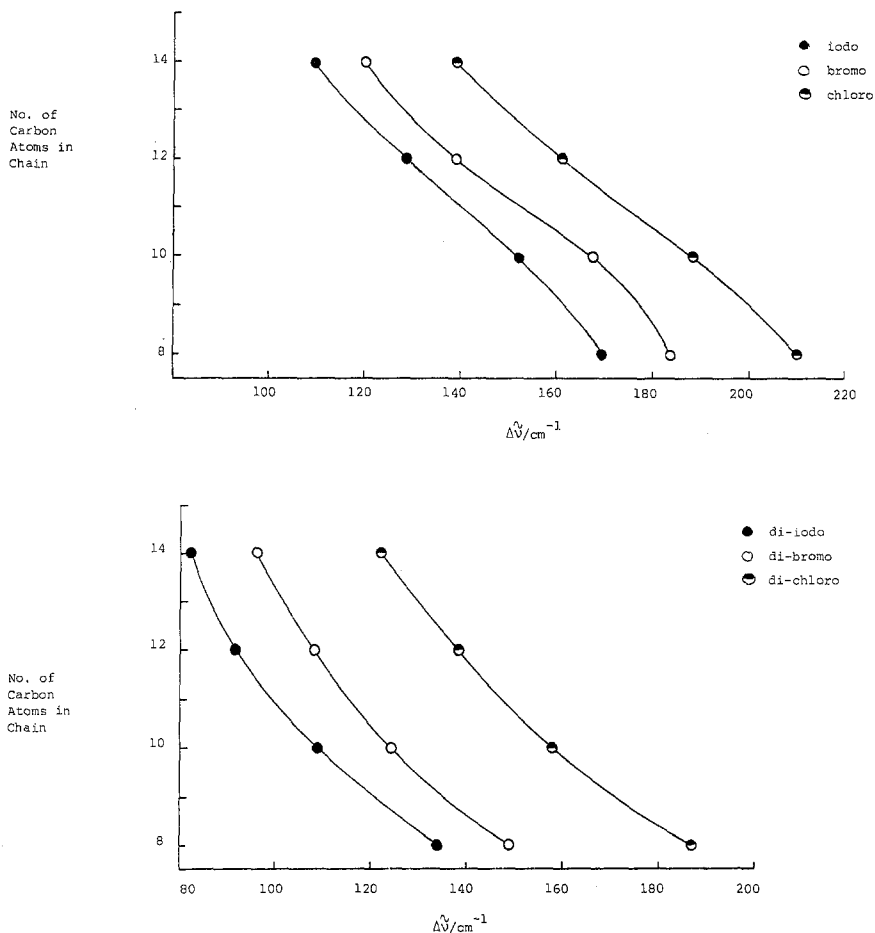


Fig. 6. Carbon chain number vs. wavenumber shifts of LAM ($m = 1$) modes for (a) upper mono- and (b) lower disubstituted n -alkanes.

As a follow-up to these calculations we are currently undertaking an extensive study of the low-frequency Raman spectra of substituted alkanes in urea inclusion compounds. An analysis of the observed LAM-modes of these molecules in their extended planar zig-zag configuration will be reported in a future publication.

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