

The LAM-1 band in the low-frequency Raman spectra of even and odd monosubstituted *n*-alkanes

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Low-frequency Raman spectra of even and odd monosubstituted *n*-alkanes have been recorded. Longitudinal acoustic modes (LAM) arising from whole-chain vibrations are described. Effects of chain length, end-group mass and temperature on the frequencies of these vibrations are discussed. The single-node LAM-1 frequencies are interpreted in terms of the chain model of Minoni and Zerbi, and are correlated with the crystal structures indicated by the high-frequency Raman spectra of the compounds.

Introduction

A number of chain-length dependent bands have been observed in the low-frequency Raman spectra of crystalline *n*-alkanes.^{1,2} Among these bands, the most informative is the whole-molecule one-node longitudinal acoustic mode (LAM-1). For the *n*-alkanes, it has been shown by experiment that the LAM-1 frequency is approximately inversely proportional to the chain length (crystal stem length).^{2–6} Within this degree of approximation, the frequencies of LAM-1 bands can be calculated using the model of an elastic rod with free ends.²

The perturbation of the LAM-1 frequencies by end effects, such as interlayer forces and the inertial masses of end groups, has been investigated theoretically by use of perturbed elastic rod models^{7,8} and crystal chain models.⁹ Experimental studies of these effects based on end-modified *n*-alkanes have been reported by several authors.^{9–15} Previous reports from our laboratories have concerned α,ω -disubstituted *n*-alkanes, and have covered a wide range of end groups.^{14,15}

In this paper we report the low-frequency Raman spectra of several even and odd monosubstituted *n*-alkanes at several temperatures in the range 173–300 K. Two aspects were considered: (i) the effect of chain length in the series of monobromoalkanes H(CH₂)_{*n*}Br where *n* lies in the range 7 to 21 (coded C_{*n*}Br); and (ii) the effect of end mass and forces in the series of monosubstituted dodecanes H(CH₂)₁₂X where X = H, Cl, Br, I, OH and NH₂ (coded C₁₂X).

Experimental

Materials

The monosubstituted *n*-alkanes were obtained from various commercial sources. All the materials were used as received.

Raman spectroscopy

Raman scattering at 90° to the incident beam was recorded by means of a Spex Ramalog spectrometer fitted with a 1403 double monochromator, and with a third (1442U) monochromator operated in scanning mode. The light source was a Coherent Innova 90 argon-ion laser operated at 514.5 nm and 300 mW. Typical operating conditions for low-frequency spectra (<250 cm⁻¹) were: bandwidth 1.0 cm⁻¹, scanning

increment 0.05 cm⁻¹, integration time 6 s. For high-frequency spectra (<1800 cm⁻¹) the conditions were: bandwidth 3.0 cm⁻¹, scanning increment 0.5 cm⁻¹, integration time 4 s. The low-frequency scale was calibrated by reference to the 9.6 cm⁻¹ and 14.9 cm⁻¹ bands in the spectrum of L-cystine.

Samples were enclosed in a capillary and held at a constant temperature (± 1 K) in the range 173–300 K by means of a Harney–Miller cell (Spex Industries Inc). The intensity of a Raman band was observed over a period of time to ensure equilibration of the sample at the given temperature. Generally, high-frequency spectra were recorded before and immediately after the low-frequency spectra, in order to confirm that samples were unchanged by exposure to the laser beam.

Spectra were recorded several times and band frequencies were obtained as averages of the observations. The uncertainty in frequency was estimated to be ± 0.5 cm⁻¹ for the low-frequency spectral region and ± 1 cm⁻¹ for the high-frequency region.

Results and discussion

Effect of chain length: C_{*n*}Br series

Representative low-frequency spectra of even and odd members of the series (samples at 173 K) are illustrated in Fig. 1 and 2. Band frequencies measured for samples at 173 K are listed in Table 1. Bands were assigned to LAM-1 by comparison of their frequencies with those in the well documented spectra of the *n*-alkanes;^{1–4} see Table 1 and the discussion below.

Comparison of the LAM-1 frequencies in Table 1 with those reported for *n*-alkanes¹ and α,ω -dibromoalkanes,^{14,15} is made in Fig. 3. The curves included in this figure were calculated using the linear-crystal model of Minoni and Zerbi,⁹ *i.e.* the layer crystal was represented in one-dimensional form, with chain and end groups represented as point masses with appropriate interactions between them. In the calculations, as in previous work, masses of $m_c = 23.292 \times 10^{-27}$ kg and $m_e = 24.963 \times 10^{-27}$ kg were assigned to chain (CH₂) and end (CH₂Br) groups, the force between chain groups was set to $f_c = 420$ N m⁻¹, and the force between chain ends was set to $f_e = 5$ N m⁻¹, this last being typical for a van der Waals interaction. The necessary equations have been given else-

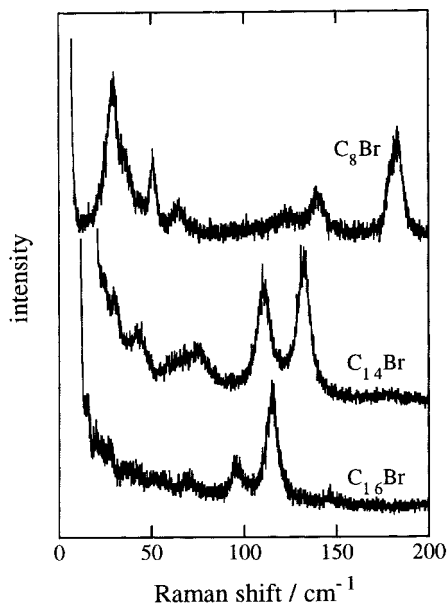


Fig. 1 Low-frequency Raman spectra of selected even monobromoalkanes ($T = 173$ K).

where.^{9,16} As seen in Fig. 3, the curves calculated for the three series fit the corresponding sets of experimental data well enough to justify the common assignment to the LAM-1.

Deviations from the calculated curves arise in a number of ways: (i) For the unsubstituted alkanes, the fit to the calculated curve is satisfactory, with the frequencies of the even members fitting well, while those of the odd members lie slightly below. (ii) A similar result holds for the dibromoalkanes, though in this case, with the exception of $C_{23}Br$, the frequencies of the odd members of the series lie well below the calculated curve. (iii) For the monobromoalkanes, there is satisfactory agreement between experiment and calculation only for $n \geq 14$. For these longer chains there is a small odd-even effect, similar in magnitude to that reported for the unsubstituted alkanes, but with the odd members of the series best fitting the calculation rather than the even members. At shorter chain lengths ($n < 14$) the reversed odd-even effect is

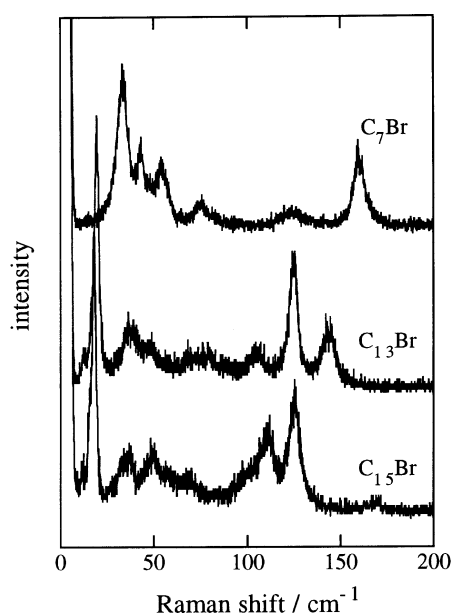


Fig. 2 Low-frequency Raman spectra of selected odd monobromoalkanes ($T = 173$ K).

Table 1 Low-frequency bands in the Raman spectra of even and odd monobromoalkanes at 173 K

n	LAM-1 frequency/cm ⁻¹	Other bands frequency/cm ⁻¹
7	222.7	14.2, 32.3, 42.7, 53.1, 74.2, 121.9, 160.2
8	183.4	29.2, 35.8, 50.2, 63.4, 123.9, 140.2
9	172.5	21.2, 29.3, 35.7, 46.7, 61.2, 102.2, 121.2
10	151.3	11.3, 23.7, 29.9, 33.7, 46.4, 102.2, 202.5
11	145.2	13, 20.3, 39.1, 47.5, 83.2, 93.2, 105.9, 178
12	127.5	6.6, 10.9, 26.5, 44.4, 73.2, 85, 157.1
13	124.0	12.3, 18.8, 36.3, 48.4, 67.3, 76.9, 104.8, 143.2, 205.6
14	131.9	12.1, 24.8, 30, 43.5, 64.2, 74.1, 110.1, 176.5
15	125.5	11.2, 17.6, 34.9, 49.1, 55.4, 68.6, 97.8, 110.7, 169.7
16	114.0	9.8, 25.6, 35.3, 64.5, 95.3
17	112.4	16.9, 35.2, 47.1, 103.3
18	106.4	13.9, 49.6, 72.1, 99.1, 131.3
20	96.4	14.4, 38.3, 47.9
21	95.8	14.3, 40.4, 85.9

most apparent, and all experimental frequencies fall below the calculated curve. Calculations based on the chosen value of $f_c = 420 \text{ N m}^{-1}$ do not reproduce the experimental values, even if f_e is lowered to zero.

The cause of this difference in the chain-length dependence of the LAM-1 frequency presumably lies in differences in crystal structure. This is well documented for the n -alkanes, where the even members of the series have a triclinic unit cell in which chain axes are tilted with respect to the end-group plane, while the odd members have an orthorhombic unit cell in which chain axes are normal to the end-group plane,^{1,17} and small differences in f_c and f_e are to be expected on this account. Unfortunately, to the best of our knowledge, crystal structures based on X-ray diffraction have not been reported

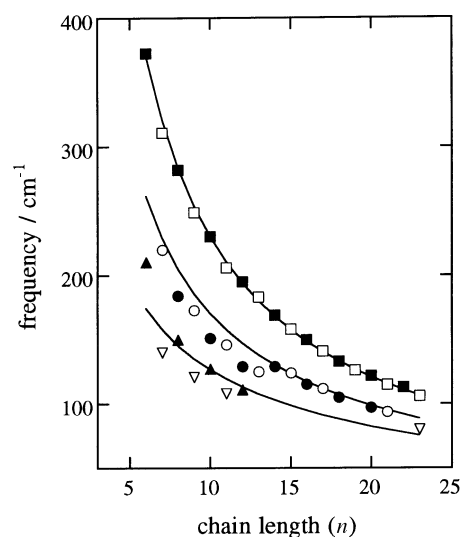


Fig. 3 Chain-length dependence of the LAM-1 frequency ($T = 173$ K) for (■, □) n -alkanes, (●, ○) monobromoalkanes and (▲, ▼) dibromoalkanes. Even members of the series are indicated by filled symbols and odd members by open symbols. The curves are calculated using Minoni and Zerbi's linear-crystal model,⁹ as described in the text.

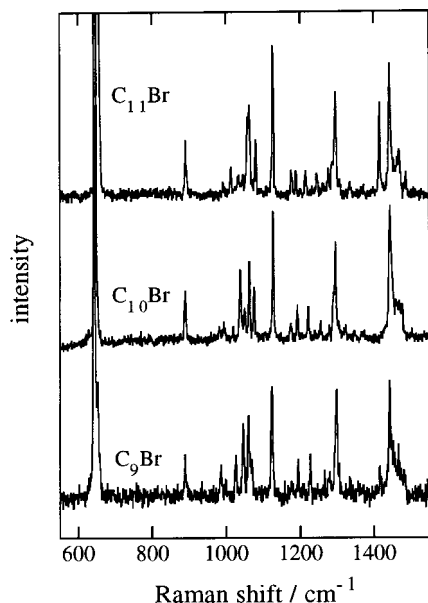


Fig. 4 High-frequency Raman spectra of selected monobromoalkanes ($T = 173$ K). Features of interest (see text) are the band at 1418 cm^{-1} in the spectra of samples C_9Br (weak) and C_{11}Br (strong) and the band at 654 cm^{-1} in the spectrum of sample C_9Br (shoulder). Neither band is found in the spectrum of sample C_{10}Br .

for the monobromoalkanes and dibromoalkanes considered here.

Differences in high-frequency Raman spectra can give information on crystal structure. For example, as described and reviewed by Boerio and Koenig,¹⁸ in the spectra of *n*-alkanes splitting of the methylene bending band near 1440 cm^{-1} provides an indicator. This crystal-field effect is seen in the spectra of alkanes with orthorhombic or monoclinic unit cells, but not in the spectra of those with triclinic and hexagonal unit cells.

The high-frequency spectra shown in Fig. 4 (samples C_9Br , C_{10}Br and C_{11}Br at 173 K) illustrate similar effects for the monobromoalkanes. Attention is drawn to two features highlighted in Fig. 5. (i) In the methylene-bending region [see Fig. 5(a)] all three spectra contain a strong band at 1444 cm^{-1} , but a band at 1418 cm^{-1} is found only in the spectra of C_{11}Br and C_9Br (weak). (ii) In the CBr-stretch region [see Fig. 5(b)], the spectrum of C_{11}Br contains a band at 654 cm^{-1} , the spectrum of C_{10}Br contains a band at 644 cm^{-1} , and the spectrum of C_9Br contains both bands, that at 654 cm^{-1} being a shoulder to the major peak.

Table 2 lists results obtained over the whole series of monobromoalkanes. The spectrum of sample C_{16}Br , like that of C_9Br , contained all four bands of interest, with the 1418 cm^{-1} and 654 cm^{-1} bands being by far the weaker. It is assumed

Table 2 Methylene-bending Raman bands and LAM-1 differences^a for even and odd monobromoalkanes at 173 K

Chain length (<i>n</i>)	Bands/ cm^{-1}	$\Delta\nu/\text{cm}^{-1}$ (LAM-1)	Possible structure
8, 10, 12	1444 and 644	ca. -20	triclinic
14	1444 and 644	zero	?
9, 11, 13	1444, 1418 and 654	ca. -10	orthorhombic
16, 18, 20	1444, 1418 and 654	-2	monoclinic
15, 17, 19, 21	1444, 1418 and 654	zero	orthorhombic
7	1444, 1418 and 644	-5	?

^a $\Delta\nu$ = difference between calculated and observed LAM-1 frequencies (see Fig. 3).

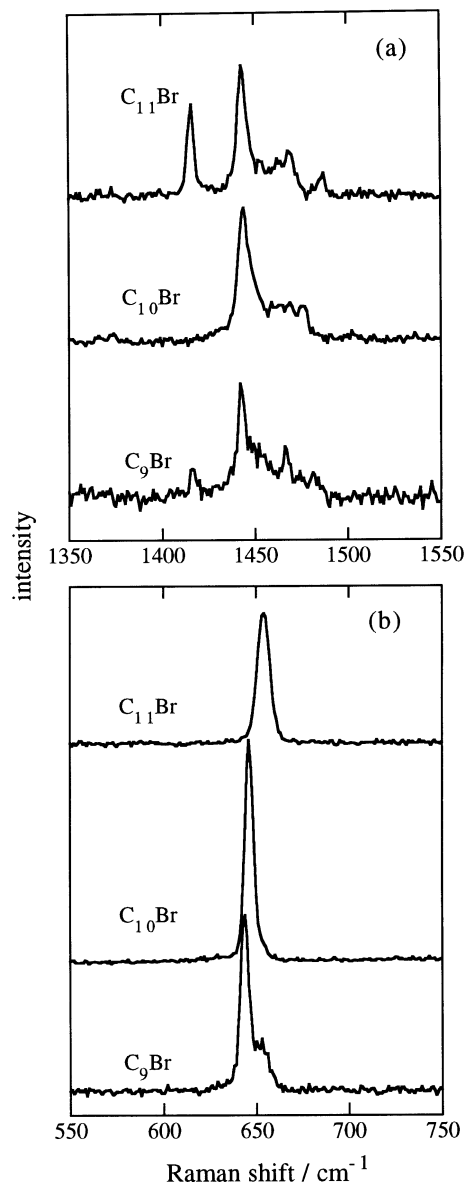


Fig. 5 High-frequency Raman spectra of selected monobromoalkanes ($T = 173$ K). Expansion of (a) the methylene-bending region and (b) the CBr-stretching region.

that these samples formed mixtures of two crystal types. Based on investigations of bromoalkanes in the liquid state, the band at 644 cm^{-1} has been assigned to stretching of the C—Br bond in the *trans* rotational state, that for the *gauche* state being found at 563 cm^{-1} .¹⁹ The relatively small variation in frequency ($644 \rightarrow 654\text{ cm}^{-1}$) found in the crystalline samples is attributed to variation in the crystal-field acting on the *trans* C—Br bond. It is assumed that the splitting giving rise to the 1418 cm^{-1} band arises from a related crystal-field effect. Overall, the results summarised in Table 2, *i.e.* the correspondence between the two effects in the high-frequency spectra and the sub-classification based on the difference in LAM-1 frequency ($\Delta\nu$) between calculation and observation (see Fig. 3), allow the tentative assignment to crystal structures shown in the last column of Table 2, which is largely based on analogy with the known structures of the *n*-alkanes.¹⁷ A transition from triclinic to monoclinic unit cell is found in the series of even *n*-alkanes at $\text{C}_{24}/\text{C}_{26}$. Possibly a similar transition occurs in the series of even monobromoalkanes, but at $\text{C}_{14}/\text{C}_{16}$, as assumed in Table 2.

Since the tentative structural assignments made (Table 2) mirror those established for the unsubstituted *n*-alkanes, they

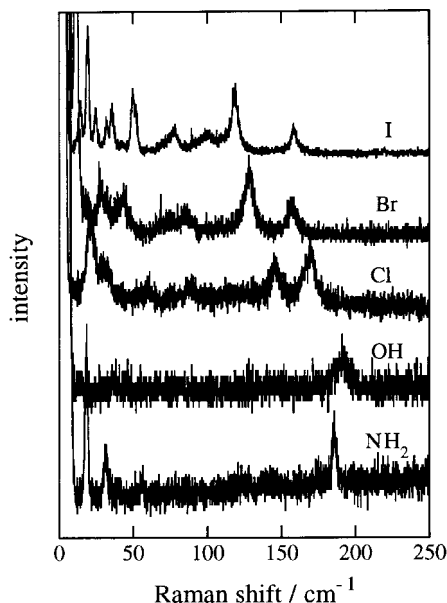


Fig. 6 Low-frequency Raman spectra of the monosubstituted dodecanes ($T = 173$ K).

do not explain the reversed even-odd effect found for the LA-1 frequencies of the monobromoalkanes compared with those of the dibromo- or unsubstituted alkanes.

Effect of end-group: $C_{12}X$ series

Low-frequency spectra obtained for the five $C_{12}X$ derivatives at 173 K are illustrated in Fig. 6. Band frequencies measured for the samples at 173 K are listed in Table 3. Comparison with results reported previously for unsubstituted¹ and α,ω -disubstituted alkanes^{14,15} allow assignment to LAM-1, as indicated in Table 3.

High-frequency spectra (not illustrated) in the methylene-bending region showed a band at 1418 cm^{-1} for $X = \text{OH}$, NH_2 and I , but not for $X = \text{H}$, Cl and Br . Following the argument presented above, this result can be used to distinguish crystals with triclinic unit cells ($C_{12}\text{H}$, $C_{12}\text{Cl}$, $C_{12}\text{Br}$) from those with orthorhombic unit cells ($C_{12}\text{OH}$, $C_{12}\text{NH}_2$, $C_{12}\text{I}$). Some difference in LAM-1 frequency might be expected on this account, but the major perturbing effect is the mass of the end group. This is illustrated in Fig. 7, where the LAM-1 frequencies of the $C_{12}X$ samples (from Table 2), together with that of dodecane itself,¹ are plotted against end-group mass. For this purpose, the end groups are systematically identified as CH_3 , CH_2NH_2 , CH_2OH etc.

Fig. 7 also shows LAM-1 frequencies reported for disubstituted C_{12} alkanes,^{14,15} and frequencies calculated for both monosubstituted and disubstituted *via* Minoni and Zerbi's linear-crystal model. As for the $C_n\text{Br}$ series discussed above, the parameters used were $m_c = 23.292 \times 10^{-27}$ kg,

Table 3 Low-frequency bands in the Raman spectra of monosubstituted n -alkanes, $\text{H}(\text{CH}_2)_{12}\text{X}$, at 173 K

X	LAM-1 frequency/ cm^{-1}	Other bands frequency/ cm^{-1}
NH_2	185.9	17.7, 31, 55.1, 125.7, 142.7, 174.1
OH	191.0	22.1, 31.1, 100.3, 183.0
Cl	168.6	20.2, 30.1, 59.9, 75.5, 89.5, 144.3
Br	127.5	6.6, 10.9, 26.5, 44.4, 73.2, 85.0, 157.1
I	118.3	13.2, 19.2, 23.6, 31.3, 35.6, 49.9, 50.9, 77.7, 99.1, 157.7

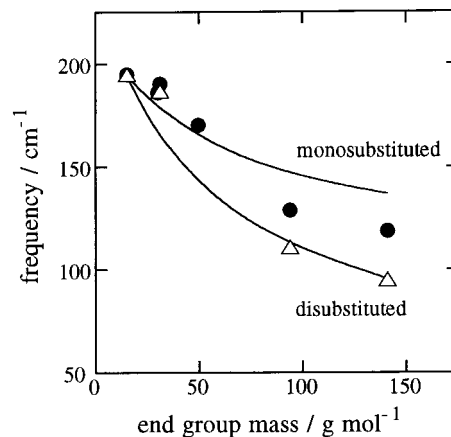


Fig. 7 Dependence of LAM-1 frequency ($T = 173$ K) on end-group mass: (●) monosubstituted alkanes and (△) disubstituted alkanes. The curves are calculated using Minoni and Zerbi's linear-crystal model,⁹ as described in the text.

$f_c = 420\text{ N m}^{-1}$ and $f_e = 5\text{ N m}^{-1}$, but with m_e in the range 24.963×10^{-27} to 233.989×10^{-27} kg according to end group. The fit is satisfactory for the disubstituted alkanes but poor for the monosubstituted alkanes. However, the approximate correspondence between experiment and theory allows common assignment of all the bands to LAM-1.

The poor fit of the data point for $C_{12}\text{Br}$ to the curve calculated with the chosen parameters has been noted above ($C_n\text{Br}$ series, see Fig. 3). It is apparent that $C_{12}\text{I}$ behaves in a similar way (see Fig. 7). At first sight, this might be taken as evidence of a similar crystal structure for these closely related compounds. However, as noted above, the high-frequency spectrum of $C_{12}\text{I}$ shows splitting of the methylene bending mode, while that of $C_{12}\text{Br}$ shows no splitting, and this indicates different structures.

The data points for $C_{12}\text{OH}$ and $C_{12}\text{NH}_2$ lie together but slightly above the curve, by $\Delta\nu \approx 11\text{ cm}^{-1}$ ($C_{12}\text{OH}$) or $\Delta\nu \approx 7\text{ cm}^{-1}$ ($C_{12}\text{NH}_2$). This increase can be compared to $\Delta\nu \approx 22\text{ cm}^{-1}$ for dihydroxydodecane, *i.e.* about twice the effect for H bonds at both ends. The increase in measured LAM-1 frequency can be reproduced in calculations by allowing for formation of hydrogen bonds. We have shown this to be so in our previous work on dihydroxyalkanes.^{14,15} Considering crystalline $C_{12}\text{OH}$ and $C_{12}\text{NH}_2$, Minoni and Zerbi would model them with a linear crystal composed of H-bonded

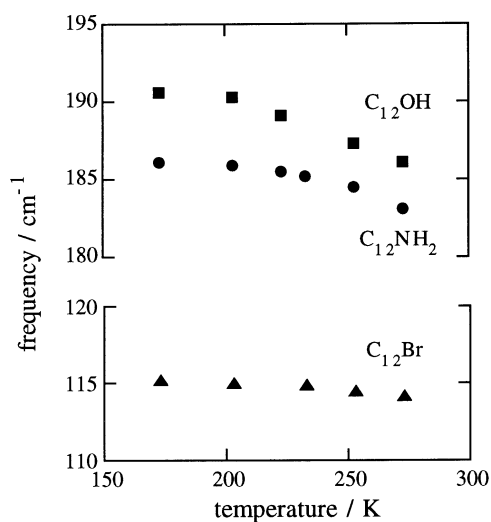


Fig. 8 Temperature dependence of the LAM-1 frequency for the monosubstituted alkanes indicated.

dimers. The necessary equations have been published.²⁰ Calculations based on the parameters listed above, retaining $f_e = 5 \text{ N m}^{-1}$ for the end force between dimers but including $f_h = 19 \text{ N m}^{-1}$ for the internal H bond of the dimer,^{14,15} gave values of LAM-1 frequency of 190.2 cm^{-1} for C_{12}OH and 186.5 cm^{-1} for C_{12}NH_2 , *i.e.* in good agreement with experiment.

Effect of temperature

The LAM-1 frequency was measured at intervals in the temperature range 173–273 K. For most samples (C_nBr , C_nCl , C_nI and the *n*-alkanes themselves) the frequency varied only by 1 cm^{-1} or so, see the results for C_{12}Br in Fig. 8. The exceptions were samples C_{12}OH and C_{12}NH_2 which formed hydrogen-bonded dimers. As seen in Fig. 8, the LAM-1 frequencies of these samples decreased by 3–4 cm^{-1} on raising the temperature from 173 to 273 K, consistent with weaker H bonds at higher temperatures. A similar value of $\Delta\nu$ has been found for alkane diols¹⁴ and stearyl alcohol,¹² while a slightly smaller value has been obtained for α -methyl, ω -hydroxy-oligo(oxyethylene)s.²⁰

Conclusions

As might be expected, considering the damping effect on longitudinal vibrational frequency of a heavy end mass, the LAM-1 frequencies of the monobromoalkanes lie between those of the *n*-alkanes and the dibromoalkanes. In all three series there is an even–odd effect, with the LAM-1 frequencies of the odd members being low for the symmetrical chains, but high for the unsymmetrical chain. High-frequency Raman spectra indicate the same differences in crystal structure as those established for the *n*-alkanes, *i.e.* even members having triclinic or monoclinic unit cells, odd members having orthorhombic unit cells. The specific cause of the reversal in even–odd behaviour remains unexplained.

Considering the series C_{12}X , one effect of changing the end group is to change the crystal structure: triclinic for $\text{X} = \text{H}$, Cl and Br , orthorhombic for $\text{X} = \text{OH}$, NH_2 and I . However, the major perturbing effect on LAM-1 frequency is the damping effect of the mass of the end group, though this is opposed by an increase in end force when hydrogen bonding is possible. For both series of compounds (C_nBr and C_{12}X), assignment of bands to LAM-1 is made possible by calculation of the longitudinal vibrational frequency *via* a simplified model of the

chains in their crystal state: in the present case, the linear crystal model of Minoni and Zerbi.

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