

# A Raman Spectroscopic Study of Molecular Interaction in Long-chain Primary Amines Systems

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The N—H, C—H and C—C stretching regions at  $3100\text{--}3400\text{ cm}^{-1}$ ,  $2800\text{--}3000\text{ cm}^{-1}$  and  $1000\text{--}1150\text{ cm}^{-1}$ , respectively, and the low-frequency accordion-like vibration region, have been investigated by Raman spectroscopy for the octyl-, nonyl-, dodecyl-, tetradecyl- and hexadecyl-normal primary amines series, at different temperatures and for different physical states. The spectra were interpreted in terms of structural changes, particularly of the conformations of the paraffin chains, the chain length and the physical state. The changes in the N—H region were associated mainly with molecular association, whereas the changes in the other spectral regions studied were associated mainly with the molecular packing of the chains.

## INTRODUCTION

Raman scattering has been increasingly used to investigate several aspects of the structural and dynamical conformation in hydrophobic regions of lipid systems.<sup>(1-4)</sup> However, so far, there has been no satisfactory study of an important class of simple lipids, the normal long-chain aliphatic amines.

In the present work, we have used Raman spectroscopy to study molecular interaction and molecular packing in octyl-, nonyl-, dodecyl-, tetradecyl-, and hexadecyl-amines.

## EXPERIMENTAL

The samples used in this study were of purum grade obtained from Aldrich-Europe and were used without further purification. Mixtures of *n*-octylamine with water were prepared from measured amounts of the amine and double distilled water in sealed glass cells which were allowed to phase equilibrate for two days in a temperature bath at about  $90^\circ\text{C}$ .

The measurements of the Raman spectra were made using a Varian Cary-82 Raman Spectrophotometer operating with a spectral slitwidth of  $3\text{--}4\text{ cm}^{-1}$  (constant over the Stokes displacement  $0\text{--}3500\text{ cm}^{-1}$ ). The light source was a Spectra-Physics Model 164 argon-ion laser operating at  $514.5\text{ nm}$ . Typically the laser was operated to give about  $300\text{--}500\text{ mW}$  power at the sample.

The samples were contained in  $1\text{ mm}$  melting point capillaries and the scattered light was collected at  $90^\circ$  to the incoming laser light. The accuracy in the reported frequencies is estimated to be  $\pm 2\text{ cm}^{-1}$ .

Sample temperatures above room temperature were achieved using a temperature bath design based on an insulated hollow aluminium jacket fitted with a ITT Vulcan heater in the solid block. A temperature accuracy better than  $\pm 2^\circ\text{C}$  was obtained for these recordings. Sample temperatures below room temperature were achieved using an Oxford Instruments

CF 100 cryostat working with a precision temperature controller EA 2349, giving a temperature accuracy of  $\pm 0.5^\circ\text{C}$ .

In the evaluation of peak intensities, Raman band heights were measured as the spectral heights above a background drawn as a straight line between minima in the spectra which is the combination of broad band luminescence with the Raman spectrum of the sample. The experimental error in these intensity measurements is of the order of 10%.

## RESULTS AND INTERPRETATION

### The N—H stretch region

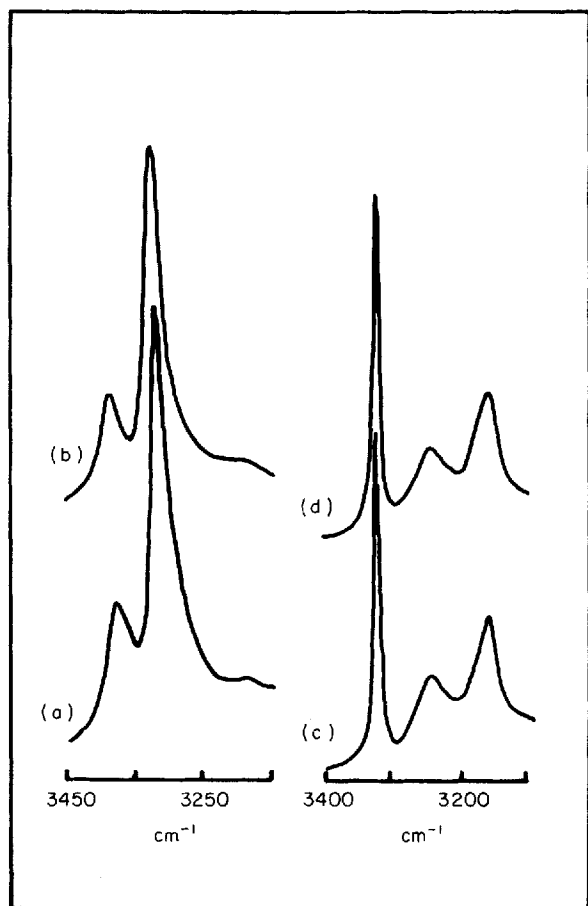
The main features of the Raman spectra of the long-chain primary amines, in the  $3100\text{--}3450\text{ cm}^{-1}$  region, for the pure liquid, the aqueous isotropic solution and the solid, are shown in Fig. 1.

In the liquid the bands at  $3380\text{ cm}^{-1}$  correspond, respectively, to the  $\text{NH}_2$  antisymmetric  $\nu_{\text{as}}$  and symmetric  $\nu_{\text{s}}$  stretchings of the free molecules;<sup>3,6</sup> the weak band at about  $3180\text{ cm}^{-1}$  is probably due to the first overtone of the  $\delta\text{NH}_2$  vibration enhanced by a Fermi resonance interaction with the  $\text{NH}_2$  symmetric stretching.<sup>7</sup>

There is no significant change in the frequency of the  $\text{NH}_2$  symmetric stretching vibration either on going from the liquid to the solid or on increasing the amine chain length.

In the solid state, the band at  $3380\text{ cm}^{-1}$  disappears, a new band at  $3250\text{ cm}^{-1}$  is observed and the band at  $3180\text{ cm}^{-1}$  is increased and shifted about  $20\text{ cm}^{-1}$  to a lower frequency.

For solid ethylamine, Perchard and co-workers<sup>7</sup> have reported a fourth band at about  $3233\text{ cm}^{-1}$ . The overlapping and the non-symmetric character of the  $3250\text{ cm}^{-1}$  and  $3162\text{ cm}^{-1}$  bands could explain the fact that it is not observed in the amines studied. These observations can probably be accounted for by the

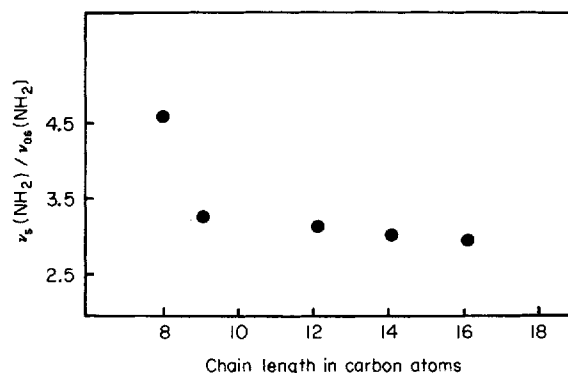


**Figure 1.** The N—H stretching vibration region in the Raman spectra of (a) liquid nonylamine at 295 K; (b) isotropic solution of octylamine–water (40.0% (w/w) amine at 295 K); (c) solid octylamine at 257 K; (d) solid dodecylamine at 295 K.

existence of two kinds of hydrogen-bonding in the solid<sup>6,8</sup> and a Fermi resonance interaction with the level  $2\delta\text{NH}_2$ .

In isotropic solutions of octylamine–water systems<sup>9</sup> there is also no significant change in the frequency of the  $3323\text{ cm}^{-1}$  band; however, on going from the isotropic solutions to the hydrated amine in a mesomorphic state this band is shifted to  $\sim 3310\text{ cm}^{-1}$ . This kind of shift has been observed for the transition from the anhydrous crystalline tetradecylamine to the gel-phase<sup>10</sup> and could be due to the change of hydrogen bond from  $\text{NH}\cdots\text{N}$  to the stronger  $\text{NH}\cdots\text{O}$ .

It is not possible to compare the relative intensities of the  $\nu_s(\text{NH}_2)$  and  $\nu_{as}(\text{NH}_2)$  bands on going from the liquid to the solid states since the  $\nu_{as}(\text{NH}_2)$  band does not appear in the solid; in the liquid, however, as shown in Fig. 2, the relative intensity  $I_{3323}(\text{cm}^{-1})/I_{3380}(\text{cm}^{-1})$  decreases drastically from octylamine to nonylamine, but is almost constant for nonyl-, dodecyl- and hexadecylamines. In the octylamine–water systems, the relative intensity decreases from 4.6 (in the pure liquid) to 3.6 (for the isotropic solution) and to 1.9 (for the hydrated amine in a liquid crystalline state). It seems reasonable to associate such a decrease for these systems with the breaking effect of water on the association of the hydrocarbon chains. On this we can interpret the behaviour of the intensity ratio  $I_{3323}(\text{cm}^{-1})/I_{3380}(\text{cm}^{-1})$  in the pure compounds with the increasing chain length,



**Figure 2.** The intensity of the  $\nu_s(\text{NH}_2)$  band relative to the intensity of the  $\nu_{as}(\text{NH}_2)$  band in the Raman spectra of liquid primary amines as a function of chain length.

as indicating that some kind of boundary behaviour exists on going from the eight-to-nine atom hydrocarbon chain. An intermolecular effect, namely, chain folding, occurs for  $n > 8$ , with important changes in the *trans/gauche* conformational distribution and the molecular environment of each chain.

### The C—H stretch region

The relative intensity of the Raman bands in the C—H stretching region has been widely used as a structural probe, providing information about the ordering and environment of the hydrocarbon moiety in lipid and related systems (see Ref. 13 and references therein). However, the information obtained by different authors is not always consistent because of different assignments of the Raman lines in that region. Peticolas and co-workers<sup>21</sup> initially assigned the  $2885\text{ cm}^{-1}$  line of phosphatidylcholine to the vibration of the terminal  $\text{CH}_3$  group and attributed the decrease in the relative intensity  $I_{2885}(\text{cm}^{-1})/I_{2850}(\text{cm}^{-1})$  in its molten state, to the increased mobility of the  $\text{CH}_3$  group. Later they revised such an assignment.<sup>24</sup> Larsson *et al.*<sup>2,10,14,15</sup> as well as Faiman and Long<sup>3</sup> and Kalyanasundaram and Thomas<sup>11</sup> adopted the former assignment. Spiker and Levin<sup>12</sup> assigned the  $2885\text{ cm}^{-1}$  line to the  $\text{CH}_2$  antisymmetric stretching vibration. Others have used the Raman intensity of the C—H bands simply as a structural probe, irrespective of the assignments<sup>22,23</sup>. More recently, Snyder and co-workers,<sup>19</sup> Okabayashi *et al.*<sup>13</sup> and Hill and co-workers<sup>20</sup> have re-examined the assignments in the complex and congested  $2800\text{--}3000\text{ cm}^{-1}$  Raman spectral region, proposing a new interpretation for the C—H bands.

According to Snyder and co-workers,<sup>19</sup> the bands at about  $2850\text{ cm}^{-1}$  and  $2880\text{ cm}^{-1}$  can be assigned to the symmetric and antisymmetric stretching vibrations, respectively, of the methylene groups,  $\nu_s(\text{CH}_2)$  and  $\nu_{as}(\text{CH}_2)$ . The antisymmetric mode is forbidden by symmetry from entering into Fermi resonance interaction and is therefore insensitive to environmental changes of the extended chain, whereas there is a strong Fermi resonance interaction between the symmetric stretching and appropriate binary combinations involving the methylene bending modes. Most of the complexity of the C—H Raman spectral region is due to this Fermi resonance interaction which affects the band structure

in dramatic ways, although it is not expected to affect significantly the total integrated intensity of the fundamentals themselves. The Raman line centred around  $2925\text{ cm}^{-1}$ , whose intensity has been correlated with the polar environment character of the chains<sup>15</sup> probably originates from that type of Fermi resonance.

If methyl groups are present, the line at about  $2873\text{ cm}^{-1}$  (usually a weak shoulder) is assigned to their C—H symmetric stretching vibrations,  $\nu_s(\text{CH}_3)$ , and the bands at  $2964\text{ cm}^{-1}$  and  $2952\text{ cm}^{-1}$  are assigned to the in-skeletal and out-of-skeletal plane C—H antisymmetric stretching vibrations,  $\nu_{as}(\text{CH}_3)$ , respectively, of the methyl groups.<sup>19</sup>

Although the total intensity of the methylene Raman fundamentals is not significantly affected by the effects of the Fermi resonance interactions, being insensitive to environmental changes of the extended chain, the value of the peak height ratio  $I_{\nu_{as}(\text{CH}_2)}/I_{\nu_s(\text{CH}_2)}$  is found to depend on the lateral packing of the extended chains and on conformational disorder. It has been used with success as an order/disorder parameter.<sup>4,14,15</sup>

In the case of the extended chain, the intensity of the  $\sim 2880\text{ cm}^{-1}$  line consists of approximately equal contributions from  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$ ; in this case, the dependence of the peak height ratio  $I_{2880}(\text{cm}^{-1})/I_{2850}(\text{cm}^{-1})$  on packing is a result of changes in the contribution of  $\nu_s(\text{CH}_2)$  while  $\nu_{as}(\text{CH}_2)$  remains nearly constant.

In the liquid state where there is conformational disorder, the  $\sim 2880\text{ cm}^{-1}$  line primarily consists of  $\nu_{as}(\text{CH}_2)$  with only a small contribution from  $\nu_s(\text{CH}_2)$ .

Evidence has been given that the value of the peak height ratio  $I_{2925}(\text{cm}^{-1})/I_{2850}(\text{cm}^{-1})$  ratio depends

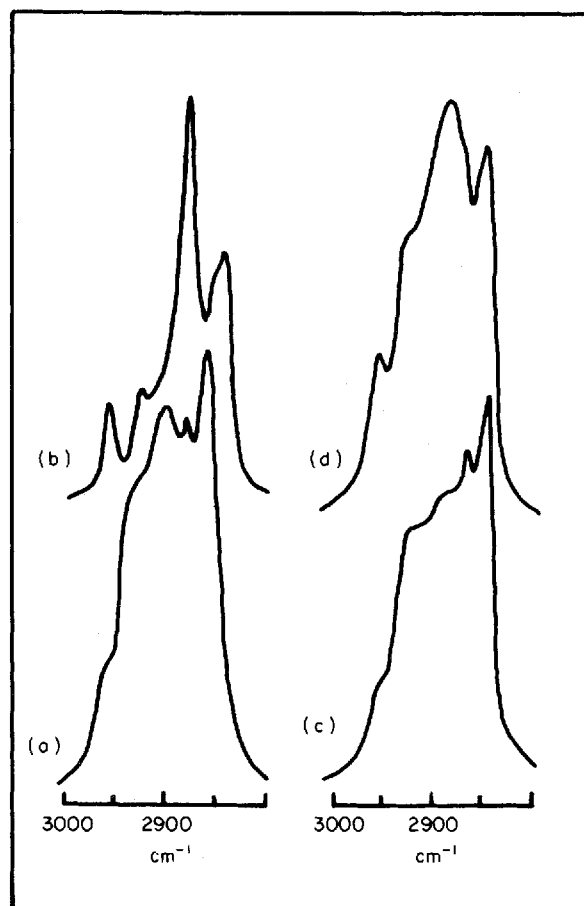


Figure 3. The C—H stretching vibration region in the Raman spectra of (a) liquid octylamine at 295 K; (b) solid octylamine at 257 K; (c) isotropic solution of octylamine–water (40.0% (w/w) amine at 295 K); (d) hydrated octylamine in mesomorphic state (25.0% (w/w) amine in water at 295 K).

Table 1. C—H Raman stretching frequencies and peak height ratios for some *n*-alkylamines systems

System	$\nu/\text{cm}^{-1}$			Peak height ratios	
	$\nu_s(\text{CH}_2)$	$\nu_{as}(\text{CH}_2)$	$\nu_s(\text{CH}_2) + 2\delta_{\text{HCH}}$	$\frac{\nu_{as}(\text{CH}_2)}{\nu_s(\text{CH}_2)}$	$\frac{I_{2925}}{I_{2850}}$
<b>Octylamine</b>					
257 K (solid)	2845	2880	2925	1.62	0.43
278 K (liquid)	2850	2888	2925	0.74	0.63
295 K (liquid)	2850	2888	2925	0.86	0.66
<b>Octylamine–water</b>					
0.8:0.2 (isotropic solution) 295 K	2850	2888	2925	0.70	0.61
0.25:0.75 (hydrated amine in mesomorphic state) 295 K	2850	2888	2925	1.14	0.77
<b>Nonylamine</b>					
295 K (liquid)	2850	2888	2925	0.83	0.65
<b>Dodecylamine</b>					
295 K (solid)	2845	2880	2925	1.78	0.33
305 K (liquid)	2850	2888	2925	0.84	0.65
323 K (liquid)	2850	2888	2925	0.77	0.64
<b>Tetradecylamine</b>					
295 K (solid)	2845	2880	2925	1.80	0.29
<b>Hexadecylamine</b>					
295 K (solid)	2845	2880	2925	1.83	0.33
323 K (liquid)	2850	2888	2925	0.86	0.62
353 K (liquid)	2850	2888	2925	0.88	0.65

upon the polar environment character of the hydrocarbon chains.<sup>14–15</sup>

Table 1 presents for the primary amines studied under different conditions of temperature, state and solution, the frequencies of the  $\nu_s(\text{CH}_2)$ ,  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2) + 2\delta_{\text{HCH}}$  modes and the two intensity ratios which have been widely used, as order/disorder and polar/apolar environmental parameters. Figure 3 illustrates the main features in the C—H stretching region of the Raman spectra of liquid, solid and aqueous octylamine.

It is clear that the changes observed for these long-chain *n*-primary amines in the C—H spectral region are comparable to those observed for *n*-paraffins in the same spectral region, namely: for the transition from the solid to the liquid there is a significant decrease in the intensity ratio  $\nu_{as}(\text{CH}_2)/\nu_s(\text{CH}_2)$  and an important increase in the intensity ratio  $I_{2925}(\text{cm}^{-1})/I_{2850}(\text{cm}^{-1})$ ; simultaneously, there is a shift to higher frequencies of the bands corresponding to the  $\text{CH}_2$  vibrations with  $\nu_s(\text{CH}_2)$  shifting from  $2845\text{ cm}^{-1}$  to  $2850\text{ cm}^{-1}$  and  $\nu_{as}(\text{CH}_2)$  from  $2880\text{ cm}^{-1}$  to  $2888\text{ cm}^{-1}$ .

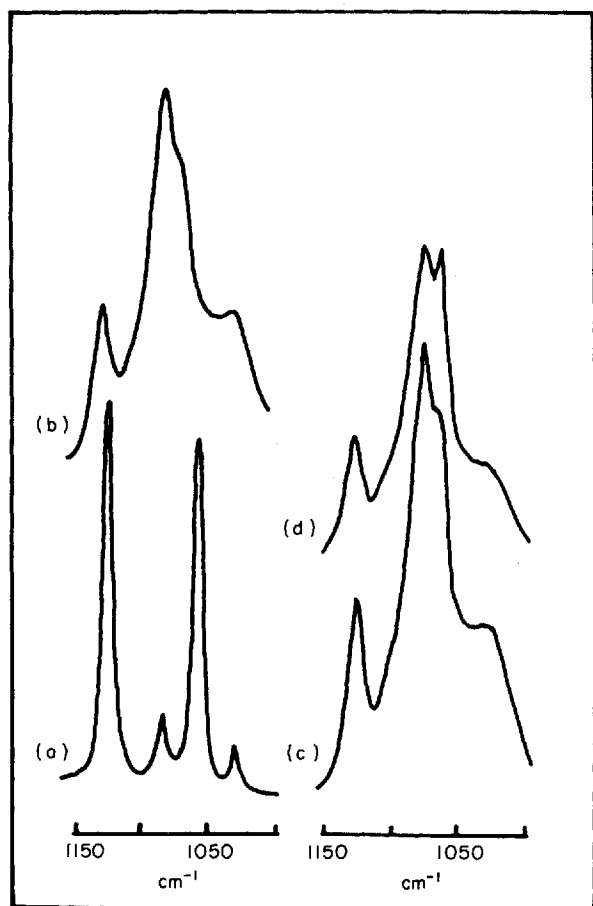
These changes are the expected result of a decrease in the amount of hydrocarbon chain in the *trans* conformation and an increase in the polar/apolar contact of the chains, with stronger external coupling between neighbouring chains on going from the solid to the liquid.

In the solid, the order/disorder parameter increases slightly with increase of chainlength; in the liquid there is no systematic change in its value with change of chain length or with change of temperature.

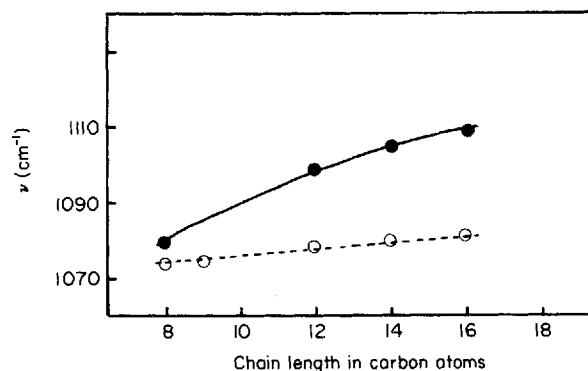
In the octylamine-water systems, the isotropic solution exhibits the spectral characteristics of the liquid amine, for both frequencies and relative intensities of the C—H stretching bands; the hydrated amine in a liquid-crystalline state shares the spectral features of the liquid amine for the frequencies but has a value intermediate between the liquid and the solid for the order/disorder parameter, and a value which is closer to the liquid than the solid, for the polar/apolar parameter. All these features must be related to the intermediate nature of the molecular packing in the mesomorphic state.

### The skeletal C—C stretching vibrations

It has been shown<sup>1,11</sup> for hydrocarbon chains that the Raman bands in the region 1050–1200  $\text{cm}^{-1}$  are due to the skeletal modes of the hydrocarbon chain arising from alternate carbon atom motions in opposite directions along the chain axis. In this region, the Raman spectra of the alkyl-amines studied (see Fig. 4) show two intense bands at 1063  $\text{cm}^{-1}$  and 1125  $\text{cm}^{-1}$  whose



**Figure 4.** The C—C stretching vibration region in the Raman spectra of (a) solid octylamine at 257 K; (b) liquid octylamine at 295 K; (c) isotropic solution of octylamine-water (40.0% (w/w) amine at 295 K); (d) hydrate octylamine in mesomorphic state (25.0% (w/w) amine in water at 295 K).



**Figure 5.** The frequency of the band in the 1070–1100  $\text{cm}^{-1}$  Raman range of primary amines in the solid (●) and liquid (○) states as a function of chain length.

frequencies are independent of the hydrocarbon chain length, within  $\pm 3 \text{ cm}^{-1}$ . These bands have been assigned to the symmetric or in-phase C—C stretching and the antisymmetric C—C stretching respectively.<sup>11</sup>

In this region, there is an additional band at 1075–1100  $\text{cm}^{-1}$  arising from all-*trans* crystalline structure vibrations. In the crystalline state, this frequency is highly dependent on the hydrocarbon chain length, increasing with the length of the chain (see Fig. 5), but the intensity does not change significantly if we take the 1063  $\text{cm}^{-1}$  or the 1125  $\text{cm}^{-1}$  band as a reference. However, in the transition to the liquid state, a broad band, much more intense than the bands at 1063  $\text{cm}^{-1}$  and 1125  $\text{cm}^{-1}$  is observed. While the intensity of this band does not vary significantly with the chain length, its frequency increases slightly with the number of carbon atoms in the chain as follows: 1075  $\text{cm}^{-1}$  for octylamine,  $\sim 1079 \text{ cm}^{-1}$  for dodecylamine, and  $\sim 1082 \text{ cm}^{-1}$  for hexadecylamine.

The appearance of this additional band indicates that the ordered crystalline and extended all-*trans* chain becomes kinked involving a change in the amine chains to a fluid configuration with a wide distribution of structures which include several *gauche* rotations.

As shown in Fig. 4, an intermediate situation occurs with the hydrated octylamine in the mesomorphic state where the band at 1063  $\text{cm}^{-1}$  compares quite well in intensity with the band at 1075  $\text{cm}^{-1}$ , intermediate between the typical solid and the pure liquid situations.

### The acoustical mode vibrations

In the low-frequency Raman spectrum of *n*-paraffins, the accordion-like longitudinal acoustical motions of the all-*trans* chain segment between folds gives rise to a series of bands below 400  $\text{cm}^{-1}$  the frequency of which varies inversely with chain length.<sup>16–18</sup> The Raman frequencies of these bands are approximately linear in  $(m/n)$ , where  $m$  is the order of the vibration and  $n$  is the number of carbon atoms in the chain. The fundamental longitudinal acoustical vibration ( $m = 1$ ) is the most intense of the series observed for a particular chain length, with the intensities of the overtones approximately proportional to  $1/m$ . For each chain length,  $n$ , there are only a limited number of frequencies intense enough for observation and these frequencies are

**Table 2. Fundamental longitudinal acoustical mode frequencies for some *n*-alkanes, *n*-fatty acids and *n*-alkylamines**

<i>n</i>	$\nu(\text{cm}^{-1})$		
	Alkanes <sup>16</sup>	Fatty acids <sup>18</sup>	Amines
8	277.9	—	255
9	248.9	—	228
12	182.6	206	184
14	162.8	184	162
16	143.7	164	144
18	128.3	145	—
20	115.9	126	—
22	103.3	105	—
24	98.1	103	—

Note. All the values in this table are values for  $T = 297$  K except the values for octylamine and nonylamine which are for  $T = 257$  K.

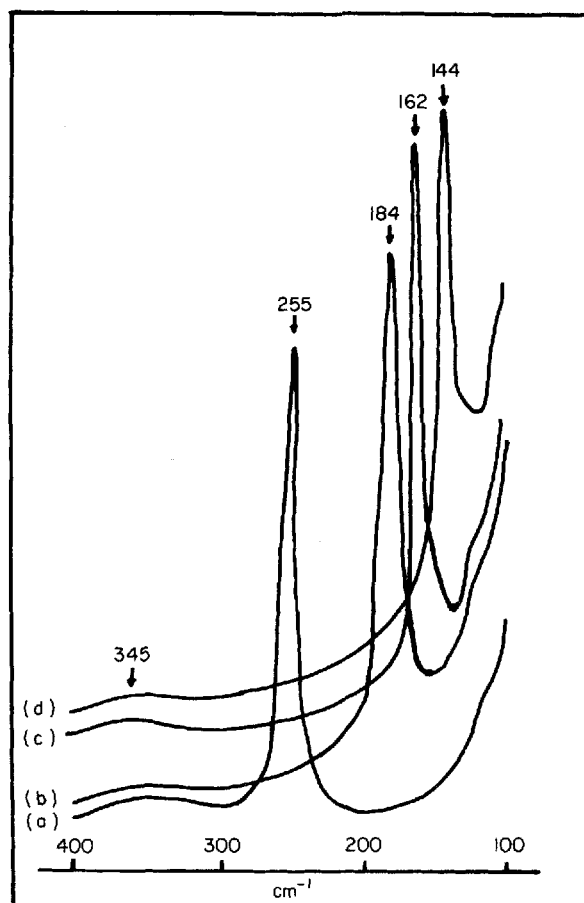
different from the frequencies observed for other chain lengths.<sup>18</sup>

Considering the actual planar zig-zag geometry and methyl end groups, Schaufle *et al.*<sup>16,17</sup> have shown that the frequencies of the accordion modes for finite polymethylene chains could be fitted to a polynomial in  $(m/n)$  of the form:

$$\Delta\bar{\nu} = A_1 + A_2(m/n) = A_3(m/n)^2 + \dots + A_7(m/n)^6$$

With values of the parameters  $A_1$ – $A_7$  determined from a least-squares treatment of the experimental frequencies, the frequencies of primary longitudinal mode for a series of  $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$  chains was calculated and good agreement with experimental values found. Warren *et al.*<sup>18</sup> extended the treatment to a series of fatty acids. A comparison of the frequency of the fundamental longitudinal mode in saturated long-chain *n*-alkanes, *n*-fatty acids and *n*-primary amines, in the solid state, is presented in Table 2.

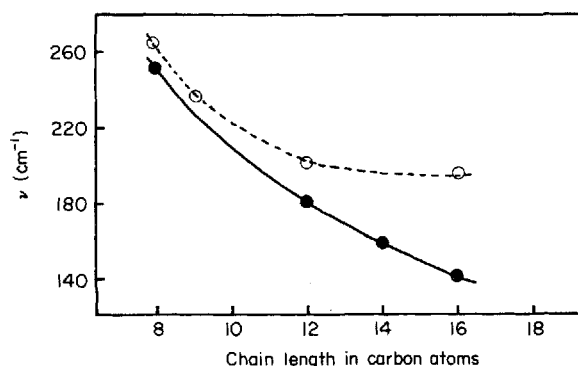
It is clear that for all three types of compounds, the frequency of the fundamental longitudinal acoustical mode decreases with increasing chainlength. Figures 6 and 7 show the variation of such a frequency for the case of the *n*-alkylamines under study. There is no significant difference between the frequency of the *n*-alkylamines and the corresponding *n*-alkanes for  $n = 12, 14$  and  $16$ , while the corresponding *n*-fatty acids exhibit a frequency higher by about  $20 \text{ cm}^{-1}$ . For lower values of  $n$ , namely for  $n = 8$  and  $n = 9$ , there is a significant difference in the frequency of the longitudinal fundamental mode of *n*-primary amines and *n*-alkanes. This difference cannot be attributed only to the different temperatures to which the values refer since it is well-known that the temperature dependence of the accordion mode frequency for the solid is small (for example, in the case of  $\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$  the accordion frequency increases only by about  $2 \text{ cm}^{-1}$  on going from  $300$  to  $77$  K). From *n*-alkanes to *n*-fatty acids and *n*-alkylamines, the carboxyl and the  $\text{NH}_2$  groups will act as a perturbation on the accordion-like motion of the hydrocarbon chain; clearly, such a perturbation decreases with the increase of the hydrocarbon chain, as would be expected. The  $\text{NH}_2$  perturbation is small and quickly becomes negligible with increase of the hydrocarbon



**Figure 6.** Raman spectra of solid *n*-alkylamines in the  $100$ – $400 \text{ cm}^{-1}$  region: (a) octylamine ( $257$  K); (b) dodecylamine ( $295$  K); (c) tetradecylamine ( $295$  K); and (d) hexadecylamine ( $295$  K).

chain (for  $n = 11$  or  $12$ ) when compared with the carboxyl group perturbation which becomes negligible only for  $n \approx 25$  to  $26$ .

On going from the solid to the liquid, the primary longitudinal acoustical mode undergoes an increase in frequency, and becomes broader and decreases in intensity. Moreover, as the temperature is raised, in the liquid state, there is a gradual increase in this frequency and a progressive decrease in intensity, as can be seen in Figs 7 and 8. Both these effects undoubtedly result from the formation of significant fractions of *gauche*



**Figure 7.** The frequency of the longitudinal acoustical mode in the Raman spectra of primary amines in solid (●—●) and liquid (○—○) states as a function of chain length.

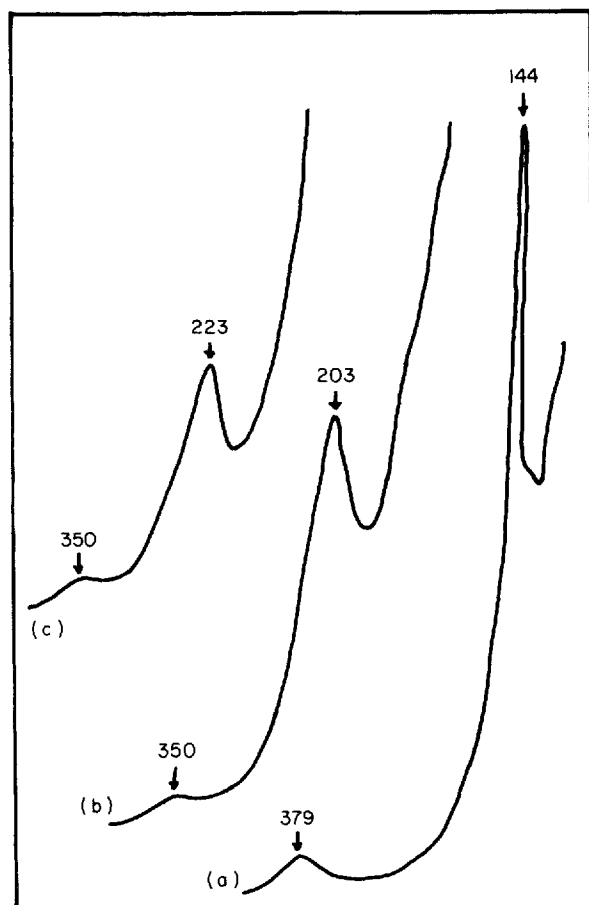


Figure 8. The Raman spectrum of hexadecylamine in the 100–400  $\text{cm}^{-1}$ , at different temperatures: (a) 295 K; (b) 323 K; (c) 353 K. Note: the numbers in this figure are wavenumbers.

separated segments within the chains: as the temperature is raised, the number of chain conformations increases.

As shown in Fig. 7 the frequency of the primary longitudinal mode in the liquid decreases with increasing chain length as in the solid. However, the difference between the frequencies of the solid and the liquid becomes progressively larger for higher number of carbon atoms of the amine chain. This result is consistent with the lower temperatures required to induce liquefaction for the shorter chains.

Finally, the aqueous solutions of octylamine also show a medium Raman band which corresponds closely to the fundamental accordion-like vibration observed either in the solid or in the pure liquid (see Fig. 9). Its frequency is independent of water content, with a value ( $\sim 260 \text{ cm}^{-1}$ ) between that for the solid and the liquid. Its intensity decreases as the water content increases; and its width is comparable with that of the pure liquid. Thus, the disruption of the all-*trans* conformation of the paraffin chain with the introduction of *gauche* linkages due to water solvation appears to be close to the same kind of disruption which occurs on going from the solid to the liquid.

Kalyanasundaram and Thomas<sup>11</sup> observed a similar broadening of the fundamental longitudinal acoustical mode in micellized CTAB and assigned it to the carbon atoms four to six  $\text{CH}_2$  units away from the polar head group: the polar head groups are anchored in the Stern-

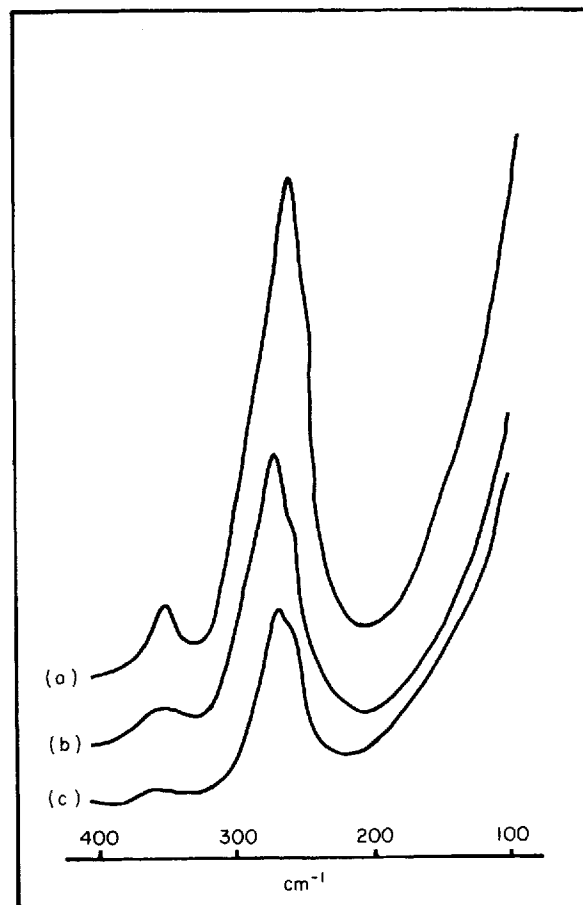


Figure 9. The Raman spectrum in the 100–400  $\text{cm}^{-1}$  region of (a) pure liquid octylamine (295 K); (b) isotropic solution of octylamine-water, 80.0% (w/w) amine (295 K); (c) hydrated octylamine in mesomorphic state, 25.0% (w/w) amine in water (295 K).

layer of the micelle, considerably restricting the motion of the hydrocarbon chain adjacent to the head group. There is, however, some evidence that in *n*-alkylamines the  $\text{NH}_2$  group acts essentially like a methyl group and does not serve to anchor the chain.<sup>25</sup> Thus, it seems that the broadening mechanism is more likely to be due to the simple increase of the random character of the hydrocarbon chains than to the differently restricted accordion-like motion of the  $\text{CH}_2$  groups due to end effects.

## CONCLUSION

From the present work it is found that in long-chain *n*-primary amines the changes of conformation and molecular packing of the hydrocarbon chains with temperature, physical state and solution have systematic effects on the band intensities and frequencies of several Raman vibrational modes. This makes possible their study by Raman spectroscopy as has been done for other lipids.

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