Low-Frequency Raman Spectra of Odd α,ω-Disubstituted n-Alkanes

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SYNOPSIS

Low-frequency Raman spectra of odd α,ω-dibromo- and α,ω-dihydroxy-n-alkanes were recorded. The longitudinal acoustic mode (LAM-1) frequencies were assigned by reference to the published results for n-alkanes and even α,ω-disubstituted n-alkanes and also by taking account of the effects of end intermolecular forces and end-group masses by use of the chain model of Minoni and Zerbi.

Keywords: Raman spectra of odd α,ω-disubstituted n-alkanes • n-alkanes, odd, and disubstituted derivatives, Raman spectra of • chain motion in even-odd alkanes, Raman study of

INTRODUCTION

The effects of end masses and forces on the single-node longitudinal acoustical modes (LAM-1) of even α,ω-disubstituted n-alkanes have been investigated experimentally by low-frequency Raman spectroscopy and interpreted theoretically[1] by the use of simple rod[2] or chain[3] models. The study[1] confirmed that the end group could be considered as an inertial mass, and that the end forces were of a magnitude appropriate for chains with van der Waals chain-end interactions (i.e., 5 N m^{-1}) except in the case of the α,ω-dihydroxy n-alkanes where the end force which best fitted the Raman data was 15 N m^{-1}, the higher value reflecting interchain hydrogen bonding.

The low-frequency Raman spectra of several odd α,ω-disubstituted n-alkanes are reported here, i.e. X(CH)$_{n-2}$X, where X = CH$_2$Br or CH$_2$OH and n is in the range 7–23. Differences exist between the low-frequency spectra of the odd and even chains, which probably are related to the differences in the packing of chains in the layer crystals of odd and even α,ω-disubstituted n-alkanes. The crystal structures of the samples are not known, but it is known[4] that LAM-1 frequencies in n-alkanes are generally in-sensitive to chain packing, which means that assignments of bands to LAM-1 can be based on the known LAM-1 frequencies of the n-alkanes[4] and their disubstituted derivatives.[1]

EXPERIMENTAL

Materials

α,ω-Dibromo-n-alkanes (n = 7, 9, 11) and α,ω-dihydroxy-n-alkanes (n = 7, 9) were purchased from Fluka AG and used without further purification. Samples of α,ω-dihydroxy and α,ω-dibromo n-tricosane (n = 23) were prepared. Consideration was given to methods of synthesis of higher n-alkane derivatives described by Zantour et al.,[5] Igner et al.,[6] and Lee and Wegner.[7] In view of the limited chain extension required, and because of the ready generation of terminal functionalities by that route, the coupling method of Zantour et al. was chosen. The preparation, starting from n-dodecandioic acid and forming n-tricosandioc acid, will be fully described elsewhere.[8] Reduction of the diacid in anhydrous toluene/diethyl-ether with borane/dimethyl-disulfide reagent gave the diol in 68% yield, and bromination of the recovered diol, using hydrobromic-acid/sulfuric-acid reagent, gave the dibromide in

66% yield. The purities of the products were ensured by chemical analysis and by ^{1}H nuclear magnetic resonance (NMR) spectroscopy.

Raman Spectroscopy

The procedure used in recording the low-frequency Raman spectra was similar to that described fully elsewhere.[1] Spectra were generally recorded over the frequency range 5–400 cm^{-1} and at several temperatures within the range 293–133 K. High-frequency spectra (to 1800 cm^{-1}) were recorded from time to time to ensure that samples were unchanged by exposure to the laser beam.

RESULTS AND DISCUSSION

Examples of spectra (T = 173 K) are shown in Figure 1. Spectra of the C_{23} diol were obtained over a limited frequency range with the sample at room temperature only (see Fig. 2), where comparison is made with a spectrum of the C_9 diol. The temperature dependence of frequency was found to be about −2 cm^{-1} per 100 K.

Band frequencies are recorded in Table I: bands of low intensity were verified by recording the spectra many times. A decrease in frequency with increase in chain length is apparent for most of the

bands in the low-frequency spectra of a given type of chain molecule (see also Figs. 1 and 2).

In this report, attention is centered on the frequencies of bands assigned to LAM-1. Because of the generally-low melting points of the samples (only the C_9 diol and the C_{23} diol and dibromide were solid at room temperature) we did not check their crystallography by x-ray diffraction. An indication of crystal structure was obtained from the methylene bending region of the high-frequency spectrum (1400–1500 cm^{-1}). Two intense bands at 1410–1415 cm^{-1} and 1440–1445 cm^{-1} were observed in the spectra of the diols, whereas the spectra of the dibromides in this region were dominated by a single intense band at 1440–1445 cm^{-1}. In the spectra of polyethylene and certain long chain alkanes, splitting of the methylene bending mode is an orthorhombic or monoclinic crystal field effect.[9]

α,ω-Dibromoalkanes

Considering first the spectra of the dibromo-n-alkanes, the frequencies of the prominent bands at the high end of the low-frequency range (see Fig. 1 and Table I) are plotted against chain length in Figure 3. Comparison is made with the frequencies of the LAM-1 bands of the even dibromo-n-alkanes[1] and the even and odd n-alkanes.[4] The assignment of the frequencies to LAM-1 is justified by this plot.
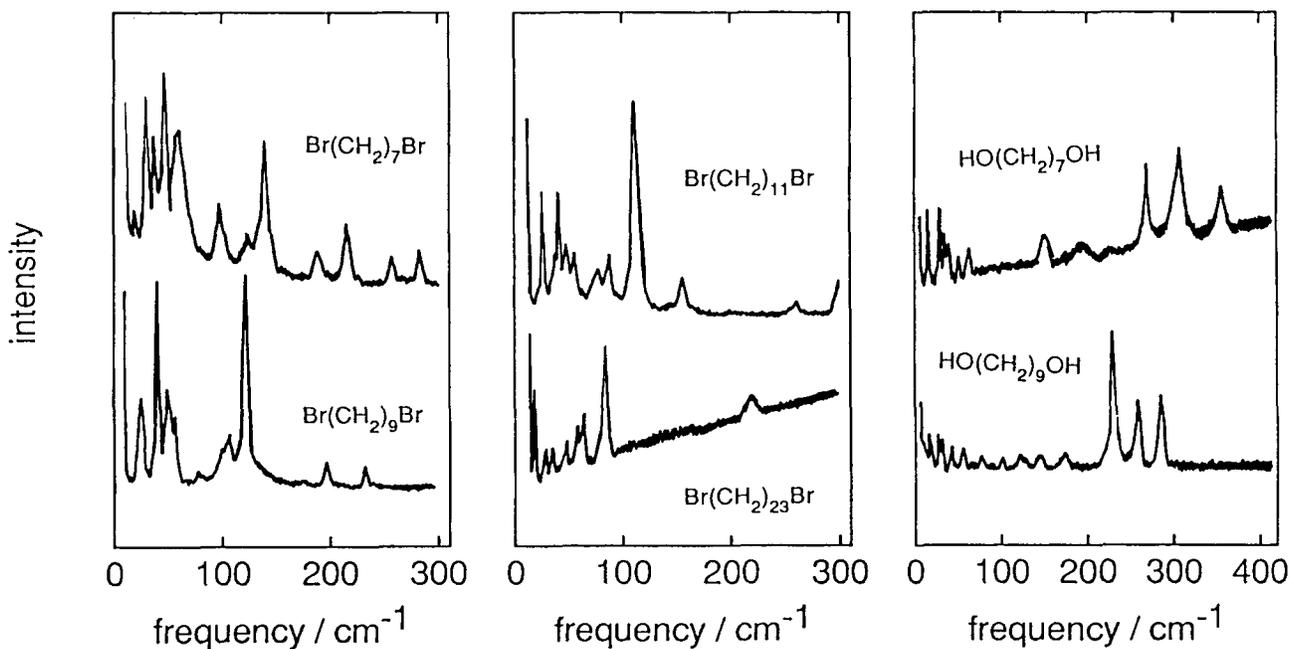
Figure 1. Low-frequency Raman spectra of odd α,ω-disubstituted n-alkanes, as indicated. T = 173 K.
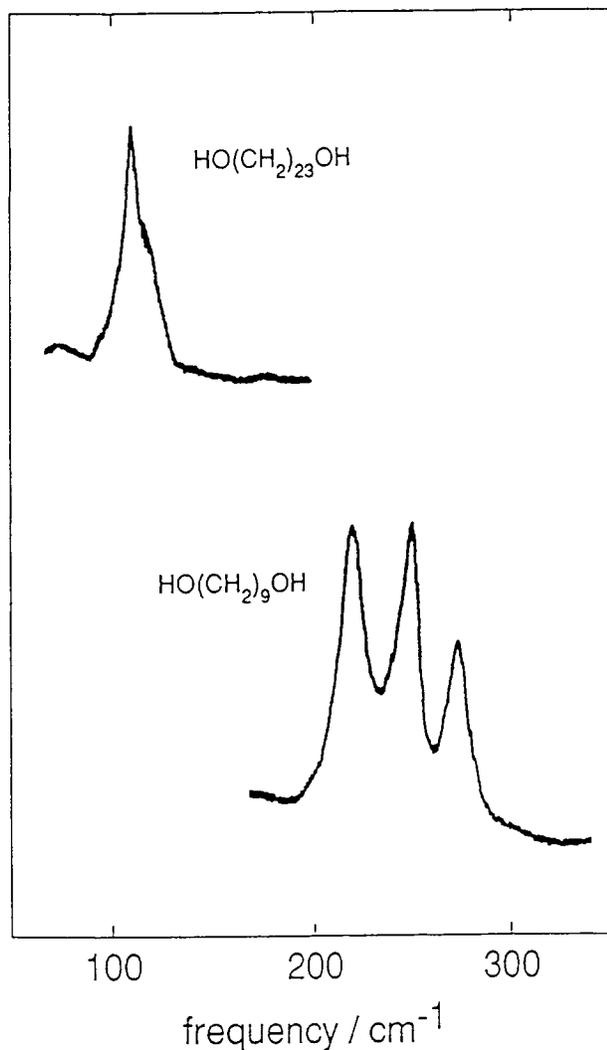
Figure 2. Low-frequency Raman spectra of odd α,ω-dihydroxy n-alkanes, as indicated. T = 293 K.

Table I. Frequencies of Raman Bands of Odd α, ω-Disubstituted n-Alkanes at 173 and 293 K

End Group	n	Frequency[a]/cm^{-1}
173 K		
CH$_2$Br	7	15, 28, 35–39, 46, 55–58, 96, 120, 140,[a] 187, 215, 255, 281
CH$_2$Br	9	(16), 23, 38, 49, 55, 78, 97–105, 121,[a] (142), (174), 198, 233
CH$_2$Br	11	(16), 21, 33–37, 43, 52, (60), 74–84, 108,[a] 152, (195), (226), 259, 298
CH$_2$Br	23	13, 24, 35, 43, 52–59, 80,[a] 216
CH$_2$OH	7	19, 31, 37, 53, 65, (83), (100), 149, 191, (220), 261*, 296, 344
CH$_2$OH	9	15, 23–27, 39, 52, 76, 99, 116, 139, 166, 218*, 248, 274
293 K		
CH$_2$OH	9	14, 25, 29, 35, (43), 49, 58, 71, (81), (106), 122, 148, 215*, 244, 269
CH$_2$OH	23	18, 33, 61, 109,[a] 118

[a] Frequencies of weak bands are in parentheses. Frequencies of bands assigned to LAM-1 are marked with an asterisk: see text.

alkanes (compared with the odd n-alkanes), but the magnitude of the effect is much smaller than that in the dibromides (see Fig. 4). The small effect in the n-alkanes correlates with more efficient packing of the end groups for the triclinic even n-alkanes, and can be reproduced by small changes in f_e in the Minoni–Zerbi calculation. The larger even-odd effect

The assignments were confirmed by fitting the data with eq. (16) of Minoni and Zerbi's report,[3] which allows calculation of the LAM-1 frequency for chain molecules in a layer crystal, i.e., for an infinite chain of molecules connected by van der Waal's intermolecular end forces. Allowance was made for differences in chain length and end-group mass, but the calculation was carried through with a constant chain force (force constant f_c = 420 N m^{-1}, which corresponds to a longitudinal modulus of E = 29 N m^{-2}). As can be seen in Figure 4, observed and calculated frequencies are in fair agreement when the end intermolecular force constant f_e = 5 N m^{-1}.

A pronounced even–odd effect is apparent in the short dibromides (n < 12, see Figs. 3 and 4). A high LAM-1 frequency is also seen for the short even n-

Figure 3. LAM-1 frequency versus alkyl chain length (n) for (●) even and odd n-alkanes and (■) even and odd α,ω-dibromo n-alkanes. T = 173 K.
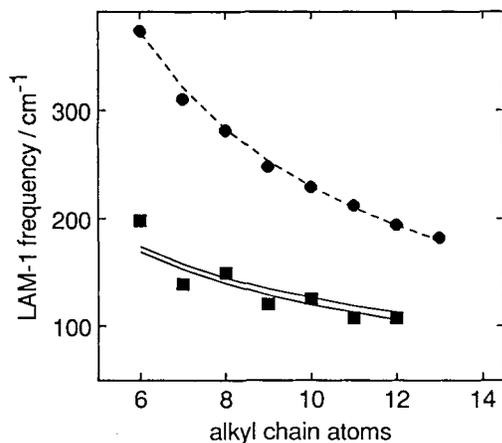
Figure 4. Application of the Minoni–Zerbi equation to the LAM-1 frequencies of (●) n-alkanes and (■) α,ω-dibromo n-alkanes: T = 173 K. Chain force constant f_c = 420 N m^{-1} and CH$_2$ chain mass m_c = 2.33 × 10^{-26} kg for all calculations: dashed line, end force constant f_e = 5 N m^{-1} and CH$_3$ end mass m_e = 2.50 × 10^{-26} kg; upper solid line, f_e = 5 N m^{-1} and CH$_2$Br end mass m_e = 1.56 × 10^{-25} kg; lower solid line, f_e = 0 N m^{-1} and CH$_2$Br end mass m_e = 1.56 × 10^{-25} kg.

in the short dibromides cannot be accommodated within the linear-chain model by varying f_e. Although the LAM-1 frequencies of the even dibromides are reasonably-well fitted with f_e = 5 N m^{-1} (see Fig. 4, upper solid curve), reducing f_e even to zero does not lower the calculated LAM-1 frequencies sufficiently to fit the results for the odd dibromides (see Fig. 4, lower solid curve). The LAM-1 frequency of the C$_{23}$ dibromide can be fitted by the Minoni-Zerbi model.

It has been shown[10] that the LAM-1 band in the C$_{20}$ dibromide at 77 K is a doublet as a result of coupling with a transverse acoustical mode (TAM). We did not observe splitting of the LAM band in our spectra at temperatures as low as 133 K. Nevertheless it is possible that TAM/LAM coupling exists and differs between even and odd dibromides, and is responsible for the pronounced even–odd effect.

α,ω-Dihydroxyalkanes

The spectra of the dihydroxy-n-alkanes are more complex than those of the dibromides. For the short chains (C$_7$ and C$_9$), three prominent bands are apparent at the high frequency end of the range (see Fig. 1). For the longer chain (C$_{23}$), the room temperature spectrum contains just one prominent band, albeit with a shoulder on the high-frequency

side and, possibly, on the low-frequency side (see Fig. 2).

The frequencies of these bands (with appropriate adjustment to equivalent temperature, 173 K) are plotted against chain length in Figure 5, where comparison is made with results for even dihydroxy-n-alkanes for which only single peaks were found,[1] with results for n-alkanes and dibromides taken from Figure 4, and with calculations based on Minoni and Zerbi's equation.

The frequency of the lowest frequency band of each of the band triplets correlates well with the results for the even diols, and, through the calculations, with the band frequency of the C$_{23}$ diol. Accordingly, the lowest frequency band of each of the band triplets is assigned to LAM-1 (as in Table I). (The origin if the triplet is unclear: assignment of LAM-1 to the central band of the triplet, which is suggested by the spectrum of the C$_{23}$ diol (see Fig. 2), remains a possibility.)

Comparing results for alkanes and diols (see Fig. 5), the damping effect of a larger end mass (CH$_2$OH vs. CH$_3$) is compensated by the effect of a larger intermolecular force, which originates in hydrogen bonding between the end planes of the layer crystal. This effect is quantified in Figure 5, where the ob-
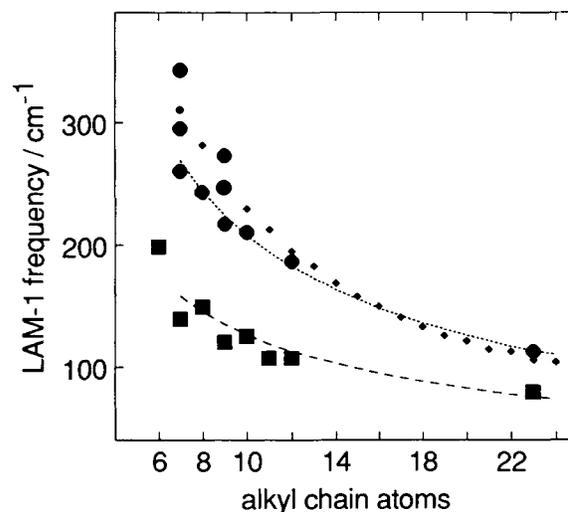
Figure 5. Low frequency Raman bands for even and odd (♦) n-alkanes, (●) α,ω-dihydroxy n-alkanes and (■) α,ω-dibromo n-alkanes: T = 173 K (adjusted from room temperature for the C$_{23}$ diol). The lines show the results of calculations based on the Minoni–Zerbi model. The dashed line represents the fit to the LAM-1 frequencies of the α,ω-dibromo n-alkanes calculated as described for Figure 4. The dotted line is calculated with f_c = 420 N m^{-1}, f_e = 15 N m^{-1}, CH$_2$ chain mass m_c = 2.33 × 10^{-26} kg, and CH$_2$OH end mass m_e = 5.15 × 10^{-26} kg.

served frequencies compare well with those calculated for chains with CH_2OH end groups and high ($f_e = 15$ N m^{-1}) end intermolecular forces.

There is an even–odd effect in LAM-1, again in the direction of the even chains having a high LAM-1 frequency.

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