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# Longitudinal Acoustic Modes in Cycloalkanes

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## Summary

The longitudinal acoustic modes (LAM) of several cycloalkanes ($(CH_2)_{14}$ to $(CH_2)_{96}$) measured by Raman spectroscopy are described. The frequency differences between the LAMs of the cycloalkanes and the corresponding n-alkanes are explained by a simple linear chain model. It is shown that the LAM-modes are practically not affected by the gauche conformations of the two folds in the cyclic molecule.

## Introduction

In order to prove the conformation of cycloalkanes to be collapsed rings and to prove the effect of chain folding on the sceletal vibrations it is useful to look at the low frequency Raman spectrum. In particular the LAMs, which have been investigated in detail for the n-alkanes (SCHAUFELE, SHIMANOUCHI, 1967), can be clearly identified because of their dependence on the molecular weight (BÖLSTLER, 1978).

## Results and discussion

The low frequency Raman spectra of the solid cycloalkanes $(CH_2)_{28}$ up to $(CH_2)_{96}$ taken at room temperature are shown in fig.1. The frequencies of the scattering peaks are found to be: $(CH_2)_{28}$: 167.6 $cm^{-1}$; $(CH_2)_{32}$: 146.1 $cm^{-1}$; $(CH_2)_{36}$: 128.3 $cm^{-1}$; $(CH_2)_{48}$: 104.3 $cm^{-1}$; $(CH_2)_{72}$: 69.7 $cm^{-1}$; $(CH_2)_{96}$: 52.5 $cm^{-1}$ within an accuracy of $\pm 1.5$ $cm^{-1}$. In comparison with the LAMs of the n-alkanes one can establish that the LAM-frequencies of the cycloalkanes are shifted to higher values. In order to explain this shift, simple model calculations were carried out:

Supposing that the LAM is determined only by the trans sequences between the folds, we have to assume that the $CH_2$-groups which form the fold, move as rigid masses on the ends of these trans sequences. We divide the molecule into two parts and describe each part as a finite linear chain. Let $\beta$ be the number of $CH_2$-groups within the fold one obtains for the total number of point masses which take part in the longitudinal vibration $n_t = 1/2 \cdot (n - 2\beta) + 2$, where n means the total number of $CH_2$-groups in the molecule. If we calculate the longitudinal vibrations of a finite linear chain with $n_t$ equal masses M we obtain the frequencies

$\omega^2 = \frac{4f}{M} \sin^2 \frac{\alpha}{2}$ with $\alpha = \frac{(2m-1)\pi}{2n_t}$ ; m means the order of the vibration and f the resulting force constant of the whole chain. Taking into account that masses $1/2 \cdot \beta \cdot M$ are localized at the ends of the linear chain, $\alpha$ has to be calculated from the equation $(\beta - 1) \tan(\alpha \cdot (n_t - 1)/2) = \cot \alpha/2$. The factor 4f/M can be taken from the LAM of the n-alkanes under the

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assumption that their force constants do not differ from the corresponding force constants of the cycloalkanes. Fig.2 shows the calculated LAM frequencies of the cycloalkanes for various values of $\beta$ in comparison with experimental values. It is evident that the various models differ considerably only for the smaller cycloalkanes ($n<40$) whereas for the greater rings there is no difference between these models. The best fitting calculated curve is obviously with $\beta = 2$ which is a model with $n_t$ equal masses (the mass at the end is not heavier). This means that a $(CH_2)_n$ ring molecule has practically the same LAM frequency as a $C_{n/2}H_{n+2}$ n-alkane, i.e. that the two gauche-conformations as part of the fold conformation at both ends of the half ring molecule do not affect the position of the LAM mode essentially (c.f. HSU, KRIMM, 1977). The shape of the LAM show clearly the existence of trans segments (which probably may be twisted weakly (c.f. TRZEBIATOWSKI, 1980)). At the transition of $(CH_2)_{22}$

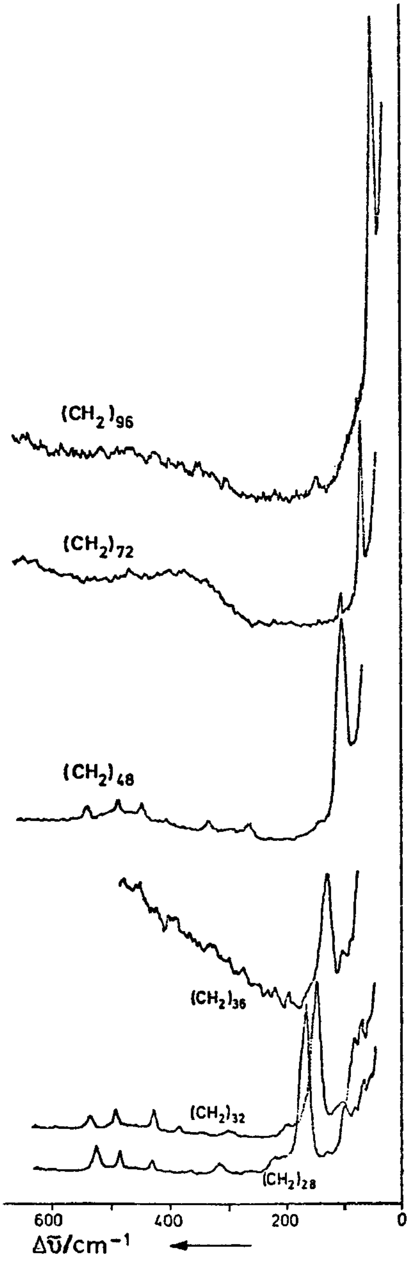

fig. 1: Low frequency Raman spectra of some cycloalkanes in the solid state.

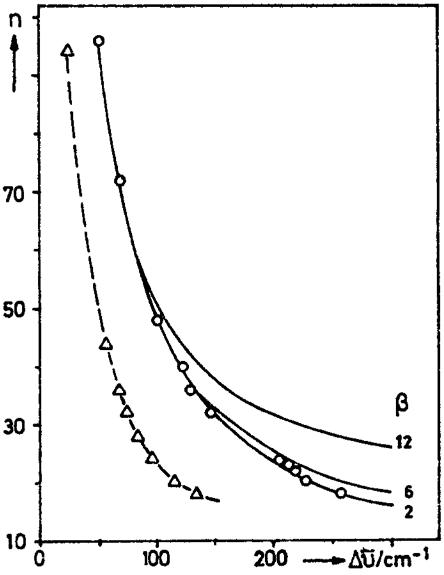

fig. 2: Experimental LAM frequencies for the n-alkanes (Δ) and cycloalkanes (○) compared to theoretical curves (n means the number of $CH_2$-groups per molecule).

and $(CH_2)_{24}$ into the high temperature phases (GROSSMANN, 1981) the relatively sharp LAM bands change into broad pseudo-LAMs, which are also found in the melt (fig.3), similar to the n-alkane liquids (SCHAUFELE, 1968).

The small peak at about 500 $cm^{-1}$, the position of which does not depend on chain length, might be analogous to the maximum frequency peak (band edge) of the $\nu_5$-branch in polyethylene (BERGHMANS et.al, 1971; HÄGELE et.al).

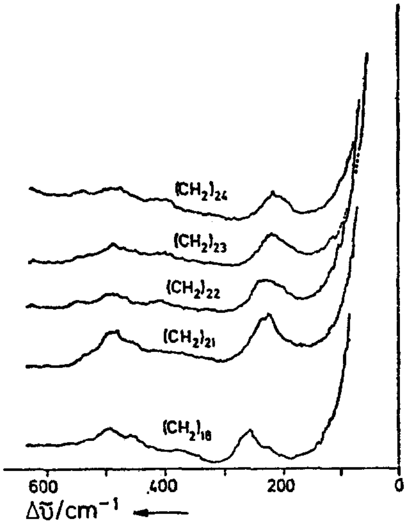

fig. 3: Low frequency Raman spectra of some cycloalkanes in the melt (rsp. in the high temperature phase of $(CH_2)_{22}$ and $(CH_2)_{24}$).

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