NOTES

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Accordionlike Skeletal Motions of $CH_3NHCONH(CH_2)_nCH_3$ (n=1—15)

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Synopsis. Solid $CH_3NHCONH(CH_2)_nCH_3$ (n=1—15) gave two intense Raman lines in the 100—500 cm^{-1} region. The frequency of one of them varied with n, but that of the other was unvarying. The n-dependent frequencies fit the theoretical ν-δ curve of C–C–C deformation of polyethylene and were, therefore, assigned to the accordion modes.

In early Raman studies of normal paraffin crystals, Mizushima and Shimanouchi[1] found sharp Raman lines which appeared at frequencies inversely proportional to the number of carbon atoms; they assigned them to the accordion-like motion of the totally symmetric skeletal deformation. Schaufele and Shimanouchi[2] elucidated the frequencies (ν) of the accordion modes of C_nH_{2n+2} molecules in terms of the phase difference (δ) of the vibrational displacements between two adjacent methylene groups.

We ourselves have previously studied the vibrational spectra of alkylureas[3-5] and pointed out that the C–N–C–N–C skeleton of the $CH_3NHCONHCH_2$– group is of a planar zigzag structure.[3] In the present study we examined the accordion modes of dialkylureas of $CH_3NHCONH(CH_2)_nCH_3$ (n=1—15). These compounds were prepared by a standard method[4] and were purified through repeated crystallization. The laser Raman spectra were excited by the 514.5 nm line and recorded on a JEOL-400D Raman spectrometer.

Two prominent Raman lines were found in the region between 100 and 500 cm^{-1}. One of them appeared around 230 cm^{-1} irrespective of n, but the other was located at a frequency which varied sensitively with n, although it became a shoulder of the libration band at about 100 cm^{-1} when $n \geqq 6$. The frequencies of the latter group of the Raman lines were approximately inversely-proportional to $n+5$ and were thus assigned to the accordion mode.

The n-dependent frequencies observed for solid $CH_3NHCONH(CH_2)_nCH_3$ are plotted against the phase difference in Fig. 1, where $\delta = 2\pi/(n+5)$ (instead of $\pi/n+5$) is used to refer to the theoretical ν-δ curve of the polyethylene crystal. The observed frequencies fit closely the theoretical curve (solid line) calculated for the ν_5 branch of the polyethylene crystal by Kitagawa and Miyazawa.[6] The ν-δ curve used has also been applied satisfactorily to the analysis of the skeletal modes of $CH_3(CH_2)_nCONH_2$.[7] Furthermore, the corresponding ν-δ plots observed for various polyethers of the $[-(CH_2)_m-O-]_n$ type have been reported to fit the theoretical ν-δ curve of the infinite polymethylene chain.[8]

Upon the determination of δ for the skeletal deformation vibrations of chain molecules with a *trans* zigzag structure, the number of constituent atoms is taken, in general, as the denominator.[2] In the present case, if the plane of the C–N–C–N–C of $CH_3NHCONHCH_2$– coincides with the *trans* zigzag plane of $-(CH_2)_nCH_3$, there will be $n+5$ atoms as the constituents of the *trans* zigzag chain of $CH_3NHCONH(CH_2)_nCH_3$ molecule; therefore $n+5$ was adopted for the denominator in the plot of Fig. 1.

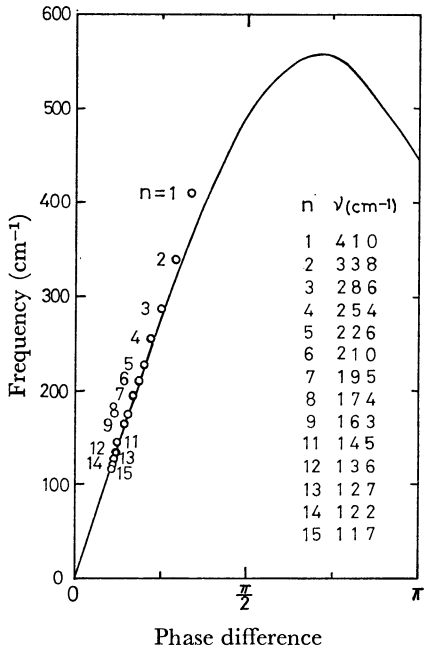

Fig. 1. The ν-δ plots for the accordionlike motion of $CH_3NHCONH(CH_2)_nCH_3$.

Usually, when n is small, the experimental ν-δ plots deviate considerably from the theoretical ν-δ curve and a correction for the effect of the end group is required.[7] Nevertheless, it is surprising that the present data for small n values fall closely on the theoretical curve without any correction for the end group. This fact may imply that all the skeletal atoms constitute a *trans* zigzag plane, and also that the deformations of NH–CO–NH and CO–NH–CH_2 (or CH_3) are effectively coupled with other skeletal deformations of the molecule just as where those parts are replaced with CH_2–CH_2–CH_2. If this consideration is correct, then it is not unexpected that the present data for n=2 fall on the theoretical ν-δ curve, because it corresponds to the case of the n=7 of C_nH_{2n+2}, for which the observed frequency fits the theoretical curve fairly well.

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