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ACCORDION-LIKE VIBRATIONS OF LONG CHAIN MOLECULES

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The application of vibration spectroscopy to chemistry is usually made by the identification of group frequencies which are supposed to be nearly independent of those of the motions of other parts of the molecule. This seems to be the most practical method, if the molecule has not a symmetrical structure. However, if it does, the overall motions of even a giant molecule can be a subject of the simple treatment.

One of the earliest investigations along this line was made in our laboratory in 1940's [1, 2]. As shown in Table 1, we observed only one strong Raman line in lower frequency region for each of n-paraffins in the solid state up to cetane ($N_c = 16$). The observed frequencies were expressed satisfactorily by the empirical equation:

$$\nu = \frac{2400}{N_c} \quad (cm^{-1}) \qquad (1)$$

when the number of carbon atoms N_c is larger than seven (see Table 1).

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TABLE 1 — *The frequencies in cm^{-1} of the accordion-like vibrations of the normal paraffin molecules in the extended form.*

Number of carbon atoms	Observed	Calculated	References
8	283	300	MIZUSHIMA and SHIMANOUCHI (1944 and 1949)
9	249	267	»
10	231	240	»
12	194	200	»
14	168	171	SHIMANOUCHI *et al.* (1974)
16	150	150	MIZUSHIMA and SHIMANOUCHI
18	133	131	SHIMANOUCHI *et al.* (1974)
20	114	120	»
22	112	109	»
24	98	100	»
28	85	86	SCHAUFELE and SHIMANOUCHI (1967)
32	76	75	»
36	67	67	»
44	56	55	»
94	26	26	»

We made the calculations of normal vibrations, the results of which are not only in agreement with this empirical equation, but also with the experimental results obtained for the molecules with $N_c < 8$ [1, 2]. It was shown that these Raman lines are to be assigned to the accordion-like motions of the whole molecules as shown in Fig. 1.

Two decades later, when the laser-Raman technique developed, SCHAUFELE and SHIMANOUCHI [3], and TAKEUCHI *et al.* [4] extendend the measurement up to n-paraffin with $N_c = 94$. The observed frequencies are satisfactorily expressed by Eq. (1).

The author does not intend to explain the recent development of our calculations of normal vibrations in this short note, but he wants to explain the accordion-like vibrations by the

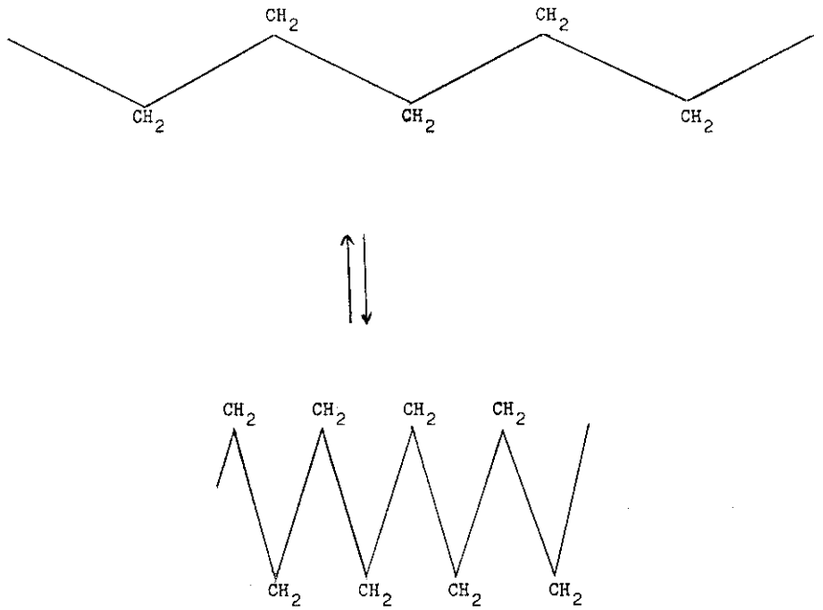

FIG. 1 — The accordion-like vibrations of the molecules of normal paraffins and polyethylene.

use of a simple model which is the longitudinal motion of a continuous rod of the length ℓ, the density ρ and Young's modulus E. Then the frequency of the vibration is given by

$$\nu = \frac{1}{2\ell}\sqrt{\frac{E}{\rho}} \qquad (2)$$

In this equation the density ρ can be calculated from the density of the unit cell of the n-paraffin crystal and the length ℓ from the number of carbon atoms N_c of the molecule as:

$$\ell = \sqrt{\frac{2}{3}} \times 1.54\ N_c \quad \text{(in Å)} \qquad (3)$$

TABLE 2 — *The accordion-like vibrations of poly-L-alanine in the α-helix form* [5].

Number of residues	Frequency in cm^{-1}
5	56
10	40
15	29
20	23
30	15
40	12
50	10
60	8
70	7
80	6
90	5

Thus from the comparison of Eq. (2) with Eq. (1), we can calculate the value of E of the extended chain molecules of n-paraffins (and also polyethylene) as 34×10^{10} Nm^{-2}. This is comparable to Young's modulus of diamond (55×10^{10} Nm^{-2}), and is a reasonable value, since this refers to that of carbon chains connected by covalent bonds as in the lattice of diamond crystal, but not to solid paraffins, the molecules of which are connected by the weak van der Waals force.

The treatment explained above can be applied to more complicated chain or helical molecules, for instance, those of polypeptides. Itoh and Shimanouchi calculated Young's modulus of poly-L-alanine in the α-helix form as 2.3×10^{10} Nm^{-2} from the frequencies of the accordion-like vibrations shown in Table 2 of this molecule [5].

The frequencies of the accordion-like vibrations of long chain molecules are in general very low so that they are excited easily at room temperature. This may have something to do with the biological aspect of protein molecules.

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