Laser-Raman Scattering by the C₃₄H₆₈ Ring Molecule

Mitsuo TASUMI^{*} and Takehiko SHIMANOUCHI

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo, Japan.

Robert F. SCHAUFELE**

Biophysics Department, Michigan State University, East Lansing, Michigan, U.S.A. (Received March 13, 1971)

ABSTRACT: Laser-Raman scattering by the $C_{34}H_{68}$ ring molecule has been measured and eight Raman bands have been observed in the region below 600 cm^{-1} . The assignments of these bands are discussed by both the Free-Segment Model and the normal-vibration calculation. It has been shown that the observed bands may be explained as arising from either the longitudinal acoustic vibrations of the long segment consisting of 15 methylene units, or the vibrations of the fold portion. Overall molecular vibrations are also discussed.

KEY WORDS Laser-Raman Scattering / Ring Molecule / C₃₄H₆₈ / Folding / Longitudinal Acoustic Vibration / Overall Molecular Vibration /

It is well established that the chains in polyethylene crystals are folded. However, the structure of the fold region is not precisely known and remains an interesting problem to be solved. A brief survey shows that there is no way to form a model having a fold structure with a relatively small number to methylene units placed at the trans and gauche (about 120° rotated from *trans*) positions with respect to the carbon-carbon single bond. This is true for the (110) as well as the (200) fold directions which, from spectroscopic^{1,2} and morphological^{3,4} studies, are thought to be the most probable cases. We, then, have to take into account some strained structures for which the equilibrium internal-rotation angles deviate considerably from the normal trans and gauche positions. In relation to this problem structural studies of methylene rings are important since these molecules inevitably have strained struc-Few such studies have been reported, tures.

however. Newman and Kay have determined the molecular and crystal structures of the ring molecule, $C_{34}H_{68}$.⁵ The Raman-scattering spectrum of this compound was measured in late 1967. A preliminary account of results, based upon eq 1, is reported in a recently issued review article.⁶ Schonhorn and Luongo have examined the infrared spectrum of $C_{34}H_{68}$ in the region of 1300 to 1400 cm⁻¹.⁷ As an extension of these studies we have conducted a more detailed analysis of the low-frequency Raman spectrum for $(CH_2)_{34}$ utilizing the same material measured by Newman and Kay. These results are reported in this paper.

EXPERIMENTAL

The sample of the ring molecule $C_{34}H_{66}D_2$ was kindly furnished by Dr. B. A. Newman to one of us (RFS). The Raman-scattering spectrum of this material was measured at the Esso Resarch and Engineering Co. utilizing a Spectra-Physics Model 125 He—Ne laser, a Spex Model 1400 double grating monochromator, together with photoelectric detection and synchronous amplification.⁸ The Raman-scattering spectrum is shown in Figure 1. This spectrum may be

^{*} Present address: Department of Biophysics and Biochemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo, Japan.

^{**} Present address: Human Biology Laboratories, College of Human Medicine, Michigan State University, East Lansing, Michigan, U.S.A.

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Figure 1. Laser-Raman spectrum of $C_{34}H_{66}D_2$.

safely regarded as that of $C_{34}H_{68}$, since the replacement of a single CH_2 group by CD_2 would not induce a great spectral change.

PRELIMINARY DISCUSSION OF THE SPECTRUM

We are most interested in the low-frequency region $(<600 \text{ cm}^{-1})$ of the spectrum, since it gives more information on the molecular structure.

The X-ray diffraction analysis of $C_{34}H_{68}^{5}$ has shown that this molecule takes a rectangular form; *i.e.*, two parallel segments consisting of 15 methylene groups which are linked together at both ends by two methylene groups (see Figure 2). It would be useful to treat the molecular vibrations of this compound from a very simple viewpoint. We assume that the molecular vibrations are localized to either the long segment (C_{15} part) or the short one (C_4 part);



Figure 2. Molecular structure of $C_{34}H_{68}$.

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in other words, the molecule is made up of two free C_{15} and two free C_4 portions. The carbon atoms at the four corners are included in both segments. We shall refer to this model as the "Free-Segment Model" (FS Model).

The normal vibrations of the C_{15} and C_4 segments may be approximated to those of npentadecane and *n*-butane, respectively. Although there are many skeletal deformation (in-plane) and torsional (out-of-plane) vibrations in a planar zigzag polymethylene chain, only the longitudinal acoustic (LA) vibrations may be observed in the Raman spectrum.^{9,10} Thus, only these vibrations will be discussed. The Raman spectrum of n-pentadecane is not yet published, but we can estimate the LA frequencies of this molecule by the following equation which has been derived by Schaufele and Shimanouchi¹⁰ and has been applied to polymethylene chains in both the solid¹⁰ and liquid¹¹ states.

$$\Delta \tilde{\nu}(\mathrm{cm}^{-1}) = A\left(\frac{m}{n}\right) + B\left(\frac{m}{n}\right)^2 + C\left(\frac{m}{n}\right)^3 + D\left(\frac{m}{n}\right)^4 + E\left(\frac{m}{n}\right)^5 + F\left(\frac{m}{n}\right)^6 \qquad (1)$$

where

 $A = 2495 \pm 86 \text{ cm}^{-1}$ $B = -(5.867 \pm 2.855) \times 10^{3} \text{ cm}^{-1}$ $C = (6.253 \pm 3.537) \times 10^{4} \text{ cm}^{-1}$ $D = -(3.485 \pm 2.058) \times 10^{5} \text{ cm}^{-1}$ $E = (7.329 \pm 5.676) \times 10^{5} \text{ cm}^{-1}$ $F = -(4.724 \pm 5.964) \times 10^{5} \text{ cm}^{-1}$

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In this equation the index *n* refers to the total number of carbon atoms and *m* is the vibration order. For the fundamental LA vibration *m* is equal to unity and for its second, third, fourth, \cdots harmonic tones *m* is equal to 2, 3, 4, \cdots respectively. The LA frequencies of *n*-pentadecane estimated by eq 1 are 153 (*m*=1), 295 (*m*=2), 411 (*m*=3), 490 (*m*=4), and 561 cm⁻¹ (*m*=5). The Raman bands arising from the modes with odd *m* would be stronger than those with even *m*. In the Raman spectrum of solid *n*-butane a band is found at 425 cm⁻¹ which is due to the symmetric bending vibration.^{9,12}

Finally we predict, from the FS Model, that $C_{34}H_{68}$ should give rise to six Raman bands, viz., 153 (s), 295 (vw), 411 (m), 425 (w), 490 (vw), and 561 cm^{-1} (w) (s, strong; m, medium; w, weak; vw, very weak). In the observed spectrum at least eight Raman bands occur below 600 cm^{-1} (Figure 1). Comparing the observed frequencies with those predicted above, we may assign the observed bands at 147, 303, 400, 431, 496, and 540 cm^{-1} to the inferred 153-, 295-, 411-, 425-, 490-, and 561-cm⁻¹ frequencies. It is rather surprising that such a simple consideration yields a reasonable explanation of the observed spectrum. However, we note that the bands at 196 and 257 cm^{-1} are left unassigned and the relative intensities of 303, 400, 431, 496, and 540 cm^{-1} are not as expected. Therefore, a normal-vibration calculation is needed to facilitate a more detailed interpretation of the spectrum.

CALCULATION OF NORMAL-VIBRATION FREQUENCIES

Although it is desirable to utilize the actual molecular geometry as determined by the X-ray diffraction method,⁵ the following two simplifications were adopted here for the convenience of calculation:

(i) The methylene group is regarded as a point-mass of 14 amu.

(ii) All the C—C bond lengths and all the C—C—C bond angles are set to 1.54 Å and $109^{\circ}28'$.

These simplifications are justified because they would not affect the results of calculation appreciably in the low-frequency region in which we are most interested. In other words, since the low-frequency modes are generally not localized in any part of the molecule, the effect arising from the simplifications would be spread out. The assumed molecular model is shown in Figure 2.

In order to get a set of force constants which is effective in the present case, the calculation of normal frequencies of the planar zigzag form of n-C₃₆H₇₄ was carried out with the same simplifications for the molecular geometry, The six valence force constants finally obtained are given in Table I together with their definitions.

Table I.Valance force constants used in the
calculation^a

<i>K</i> (C–C)	4.622 md/A
H (C-C-C)	1.000 mdA
Y (int. rot.)	0.087 mdA
k (C-C, C-C)	0.132 md/A
h (C–C–C, C–C–C)	0.300 mdA
f (C-C, C-C-C)	0.170 md

* K (C-C), H (C-C-C), and Y (int. rot.) are the diagonal force constants for the C-C stretching, the C-C-C bending, and the internal-rotation coordinates, respectively. The constants k and h are, respectively, the interaction terms between the adjacent C-C stretching and the adjacent C-C-C bending coordinates. The constant f represents the interaction term between the C-C stretching and C-C-C bending coordinates attached to the same carbon atom.

The values of force constants were determined by the trial-and-error method so as to get the best fit between the calculated and observed LA frequencies. In Table II the calculated LA frequencies are compared with the observed values.

Table II. Calculated and observed frequencies of longitudinal acoustic vibrations of $n-C_{36}H_{74}$

т	Calcd freq., cm ⁻¹	Obsd freq., ^a cm ⁻¹
1	63	67
3	187	189
5	301	303
7	412	403
9	501	475

^a Observed data are taken from ref 10.

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	A_{g}		$\mathbf{B}_{\mathbf{g}}$			$\mathbf{A}_{\mathbf{u}}$		\mathbf{B}_{u}			
Free	q., cm-	¹ Mode	Free	q., cm−	¹ Mode	Free	q., c m−	¹ Mode	Free	1., cm-	¹ Mode
ν_1	563	x, z	V17	545	<i>x</i> , <i>z</i>	V32	544	<i>x</i> , <i>z</i>	V47	563	<i>x</i> , <i>z</i>
ν_2	489	end	ν_{18}	509	<i>x</i> , <i>z</i>	ν_{33}	509	<i>x</i> , <i>z</i>	v_{48}	459	<i>x</i> , <i>z</i>
ν_3	450	<i>x</i> , <i>z</i>	ν_{19}	393	<i>x</i> , <i>z</i>	ν_{34}	486	end	ν_{49}	437	x
ν_4	430	<i>x</i> , <i>z</i>	ν_{20}	370	<i>x</i> , <i>z</i>	ν_{35}	362	<i>z</i> , <i>x</i>	ν_{50}	365	x, end
ν_5	303	<i>x</i> , <i>z</i>	ν_{21}	298	<i>x</i> , <i>z</i>	ν_{36}	332	<i>x</i> , <i>y</i>	ν_{51}	315	<i>z</i> , <i>x</i>
ν_6	255	<i>z</i> , <i>x</i>	ν_{23}	257	<i>z</i> , <i>x</i>	ν_{37}	256	<i>x</i> , <i>y</i>	ν_{52}	215	z, x, y
ν_7	211	У	$ u_{23}$	209	` <i>Y</i>	ν_{38}	210	y, z	ν_{53}	210	y, z
ν_8	192	y, x, z	ν_{24}	190	У	ν_{39}	202	z, y	ν_{54}	191	У
ν_9	169	У	$ u_{25}$	173	У	ν_{40}	180	y, z	ν_{55}	161	У
ν_{10}	145	<i>x</i> , <i>y</i>	ν_{26}	145	z, x	ν_{41}	144	z, y	ν_{56}	151	y, x
ν_{11}	130	<i>x</i> , <i>z</i>	ν_{27}	121	У	ν_{42}	121	y, z	ν_{57}	145	<i>x</i> , <i>y</i>
ν_{12}	94	z, y	ν_{28}	113	У	$ u_{43} $	101	y, z	ν_{58}	90	<i>z</i> , <i>y</i>
$ u_{13}$	68	y, z	ν_{29}	53	y, z	V44	53	z, y	ν_{59}	78	y, z
ν_{14}	62	y	ν_{30}	42	z, y	ν_{45}	35	y, z	ν_{60}	61	y
ν_{15}	21	z, y	ν_{31}	17	х, у	ν_{46}	13	z, y	ν_{61}	23	y, z
ν_{16}	13	y, z							ν_{62}	14	z, y

Table III. Calculated frequencies of $C_{34}H_{68}$ in the region lower than 600 cm⁻¹

The normal-vibration frequencies of cyclic $C_{34}H_{68}$ were then calculated. The force constants related to the *gauche* linkage were set equal to those of the *trans* which are listed in Table I. The model of Figure 2 has the symmetry C_{2h} and 96 internal vibrations. These are classified into 25 A_g, 23 B_g, 24 A_u, and 24 B_u normal modes. The numerical calculation was carried out on a HITAC-5020E of the Computer Centre of the University of Tokyo using the programs developed by Shimanouchi and others.¹³

RESULTS AND DISCUSSION

Of 96 normal vibrations we are interested only in the modes which have frequencies lower than 600 cm⁻¹. Due to the simplification of reducing the methylene group to a point-mass, the results of calculations in the region higher than 600 cm^{-1} are less reliable. In the region below 600 cm^{-1} the species A_g , B_g , A_u , and B_u have 16, 15, 15, and 16 normal vibrations, respectively. The calculated frequencies of these normal vibrations are listed in Table III.

We have calculated the relative atomic displacements of each normal mode. However, since it would be too space-consuming to show the vibrational patterns of all these modes, we indicate only the directions (x, y, z) in which the atomic displacements occur. The mode in

which the atoms vibrate in the x-, and z-directions is similar to the in-plane skeletal mode (ν_5 branch) of the planar zigzag polymethylene chain.¹⁴ The mode of the y-direction corresponds essentially to the torsional vibration around the C—C bond $(\nu_9 \text{ branch})$.¹⁴ From the comparison of the calculated and observed frequencies the assignments of observed Raman bands may be made as shown in Table IV. In the first place we note that, unlike the FS Model, the 196and 257-cm^{-1} bands may be assigned on the basis of the present calculation. The vibrational patterns of the modes listed in Table IV are shown in Figures 3 to 14. It is seen from these figures that the modes corresponding approximately to the LA vibrations of m=1 (accordion vibration), 2, 3, 4, and 5 are ν_{10} (145 cm⁻¹), ν_{21} (298)

 Table IV.
 Assignments of observed Raman

 bands in the region lower than 600 cm⁻¹

Obsd freq., cm ⁻¹	Assignment			
540	v ₁ (563),	ν ₁₇ (545)		
496	ν_2 (489),	ν ₁₈ (509)		
431	ν ₄ (430)			
400	v19 (393)			
303	ν ₅ (303),	v21 (298)		
257	ν_6 (255),	v22 (257)		
196	ν ₈ (192)			
147	ν ₁₀ (145)			



Figure 3. Vibrational pattern of ν_1 . The relative atomic displacements of the portion shown by bold line in Figure 2 are indicated. The displacements of x-direction of C₄ part are indicated by $+\rightarrow$ (+direction) \leftarrow - (-direction).



Figure 4. Vibrational pattern of ν_2 .



Figure 6. Vibrational pattern of ν_5 .



Figure 7. Vibrational pattern of ν_6 .



Figure 8. Vibrational pattern of ν_8 .



Figure 9. Vibrational pattern of ν_{10} .





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Figure 11. Vibrational pattern of ν_{18} .



Figure 12. Vicrational pattern of ν_{19} .



Figure 13. Vibrational pattern of ν_{21} .



Figure 14. Vibrational pattern of ν_{22} .

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cm⁻¹), ν_4 (430 cm⁻¹), ν_{18} (509 cm⁻¹), and ν_1 (563 cm⁻¹), respectively. These frequencies may be compared with those estimated by the FS Model, viz., 153, 295, 411, 490, and 561 cm⁻¹. It is interesting that the normal-vibration calculation and the estimation by the FS Model gave frequencies quite close to each other. This seems to support the idea that the LA frequencies, particularly the accordion frequency, of the planar zigzag chain in the folded polyethylene single crystal might be estimated by the FS Model without much error. It is undoubtedly necessary, however, to check the validity of this conclusion by studying other large ring molecules. The mode ν_8 also has an accordion-vibration component. This explains the relatively strong intensity of the 196-cm⁻¹ band. The ν_6 and ν_{22} modes may be assignable to the 257-cm⁻¹ band. The intensity of this band may come from the symmetric deformation vibration of the C₄ part of ν_6 (Figure 7). It would be better to assign the 303- and 496cm⁻¹ bands to ν_5 and ν_2 , since the modes with even m numbers (ν_{21} and ν_{18}) are expected to be weak in the Raman spectrum. The ν_5 mode has the component of the LA vibration of m=3. The ν_2 mode is localized almost purely to



Figure 15. Overall vibrations of $C_{34}H_{68}$: (a), elongation; (b), breathing; (c), rhombus-type; (d), twisting; (e), trapezoid-type; (f) bending-y; (g), bending-z.

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the C_4 part. By the FS Model its frequency was estimated at 425 cm^{-1} . The higher shift of frequency from 425 to 496 cm^{-1} may be accounted for by the fact that the C_4 part is not free in the cyclic molecule. It is not unreasonable that the FS Model becomes a poor approximation for the vibrations of a short segment linking larger segments. The bands at 431 and $540 \,\mathrm{cm}^{-1}$ are assigned to the odd *m* LA vibrations (ν_4 and ν_1). As they are not pure LA vibrations (Figures 3 and 4), there is no simple estimation of their relative intensities. The 400-cm⁻¹ band is assigned to ν_{19} . The vibrational pattern of ν_{19} is rather complicated (Figure 12) and the origin of the intensity of ν_{19} is not very clear. It is noted that this mode has a component of torsional vibration of the end portion.

Next, we mention the overall vibrations (the deformations over the entire molecule). In Figure 15 the vibrational patterns of six overall vibrations are given schematically. Of these only the elongation vibration (ν_{10}) is observed at 147 cm⁻¹. The trapezoid-type vibration (ν_{57}) has the same calculated frequency with ν_{10} . This shows that the accordion-type vibrations of parallel long segments interact only weakly with each other. The other modes, viz., breathing, rhombus-type, twisting, and bending, have much lower frequencies of almost 13 to 23 cm^{-1} . The measurement of this region of the spectrum will give valuable additional information in the study of molecular structure.

In conclusion we may say that the study of the Raman spectrum of large ring molecules reveals important information regarding the lengths of planar zigzag segments. The information obtained, thereby, is also of considerable value in elucidating the molecular structure of folded single crystals.

After completing this paper (actually, after submitting it to this journal) we found a paper by Peticolas, *et al.*,¹⁵ which reported the observation of Raman bands due to the accordion vibrations of folded chains in single crystals of polyethylene. The frequencies observed are in the range 10—40 cm⁻¹, depending upon the annealing temperature. The differences between the fold lengths calculated from these frequencies and those obtained from small-angle X-ray scattering were found to be no greater than 10%. Peticolas, *et al.*, attributed the differences to end effects. Our present study on $C_{34}H_{68}$ shows that end effects (or cyclization effects) do not cause a significant change in the accordion frequency of the all-*trans* C_{15} segment. Therefore, more detailed experimental and theoretical studies are necessary to clarify whether the differences in fold lengths derived by the two methods are really due to end effects. In any case, Raman spectroscopy seems to provide a useful tool for the investigation of structures of polymer single crystals.

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