Analysis of Skeletal Deformation Vibration Spectra in Relation to the Molecular Structure

Tsunetake FUJIYAMA

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

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Deformation vibrations associated with displacements of skeletal heavy atoms are mainly discussed. It is shown that skeletal deformation vibrations are sensitive to the change of an azimuthal angle θ and that the frequencies of the vibrations are specific for the structure of rotational isomers. The θ-dependency of skeletal deformation vibrations corresponds exactly to that of elements of a kinetic energy matrix $\bar{G}$. The results emphasize the simplicity and the usefulness of the approximate normal coordinate treatment in which only skeletal heavy atoms are taken into account.

The concept of group frequencies has played an important role in the interpretation of vibration spectra, and it has contributed greatly to the progress of vibration spectroscopy. On analysing the spectra of large molecules, however, it is difficult to find those appropriate frequencies in the so-called finger print region because of the complexity of the coupling between the group frequencies and the overlapping of vibration bands. Sometimes the normal coordinate treatment affords a useful solution of the problem. However, many of the molecules which arouse great interest of chemists are composed of many atoms and the normal coordinate treatment for such molecules is often time consuming. Moreover, it is not always easy to obtain a reasonable set of force constants that can explain very complicated spectra.

A series of studies on molecular structures for various aliphatic compound showed that it is very hard to make a complete analysis of the vibration spectra of the molecules which have internal rotation axes because of their complexity. In order to overcome the difficulties we tried to find the absorption bands which are sensitive to the change of geometry of rotational isomers and are easily found in the spectra free from the overlapping of other absorption bands. The skeletal deformation vibrations are just the absorption bands satisfying the above requirements and will become still more useful with the remarkable progress in far-infrared spectrometers and laser-Raman instruments. Details of the spectral data used in the present report will be found in the references.[1-3]

Basic Concept

Intrinsic Frequency. The vibrations discussed herewith are deformation vibrations associated with displacements of skeletal heavy atoms of a given molecule. The basic concept of the vibrations will be drawn from the vibration frequencies of the CH_3CH_2X type molecules, because a molecule of this type has only one skeletal deformation vibration.

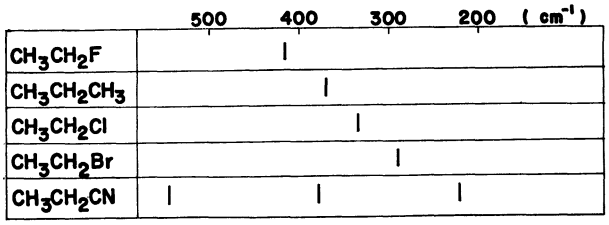

Fig. 1. Observed frequencies for CH_3CH_2X type molecules.

Figure 1 shows the observed frequencies of CH_3CH_2X type molecules. It is clear that the frequency of the deformation vibration decreases with the increase of the mass of atom X. This implies that deformation vibration frequency is determined mainly by the diagonal element of a kinetic energy matrix $\bar{G}$ corresponding to a coordinate $\Delta\alpha_{CCX}$, where $\Delta\alpha_{CCX}$ represents the change of the angle C–C–X. The calculated diagonal elements of $\bar{G}$ matrices for the CH_3CH_2X type molecules are compared with the observed deformation vibration frequencies in Table 1, where g_{CCX} denotes the diagonal element of $\bar{G}$ matrix corresponding to the coordinate $\Delta\alpha_{CCX}$ in $amu^{-1}\cdot A^{-2}$, ν the deformation vibration frequency in cm^{-1}, and A or f_{CCX} is defined by the relations

Table 1. Relation between frequencies and diagonal elements of $\bar{G}$ and $\bar{F}$ matrices of CH_3CH_2X type molecules

Molecule	ν (cm^{-1})	A (amu^{-1} A^{-1} md)	g_{CCX} ($amu^{-1}A^{-2}$)	f_{CCX} (md A)
CH_3CH_2F	415	0.103	0.168	0.61
$CH_3CH_2CH_3$	371	0.082	0.163	0.50
CH_3CH_2Cl	336	0.066	0.126	0.52
CH_3CH_2Br	290	0.053	0.115	0.46

$$A = \frac{4\pi^2 c^2}{N}\nu^2, \tag{1}$$

and

$$f_{CCX} = A/g_{CCX}. \tag{2}$$

In these equations f_{CCX} is expressed in md·A, A is in $amu^{-1}\cdot A^{-1}\cdot md$, while N and c represent the Avogadro number and the velocity of light, respectively. We see that a close relationship exists between g_{CCX} and A as expected. The observed frequencies of Fig. 1 are not assigned exactly to the CCX deformation modes, but they might be considered, to the first approximation,

1) T. Fujiyama, MA thesis submitted to the University of Tokyo (1963).

2) T. Fujiyama, Ph. D. thesis submitted to the University of Tokyo (1966).

3) Tables of Molecular Vibrational Frequencies, Part 1, U. S. Department of Commerce, N. B. S, (1967), and the references cited therein,

to be the *intrinsic frequencies* of the deformation vibrations expressed by the coordinate $\Delta\alpha_{CCX}$. The f_{CCX}'s are values calculated by Eq. (2), and not the real values of $\bar{F}$ matrices. However, the values can be used for the estimation of the intrinsic frequencies.

The frequencies of CH_3CH_2CN exhibit quite exceptional behaviour in the group, because the molecule has two extra vibrations occurring from the linear part of a cyanide group. The intrinsic frequency of a CCN bending vibration is expected to be near 370 cm^{-1}, because the degenerate CCN bending vibration of CH_3CN occurs at 370 cm^{-1}. The CCC deformation vibration and the parallel component of the CCN bending vibration have strong mutual interaction because of the closeness of their unperturbed frequencies, and separate into 544 cm^{-1} and 226 cm^{-1}, leaving the unperturbed perpendicular component of the CCN bending vibration at 378 cm^{-1}. We designate these three vibrations occurring at 544, 226, and 378 cm^{-1} as A, C, and B type vibrations of a cyanide group,

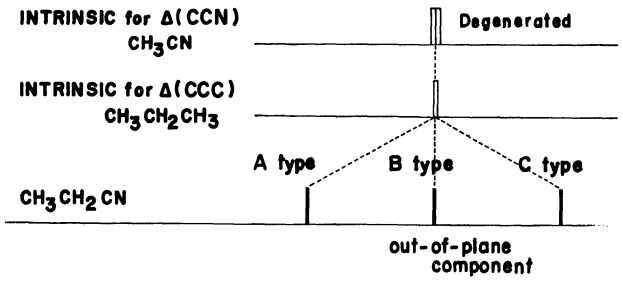

Fig. 2. Frequency diagram for CH_3CH_2CN.

respectively. Figure 2 shows the frequency diagram for CH_3CH_2CN. It seems better to classify CH_3CN into a CH_3CH_2X group rather than CH_3CH_2CN as far as skeletal deformation vibrations are concerned. Then the intrinsic frequency for a cyanide group may be chosen near 370 cm^{-1} referring to the spectra of CH_3CN. However, much clearer pictures would be obtained if one chooses the frequencies of CH_3CH_2CN as the intrinsic frequencies of cyanide compounds. The choice of an intrinsic frequency may be changed inaccordance with the characteristics of a given molecule so as to make the results of spectral analysis clearer and simpler.

Coupling between Intrinsic Frequencies. As intrinsic frequencies can be obtained from the observed frequencies of CH_3CH_2X type molecules, the next step is to estimate the feature and the degree of interaction between them.

$CH_3CH_2CH_2X$ Type Molecules: This type of molecule is expected to have two skeletal deformation vibrations corresponding to the coordinates, $\Delta\alpha_{CCC}$ and $\Delta\alpha_{CCX}$ whose intrinsic frequencies are known from the observed frequencies for $CH_3CH_2CH_3$ and CH_3CH_2X, respectively. The $\bar{G}$ and $\bar{F}$ matrices of this type of molecules are

$$G = \begin{array}{c} \begin{matrix} \text{other coordinates} & \Delta\alpha_{CCC} & \Delta\alpha_{CCX} \end{matrix} \\ \begin{pmatrix} & & \\ & g_1 & c \\ & c & g_2 \end{pmatrix} \end{array}, \qquad (3)$$

$$F = \begin{array}{c} \begin{matrix} \text{other coordinates} & \Delta\alpha_{CCC} & \Delta\alpha_{CCX} \end{matrix} \\ \begin{pmatrix} & & \\ & f_1 & \\ & & f_2 \end{pmatrix} \end{array}, \qquad (4)$$

where the matrix elements g_1 and f_1 are associated with the coordinate $\Delta\alpha_{CCC}$, g_2 and f_2 are associated with the coordinate $\Delta\alpha_{CCX}$, and c is the cross term of the coordinates $\Delta\alpha_{CCC}$ and $\Delta\alpha_{CCX}$. Of these five elements, only c depends on the angle θ through the relation:

$$c = \text{Constant} \times \cos\theta, \qquad (5)$$

where θ is the azimuthal angle of the skeleton C–C–X.

Consider, to a first approximation, the two dimensional parts of the matrices $\bar{G}$ and $\bar{F}$, which are indicated in Eqs. (3) and (4). The frequencies of the two deformation vibrations are then expressed as

$$\nu_{\pm} = [(g_1f_1+g_2f_2) \pm \sqrt{(g_1f_1-g_2f_2)^2+4c^2f_1f_2}]/2. \qquad (6)$$

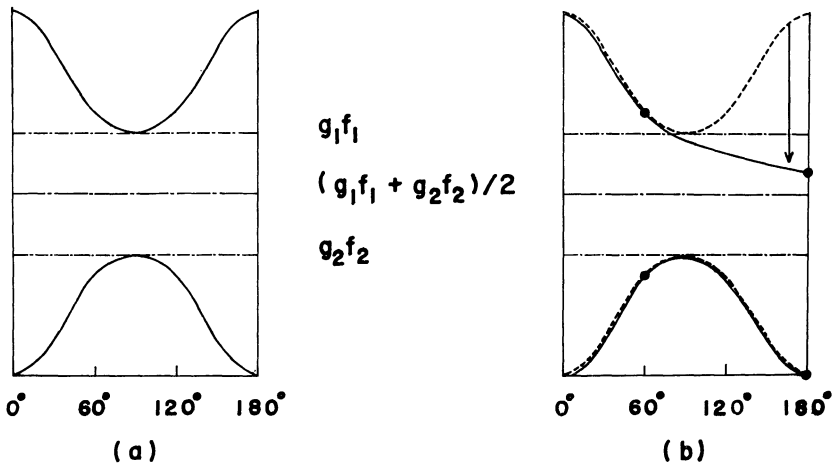

Fig. 3. θ-dependency of skeletal deformation vibration.
(a) Effect of deformation-deformation interaction.
(b) Effect of stretching-deformation interaction.

Equation (5) shows that the element c is zero when θ is 90° and has the largest value when θ is 0° or 180°. Thus, we can understand from Eq. (6) that frequency separation of these two vibrations, $\nu_+ - \nu_-$, is the largest for $\theta=0°$ or for $\theta=180°$ and the smallest for $\theta=90°$. Figure 3(a) shows the θ-dependency for the skeletal deformation frequencies. If c is zero, ν is either g_1f_1 of g_2f_2, which is the intrincis frequency associated, respectively, with $\Delta\alpha_{CCC}$ or $\Delta\alpha_{CCX}$.

The effects of the other vibrations such as a stretching vibration of C-X bond are considerable in this case. In addition to deformation-deformation interaction, we have to consider the effect of stretching-deformation interaction. It is known that the effect of the latter interaction if remarkable when azimuthal angle θ takes a value larger than 90°.[5] Usually the frequency of C–X stretching vibration is higher than those of deformation vibrations. Therefore the effect is remarkable only for ν^+ of Eq. (6). Thus, the θ-dependency of the skeletal deformation frequencies of $CH_3CH_2CH_2X$ type molecules leads to that shown in Fig. 3 (b).

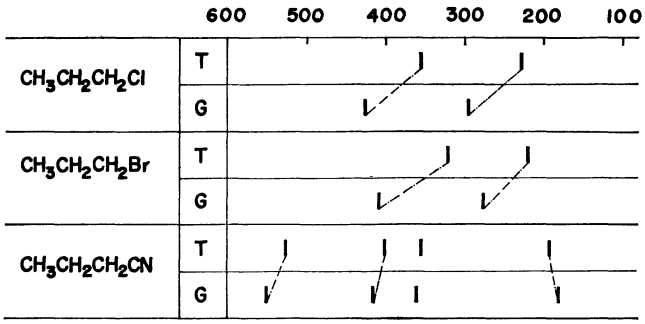

Fig. 4. Observed frequencies for $CH_3CH_2CH_2X$ type molecules.

The observed skeletal deformation frequencies of the $CH_3CH_2CH_2X$ type molecules are summarized in Fig.4. Recall that *trans* (hereafter T) and *gauche* (hereafter G) forms of these molecules correspond to the values of azimuthal angles of 180° and 60°, respectively. Then the correspondence of Fig. 3(b) and Fig. 4 is most striking.

For $CH_3CH_2CH_2CN$, it is convenient to consider the coupling between the intrinsic frequencies taken from CH_3CH_2CN and the additional intrinsic frequency taken from $CH_3CH_2CH_3$. In this case, it is sufficient to consider the interaction between the A and the C type vibrations of cyanide group and the intrinsic vibration for $\Delta\alpha_{CCC}$; the type B vibration of cyanide group is perpendicular to the plane of the skeleton. The interaction of the A and the C type vibrations with the additional $\Delta\alpha_{CCC}$ vibration is also very small, because these frequencies are well separated from each other. One remarkable change thus expected is a slight lowering of the frequency of the type A deformation for the T form due to the stretching-deformation interaction. Figure 5 shows the frequency diagram for $CH_3CH_2CH_2CN$.

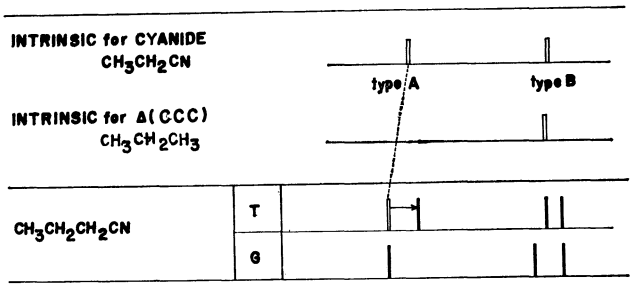

Fig. 5. Frequency diagram for $CH_3CH_2CH_2CN$.

It is interesting to note that the stretching-deformation interaction pushes the C–X stretching vibration of T form up to higher frequency side. This situation explains the well-known empirical rule which correlates molecular conformation and the C–Cl stretching frequencies.[4]

XCH_2CH_2X Type Molecules: The deformation vibrations of these molecules are analyzed satisfactorily by taking into account the two vibrations corresponding to the coordinates $\Delta\alpha_{CCX}$'s. Therefore, a similar approach used in the last section may be applied for this case. The only difference comes from the fact that the two intrinsic frequencies are identical, *i.e.*, $g_1f_1=g_2f_2$. Thus, the extent of coupling becomes most sensitive for

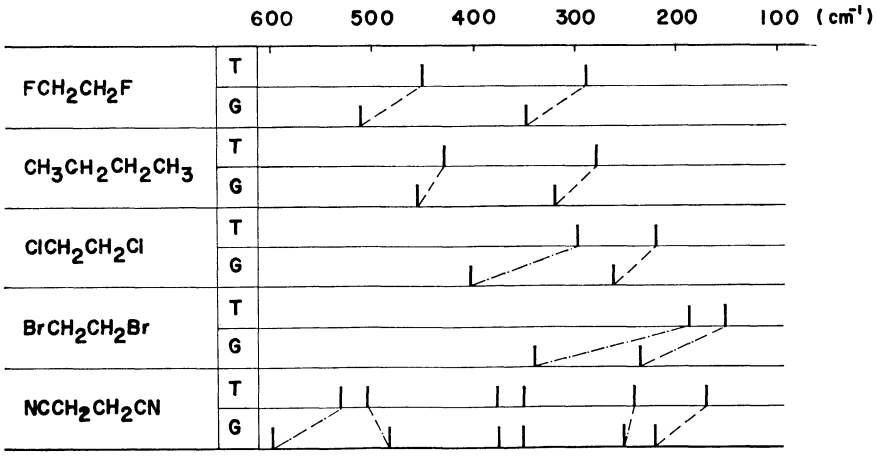

Fig. 6. Observed frequencies for XCH_2CH_2X type molecules.

4) T. Shimanouchi, S. Tsuchiya, and S. Mizushima, *J. Chem, Phys.*, **30**, 1365 (1959).

5) Here, the term stretching is used symbolically. The frequency of the stretching vibration under consideration is the lowest of all the other vibrations which interact with skeletal deformation vibrations indirectly. For a complete description of the deformation-stretching interaction, see I. Nakagawa, *Nippon Kagaku Zasshi*, **76**, 813 (1955), and the related reports cited therein.

the change of the element c of Eq. (6). Figure 6 shows the observed frequencies for XCH_2CH_2X type molecules and the close similarity of Fig. 4 and Fig. 6 is quite obvious.

For succinonitrile, the vibration frequencies of type A and type C exhibit similar patterns, respectively, in the 600—500 cm^{-1} and the 250—150 cm^{-1} regions. The B type vibrations locate in the region of 350—380 cm^{-1} and change their frequencies little for all θ.

Application to More Complicated Molecules

$XCH_2CH_2CH_2X$ Type molecules. This type of molecule has three skeletal deformation vibrations associated with the coordinates $\Delta\alpha^1_{CCX}$, $\Delta\alpha_{CCC}$, and $\Delta\alpha^2_{CCX}$. The submatrix of $\bar{G}$ corresponding to the three deformation coordinates is given as:

$$\bar{G} = \begin{array}{c} \begin{matrix} \Delta\alpha_{CCC} & \Delta\alpha^1_{CCX} & \Delta\alpha^2_{CCX} \end{matrix} \\ \begin{pmatrix} A & & \\ C_1 & B & \\ C_2 & D & B \end{pmatrix} \end{array}, \qquad (7)$$

where A and B are independent of θ, C_1, C_2, and D are related with θ by the relations:

$$C_1 = \text{Constant} \times \cos\theta_1, \qquad (8)$$

$$C_2 = \text{Constant} \times \cos\theta_2, \qquad (9)$$

and $$D = \text{Constant}\,(\sin\theta_1 \sin\theta_2 - (1/3)\cos\theta_1 \cos\theta_2). \qquad (10)$$

In these equations, θ_1 and θ_2 are two azimuthal angles made by the skeleton of $XCH_2CH_2CH_2X$ and the coefficients are calculated by assuming all the valence angles are tetrahedral. For this case we may well consider the coupling of the skeletal deformation vibrations in two steps, of which the first is the interaction between $\Delta\alpha^1_{CCX}$ and $\Delta\alpha^2_{CCX}$. The second is that between $\Delta\alpha_{CCC}$ and the two resultant vibrations from the first step. The matrix element D plays a dominant role in the first stage, while C_1 and C_2 do in the second process. If we use the matrix expression, the first process corresponds to stransforming the three deformation coordinates by an unitary matrix $\bar{U}$, where

$$\bar{U} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \qquad (11)$$

After the trasformation, the matrix **G** of Eq. (7) becomes

$$\bar{G}_s = \bar{U}\bar{G}\tilde{\bar{U}} = \begin{array}{c} \begin{matrix} S_1 & S_2 & S_3 \end{matrix} \\ \begin{pmatrix} A & & \\ (C_1+C_2)/\sqrt{2} & B+D & \\ (C_1-C_2)/\sqrt{2} & 2 & B-D \end{pmatrix} \end{array} \qquad (12)$$

and the relation between the two sets of coordinates is

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \bar{U} \times \begin{pmatrix} \Delta\alpha_{CCC} \\ \Delta\alpha^1_{CCX} \\ \Delta\alpha^2_{CCX} \end{pmatrix} \qquad (13)$$

Consider the three rotational isomers, TT, TG, and GG of the $XCH_2CH_2CH_2X$ type molecules, then the magnitude of D is calculated for these three rotational isomers from Eq. (10) as:

$$D(\text{TT}) : D(\text{TG}) : D(\text{GG}) = 2 : 1 : 4.$$

Thus the frequency separation due to the first step coupling is expected to be that of Fig. 7.

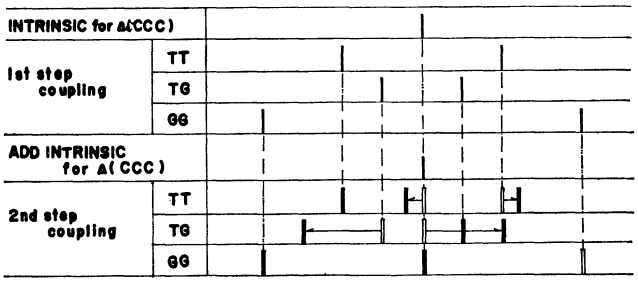

Fig. 7. Frequency diagram for $XCH_2CH_2CH_2X$ type molecules.

The second step is explained by the magnitude and the θ-dependency of C_1 or C_2. The magnitudes of (C_1+C_2) and (C_1-C_2) give the measures of coupling between S_1 and S_2, or between S_1 and S_2, respectively. Referring to the calculated C_1 and C_2 values and to the intrinsic frequency of S_1 obtained from $CH_3CH_2CH_3$, we can expect the frequencies of $CH_3CH_2CH_2CH_2CH_3$, the results of which are shown in Fig. 7. In fact, the observed frequencies given in Fig. 8 for pentane follow the expected pattern reasonably.

As for $NCCH_2CH_2CH_2CN$, the first step coupling is essential, because the intrinsic frequencies for cyanide groups are far apart from that of the intrinsic frequency for $\Delta\alpha_{CCC}$. Both the A type and the C type frequencies of cyanide groups exhibit the patterns quite close to that expected from the first step interaction. They are found, respectively, in the region of 600—400 cm^{-1} and of 200—100 cm^{-1}. The frequencies observed in the region of 400—300 cm^{-1} correspond to the $\Delta\alpha_{CCC}$ and type B vibrations of cyanide groups.

From the analogy of the cyanide compounds, it is convenient to designate the frequencies separated into the higher and the lower frequency regions by the first step coupling as A type and C type deformation vibrations, respectively, and to designate the additional

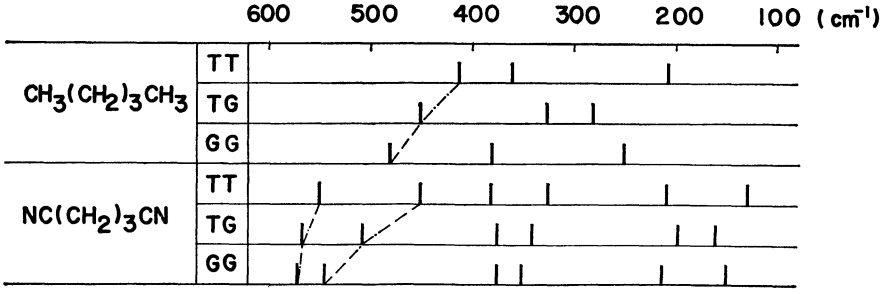

Fig. 8. Observed frequencies for $XCH_2CH_2CH_2X$ type molecules.

intrinsic frequencies for the second step coupling as B type deformation vibration. Generally, the deformation vibrations of type A occur in the region around 600—400 cm^{-1} and are appropriate vibration to study molecular conformation. The frequencies of the A type vibrations are moderately sensitive to the change of azimuthal angles and their relative locations originated from different rotational isomers are fairly analogous with different molecules. On the other hand, the B and the C type vibrations are not always useful for the purpose. Although the C type vibrations are also sensitive to the molecular geometry, the coupling effects with torsional vibrations spoil the structural specificity of the spectral pattern. The frequencies of B type vibrations are almost the same as those of intrinsic freuqencies and, therefore, insensitive to molecular structures. The spectral analysis of CH_3-$CH_2CH_2CH_2Cl$ is the most striking example demonstrating this conclusion.

$CH_3CH_2CH_2CH_2Cl$: This molecule has five possible rotational isomers, TT, GT, TG, GG, and GG'. A similar approach used in the last section is applicable to this case.

The matrix element D of Eq. (7) changes its magnitude in accordance with the conformation of the molecule. The magnitude of D is calculated for the five possible rotational isomers from Eq. (10) as:

$$D(\mathrm{TT}):D(\mathrm{GT}):D(\mathrm{TG}):D(\mathrm{GG}):D(\mathrm{GG}') = 2:1:1:4:5$$

Thus, the general pattern of the frequency separations due to the first step coupling is expected to be that of

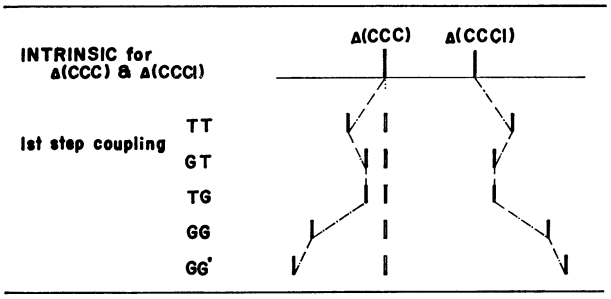

Fig. 9. Frequency diagram for $CH_3CH_2CH_2CH_2Cl$.

Fig. 9. If we neglect the second step interaction, it is clear that the A type vibrations occur in the region around 500—400 cm^{-1}. With reference to the A type vibrations of $CH_3CH_2CH_2CH_2CH_3$ of Fig. 8, the highest and the lowest frequencies of the A type vibrations of $CH_3CH_2CH_2CH_2Cl$ are expected, respectively, to be 500 cm^{-1} and 370 cm^{-1}, since the intrisic frequency for $\Delta\alpha_{CCCl}$ is lower than that of $\Delta\alpha_{CCC}$. The frequency diagram of Fig. 7 indicates that the A type vibrations of GT and TG forms are shifted to the higher frequency side by the second step coupling effect. Thus, the A type vibrations of this molecule are expected to occur in the frequency order:

$$\nu(\mathrm{GG}') > \nu(\mathrm{GG}) > \nu(\mathrm{TG}) \gtrsim \nu(\mathrm{GT}) > \nu(\mathrm{TT}).$$

Figure 10 shows the observed infrared spectra of liquid $CH_3CH_2CH_2CH_2Cl$ in the region of 700—200 cm^{-1}. Actually, four bands are seen in the A region of the spectra, namely 472, 456, 435, and 380 cm^{-1}. This

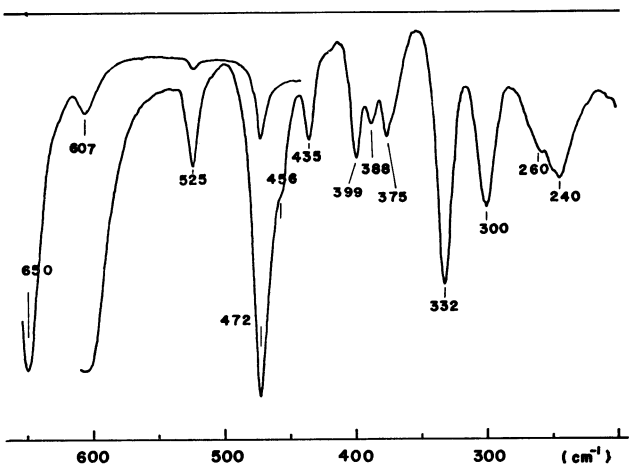

Fig. 10. Infrared spectra of liquid $CH_3CH_2CH_2CH_2Cl$ in the region of 700—200 cm^{-1}.

indicates the existence of at least four rotational isomers in liquid $CH_3CH_2CH_2CH_2Cl$. A more detailed analysis of the spectra including the B and the C type vibrations will be reported elsewhere.

Molecules Having Side Chains. We have discussed so far the normal chain molecules. The skeletal deformation vibrations of molecules having side chains are also interesting. The intrinsic frequencies of these molecules are reasonably obtained from the vibration spectra of $(CH_3)_2CHX$ type molecules.

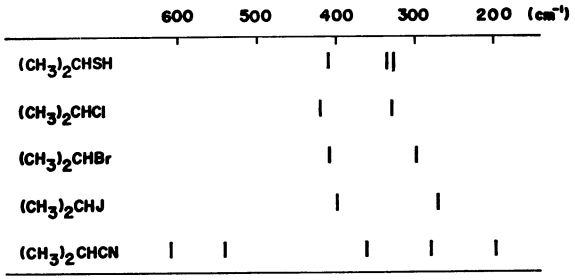

Fig. 11. Observed frequencies for $(CH_3)_2CHX$ type molecules.

$(CH_3)_2$ CHX type molecules: The observed frequencies for the molecules of this type are summarized in Fig. 11. These molecules have three skeletal deformation vibrations, of which two are of the species A' and the other is of the species A''. The A'' vibration which is called an out-of-plane bending vibration is expected to show strong frequency dependency on the mass of X atom. The A' vibrations are assigned either to CH_3–C–CH_3 bending or to inplane C–X bending vibration. It is seen from Fig. 11 that the former exhibit almost the same frequency regardless of the X atom. The slight difference in frequency may be attributed to the effect of the intraction with the C–X stretching vibration.

For $(CH_3)_2CHCN$ also, the intrinsic frequencies can be found as is the case for CH_3CH_2CN. Define the internal coordinates, $\Delta\alpha_1$, $\Delta\alpha_2$, $\Delta\alpha_3$, $\Delta\beta_s$, and $\Delta\beta_p$, which are associated with the skeletal displacements of $(CH_3)_2CHCN$ molecule, then the symmetry coordinates which define the approximate vibrational modes of the molecule are:

$$S_1 = (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)/\sqrt{6}$$
$$\sqrt{2}S_2 = (\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3)/\sqrt{3} - \Delta\beta_p,$$
$$\sqrt{2}S_3 = (\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3)/\sqrt{3} + \Delta\beta_p, \quad (14)$$
$$\sqrt{2}S_4 = (\Delta\alpha_2 - \Delta\alpha_3)/\sqrt{2} - \Delta\beta_s,$$
and $$\sqrt{2}S_5 = (\Delta\alpha_2 - \Delta\alpha_3)/\sqrt{2} + \Delta\beta_s,$$

where $\Delta\alpha_1$ corresponds to the change of an angle CH_3–C–CH_3, $\Delta\alpha_2$ and $\Delta\alpha_3$ to those of CH_3–C–CN, and $\Delta\beta_s$ and $\Delta\beta_p$ to the parallel and the perpendicular bending of C–C≡N part, respectively. The coordinates, S_1, S_2, and S_3, belong to A' species, while S_4 and S_5 to A'' species. The S_2 and the S_4 vibrations are called A type intrinsic vibrations of a cyanide group and occur in the region of 600—550 cm^{-1}. The S_3 and the S_5 vibrations are called C type vibrations of a cyanide group and occur in the region of 300—100 cm^{-1}. The CH_3–C–CH_3 deformation vibration occurring at 360 cm^{-1} corresponds to the coordinate S_1 and is called B type vibration. The frequency of the B type vibration is close to the intrinsic frequency of $\Delta\alpha_{CCC}$ for normal chain molecules. These five frequencies of $(CH_3)_2$-CHCN molecule can be chosen as the intrinsic frequencies of the cyanide group attached to a secondary carbon atom, the details of which are seen in the lower part of Fig. 13.

$CH_3CH(CN)CH_2CH_3$: 2-cyanobutane is chosen as an appropriate example of application to secondary substituted molecules with an internal rotation axis. In addition to the five intrinsic frequencies obtained from $(CH_3)_2CHCN$, it is enough to consider one skeletal deformation vibration corresponding to the coordinate $\Delta\alpha_{CCC}$, whose intrinsic frequency is supposed to be near 370 cm^{-1}. The first step coupling takes place between the two vibrations, $\Delta\alpha_{CCC}$ at 370 cm^{-1} and the B type vibration of $(CH_3)_2CHCN$ at 360 cm^{-1}. As already discussed, this type of coupling has the most serious effect on frequencies when the molecule takes T form. The second step coupling corresponds to the interaction of the A type vibrations of cyanide part with the resultant vibrations from the first step interaction. The effect of the interaction is strong when the molecule takes G form both for the out-of-plane and the in-plane vibrations of the type A. When the molecule takes T conformation, the frequency shift due to the coupling is expected to be very small, so that the vibration of the A type would not be affected much. Thus, we can expect the frequency diagram of this molecule as shown in Fig. 12.

Figure 13 shows the observed inrfared spectra of liquid 2-cyanobutane in the region of 700—100 cm^{-1} together with the skeletal deformation frequencies of $(CH_3)_2CHCN$ at the bottom. From the spectra the existence of at least two rotational isomers is concluded because there appear thirteen bands in the region of 600—100 cm^{-1} when only six skeletal deformation vibrations are expected for each rotational isomer. It is seen in the figure that there exist four bands with strong intensities in the 600—500 cm^{-1} region where the A type vibrations of cyanide group are expected to occur. The bands at 577 cm^{-1} and 528 cm^{-1} increase their relative intensities in the low temperature spectra, while those at 602 cm^{-1} and at 555 cm^{-1} follow the reverse tendency. This implies that those frequencies correspond, in pairs, to the stable rotational isomers T and G. From the frequency diagram of Fig. 12, we may conclude that the pair at 577 and 528 cm^{-1} is assigned to that of T form, while the pair at 602 and 555 cm^{-1} is assigned to that of G form. It is also understood that the T form is a more stable rotational isomer. It should be noticed that two bands are found at 666 and 492 cm^{-1} in the spectra of Fig. 13. These may also be of the A type and may be assigned to the rotational isomer G which is assumed to be most unstable form. In fact, the bands disappear in the low temperature spectra.

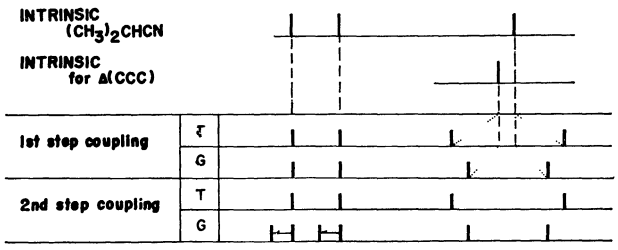

Fig. 12. Frequency diagram for $CH_3CH(CN)CH_3CH_2$.

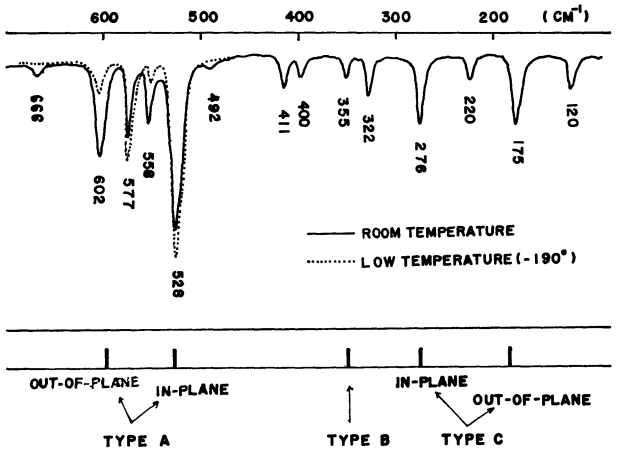

Fig. 13. Infrared spectra of liquid $CH_3CH(CN)CH_2CH_3$. Solid line: room temperature, Dotted line: low temperature (−190°C, glass) Bottom: observed frequencies for $(CH_3)_2$-CHCN.

Discussion

It was shown in the former sections that the molecular conformations of same complicated molecules could be determined by the analyses of skeletal deformation vibrations. The process of the analysis may be summarized as follows.

(a) Find the intrinsic frequencies from the simpler molecules which have the similar chemical structures or substituents as those of molecules in question. The molecules suitable for this purpose are of the type CH_3CH_2X, $(CH_3)_2CHX$, and $(CH_3)_3CX$. The choice of the intrinsic frequencies should be made so as to make the analyses simpler.

(b) Consider the coupling between the intrinsic frequencies. The frequency shift due to the coupling can be estimated from the off-diagonal elements of

$\bar{G}$ matrix associated with the two coordinates of the intrinsic frequencies in question.

(c) We may consider the couplings in several steps. The resultant frequencies from one interaction step will play a role as the intrinsic frequencies in the next process.

(d) When the matrix elements of $\bar{G}$ depend on the azimuthal angle θ, the frequencies involved are naturally θ-dependent. When the diagonal elements of the deformation coordinates involved have θ-dependency, it is not very hard to determine the structure of the molecule by comparing the observed frequencies with the expected values for skeletal deformation frequencies. Therefore, when off-diagonal elements of $\bar{G}$ matrix are θ-dependent, it is desirable to make transformation which brings the θ-dependency into the diagonal parts.

(e) Sometimes it is necessary to take into account the effect of the stretching vibrations, the frequencies of which are located close to those of the skeletal deformation vibrations. The effect is important when the substituents X are composed heavy atoms, because the stretching vibration frequencies come close to those of the skeletal deformations. The effects are often θ-dependent.

(f) Throughout the analyses, a $\bar{F}$ matrix is tacitly assumed to be diagonal. The validity of the assumption can hardly be guaranteed theoretically, but the good correspondence between the expected and the observed spectral patterns indicates the practical usefulness of the method.

The above discussions lead to the very important conclusion about the normal coordinate treatment of complicated molecules. It is good enough to take into account the skeleton of a given molecule in the calculation, if the determination of the molecular structures of rotational isomers is the main object of the calculation. In that case the force constants used for the calculations are purely empirical parameters appropriate to explain the vibration frequencies produced by the displacements of heavy atoms. Mostly it is possible to choose the suitable set of force constants to explain spectra of skeletal deformation region. The simplicity and usefulness of such treatment may easily be understood by considering the size of the secular determinant to be solved. In the case of *n*-butylchloride, for example, the determinant is 36 in its order if all the atoms were considered, while mine order matrix is necessary if we neglect the light atoms.

It must be emphasized here, however, that the estimated frequencies from the above processes are of course not exact. It is always necessary to compare the expected frequencies with the observed as a group or as a pattern. Vital to this type of work is the isolation of the bands originating from one rotational isomer from those of the others. This can be done by examining the effects of temperature and of solvents on the spectra as well as by observing the spectra in various phases.

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