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COMMISSION ON
MOLECULAR STRUCTURE AND SPECTROSCOPY
in conjunction with
THE SCIENCE COUNCIL OF JAPAN

# MOLECULAR STRUCTURE AND SPECTROSCOPY

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Special Lectures

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# SPECIAL LECTURES

# JAPANESE RESEARCHES ON INTERNAL ROTATION

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## INTRODUCTION

Researches on internal rotation have been made in Japan, for the most part at the University of Tokyo, for the past thirty years. The substances studied range from very simple ones to polymers, including those of biological interest. Thus, it is impossible to refer to all of the researches in a paper of this size. The author, therefore, directs attention to a few groups of substances, and explains the experimental results briefly so that he can outline the basic idea for this series of researches.

One of the incentives for starting these researches was provided by the study on the anomalous dispersion and absorption of undamped short electric waves made by the author[1-3] in the 1920's. The refractive index of some substances drops from a large value in the radio frequency region to a much smaller value in the infra-red region, the latter values being not much different from those usually observed in the visible region. This result was explained more reasonably by the dipole theory of Debye than by the electron theory of Schrödinger. In a simple case the dispersion is caused by the orientation of a dipole molecule as a whole, but the situation becomes more complicated if the molecule has an axis of internal rotation. Thus we became interested in studying the rotation of two halves of a molecule relative to each other, a rotation which organic chemists supposed for some time to be completely free. As will be shown below, there are actually several potential minima in one complete rotation giving rise to rotational isomers, but they are usually not separable from each other, as the potential barrier hindering the internal rotation is so low that the equilibrium among the isomers is readily reached.

## RAMAN EFFECT AND INFRA-RED ABSORPTION

It will be convenient to start the discussions with the experimental results obtained with symmetrical 1,2-dihalogenoethanes, $XH_2C—CH_2X$, in the solid state[7, 14, 15]. The Raman and infra-red bands are considerably decreased in number on solidification, and the frequencies of the Raman bands are found to be completely different from those of the infra-red bands[31]. In other words, the alternate exclusion principle holds for those two kinds of spectra. This shows that molecules in the solid state are in a form which has a centre of symmetry as shown in *Figure 1a*. Let us call this form the *trans* form.

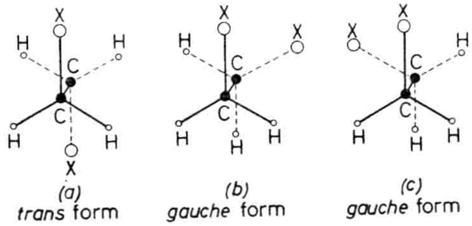


*Figure 1.* Stable molecular forms of $XH_2C—CH_2X$

The normal modes of vibrations of this form were calculated, and the observed Raman frequencies were shown to correspond to the symmetric vibrations to the centre, and the observed infra-red frequencies to the anti-symmetric vibrations[6, 43, 47]. In the case of molecules of the type of $XH_2X—XH_2Y$, the alternate exclusion principle no longer holds, but the normal vibration calculation shows that the molecules in the crystalline state exist only in the *trans* form.

In the gaseous and liquid states many other bands are observed in addition to those of the bands in the solid state (see *Figure 2*). Some of them were shown to be the forbidden bands of the *trans* form which became active due to the deformation of molecules in the liquid state[23]. However, many of them arise from the vibrations of other molecular forms, the azimuthal angles of which differ from that of the *trans* form by *ca.* ±120° [19, 43, 48]. They are called the *gauche* forms (see *Figure 1*). There are two different *gauche* forms which are non-superposable mirror images and, therefore, each of them is an optially active form. It is interesting that the ligand $NCS{\cdot}CH_2–CH_2{\cdot}SCN$ in the platinum complex was shown to adopt the *gauche* form[79]. This gives rise to an optical activity of a new type which would not exist if the ligand

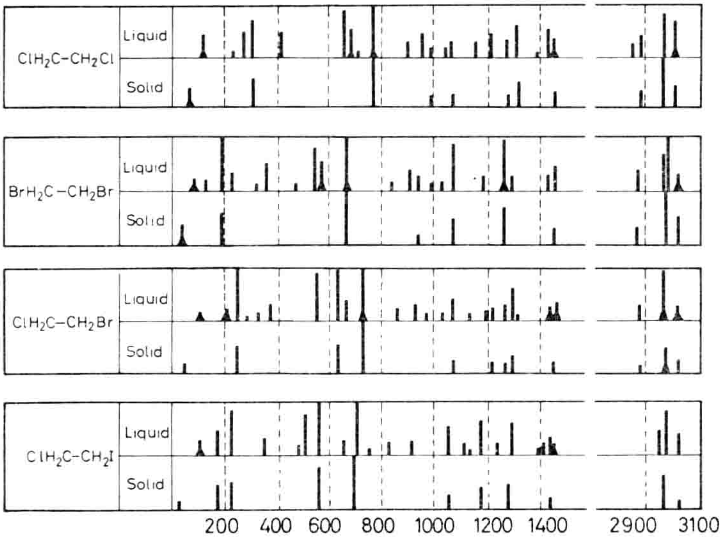


*Figure 2.* Raman lines of $XH_2C—CH_2Y$ in the liquid and solid states

were in the *cis* form, as has been tacitly assumed in classical coordination chemistry.

Some trisubstituted ethanes are expected to have three kinds of rotational isomers. This was shown to be actually the case for $ClCH_2CHClCH_3$ and $CH_3CHClCH_2CH_3$[85].

In our normal vibration calculations[43] a reasonable type of potential function was used with transferable force constants[65]. By this and also by the product and sum rules for rotational isomers found by us[43], the azimuthal angles of the *gauche* form could be determined by the spectroscopic method. The result was nicely confirmed by other experimental methods to be described below. Furthermore, the nature of each vibration was determined by calculating the distribution of potential energy among symmetry coordinates[83].

For the gaseous 1,2-dichloroethane the rotation–vibration spectrum was also measured and the assignment of the observed frequencies was confirmed by studying the fine structure, or the envelope of the bands[60].

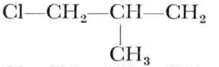
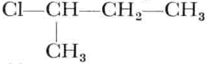
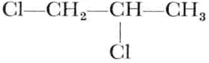
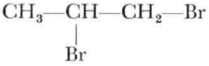
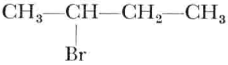
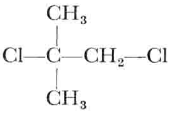
It is to be noted that the normal vibration calculations referred to above were made for the *trans* and *gauche* molecules without taking into account the torsional vibrations about the axis of the C—C bond. These make the most significant contribution to the specific heat and entropy at low temperatures, and also provide us with information for the height of the potential barrier hindering the internal rotation. Therefore, the determination of these values is one of the most important problems in the investigation of internal rotations.

The Raman lines at 125 $cm^{-1}$ and 91 $cm^{-1}$ of $ClH_2C—CH_2Cl$ and $BrH_2C—CH_2Br$, respectively, in the liquid state are concluded to be the torsional frequencies of the *gauche* forms, the corresponding vibrations of the *trans* form are inactive in the Raman effect, but could be observed as absorption in the far infra-red region: 122 $cm^{-1}$ (gas) and 134 $cm^{-1}$ (liquid) for $ClH_2C—CH_2Cl$ and 118 $cm^{-1}$ (gas) and 127 $cm^{-1}$ (liquid) for $BrH_2C—CH_2Br$[58].

So far only the values of frequencies have been discussed in relation to the internal rotation. In addition to these studies, intensities of Raman and infra-red bands have been measured at different temperatures and in various states[31, 44, 51]. From these measurements the change of the ratio of the *trans* and *gauche* molecules with temperature was determined, hence also the energy difference between the two forms (see *Table 1*). From *Table 1* it is seen that the energy difference depends considerably on the states. For example, that of the *trans* and *gauche* molecules of $ClH_2C—CH_2Cl$ in the gaseous state is 1·14 kcal/mole, whereas it is almost zero in the liquid state. This is explained as being due to the interaction between a molecular dipole and its induced moment in the surrounding media in the liquid state. The interaction was calculated to be 1·0 kcal/mole for the *gauche* molecule, whereas it vanishes for the *trans* molecule with no moment[26]. For this reason the *gauche* molecule is decreased in energy and becomes as stable as the *trans* molecule in the liquid state.

It is to be noted that although a considerable intensity change of vibration bands was found with change of state, the values of the frequencies are almost constant in all states. This means that the molecular forms (or

*Table* 1. Stable configurations of rotational isomers (*T* denotes the *trans* form and *G* the *gauche* form; figures in parentheses attached to the less stable isomers denote the energy difference in kilocalories per mole)

| *Molecule* | *Solid* | *Liquid* | *Gas* |
|---|---|---|---|
| $ClH_2C{-}CH_2Cl$ | *T* | *T*, *G*(*ca.* 0) | *T*, *G*(1·14) |
| $BrH_2C{-}CH_2Br$ | *T* | *T*, *G*(0·73) | *T*, *G*(1·70) |
| $ClH_2C{-}CH_2Br$ | *T* | *T*, *G*(0·42) | *T*, *G*(1·46) |
| $ClH_2C{-}CH_2I$ | *T* | *T*, *G* | |
| $CH_3CH_2{-}CH_2CH_3$ | *T* | *T*, *G*(0·8) | *T*, *G* |
| $CH_3CH_2{-}CH_2Cl$ | *T* | *T*, *G*(*ca.* 0) | *T*, *G* |
| $CH_3CH_2{-}CH_2Br$ | *T* | *T*, *G*(*ca.* 0) | *T*, *G*(*ca.* 0) |
| $HOH_2C{-}CH_2Cl$ | *G* | *G*, *T* | *G*, *T*(0·95) |
|  $Cl{-}CH_2{-}\underset{\underset{CH_3}{\vert}}{CH}{-}CH_2$ | — | — | *T*, $G_I$(0·2) |
|  $Cl{-}\underset{\underset{CH_3}{\vert}}{CH}{-}CH_2{-}CH_3$ | — | *T*, $G_I$ | *T*,$G_I$(0·7) |
|  $Cl{-}CH_2{-}\underset{\underset{Cl}{\vert}}{CH}{-}CH_3$ | — | *T*, $G_I$(0·2), $G_{II}$(0·9) | *T*, $G_I$(1·2), $G_{II}$(1·9) |
|  $CH_3{-}\underset{\underset{Br}{\vert}}{CH}{-}CH_2{-}Br$ | — | *T*, $G_I$(1·0) | *T*, $G_I$(1·7) |
|  $CH_3{-}\underset{\underset{Br}{\vert}}{CH}{-}CH_2{-}CH_3$ | — | — | *T*, $G_I$(0·7), $G_{II}$(1·3) |
|  $Cl{-}\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}{-}CH_2{-}Cl$ | *T* | *T*, *G*(*ca.* 0) | *T*, *G*(less stable) |

conformations) of rotational isomers are not much affected by neighbouring molecules, although their relative energies change considerably with surrounding media.

## DIPOLE MOMENT

The measurement of the dipole moment was our first experimental step towards the investigation of internal rotation[5]. This alone provides us with information on the mean state of internal rotation[8–16]. However, since the existence of rotational isomers was established by the spectroscopic studies, the dielectric data can be used for the determination of the relative amount of rotational isomers, provided that each of them has a different dipole moment[20, 50, 104].

For example, the apparent change of dipole moment of $ClH_2C{-}CH_2Cl$ with temperature is explained as due to the change of the relative number of *trans* and *gauche* molecules, where the *trans* molecule has no, or almost no, moment and the observed dipole moment arises from the dielectric contribution of the *gauche* molecule. Therefore, the dielectric data can be used for the calculation of the energy difference between the rotational isomers, and the result is found to be in good agreement with those of the intensity measurements explained above[22]. Similar studies have been made for many other substances in the gaseous state as well as in non-polar dilute solutions.

The chair form and the boat form of the cyclohexane ring arise from the different internal rotation states about the C—C axis. The molecular structure of various cyclohexane derivatives has been studied in relation to this problem by dielectric measurements as well as by spectroscopic investigations[106]. It may not be out of place to mention that the explanation given of the dielectric measurement on some 1,4-disubstituted cyclohexanes is wrong. For example, the dipole moment of 1,4-cyclohexanedione was reported to be very large (1·4D) and, consequently, a large number of molecules would appear to be in the boat form. However, this was based on the assumption that the atomic polarization is small as is usually the case. However, this does not hold in this case, because a low frequency deformation vibration anti-symmetric to the centre of the chair form absorbs very strongly (due to the large moment of the C=O group) and the atomic polarization will become very large. In other words, even if all the molecules are in chair form, the result of the dielectric measurement may still be explained satisfactorily.

## ELECTRON DIFFRACTION

Electron diffraction investigations in the gaseous state were made in order to see if experimental results compatible to those of spectroscopic and dielectric measurements could be obtained[25, 29, 97–103]. For example, for $ClH_2C—CH_2Cl$, the observed intensity maxima and minima are expected to appear at such positions as to coincide with those of the theoretical intensity curves calculated for the mixture of the *trans* and *gauche* isomers. Actually, of the theoretical curves calculated for various compositions of rotational isomers, that of the molar fraction obtained from the spectroscopic and dielectric measurements was found to be in good agreement with the result of diffraction experiments[25].

Diffraction investigations can also be applied in determining the height of the potential barrier hindering the internal rotation[95, 96]. For example, for $Cl_3C–CCl_3$ in the staggered form and with high potential barrier, the torsional motion is separable from other motions and, therefore, from the observed total mean amplitude, that for the Cl · · · Cl pair can be obtained by subtraction. It turns out that that of the *gauche* Cl · · · Cl pair is sensitive to the barrier height and thus its value is calculated as 10·8 kcal/mole. For $Cl_3Si–SiCl_3$ with low barrier, the scattering intensity of a molecular model is calculated, taking weighted average over-all values of internal rotation angle. The height of the barrier is found to be 1 kcal/mole which corresponds to almost free rotation in agreement with spectroscopic investigations. It is interesting that for $Cl_3Si—CCl_3$ an intermediate barrier height of 4·3 kcal/mole was obtained[96].

## ENTROPY

The experimental results explained above have supplied us with all the molecular data necessary for the calculation of statistical entropy. We are now able to compare this value with the third law value obtainable from thermal measurements. This comparison was made for $ClH_2C$—$CH_2Cl$ and $BrH_2C$—$CH_2Br$[24, 30]. The agreement between the statistical entropy and third law entropy was satisfactory. This again confirms our values of the molecular constants of the *trans* and the *gauche* molecules and of their equilibrium ratio.

The determination of the entropy difference between the rotational isomers by the spectroscopic method deserves a brief explanation[41]. The intensities of two absorption bands, of which one is assigned to one isomer and the other to another isomer, are compared in frequency and in molecular absorption coefficient with a standard band which is common to both isomers (as is often the case for a certain C—H stretching band). Such an experiment was made at different temperatures for $ClH_2C$—$CH_2OH$ and from the result the entropy difference was calculated as 3·4 e.u. This value is understandable in view of the fact that only the *gauche* isomer has an internal hydrogen bond[41]. This would reasonably explain the entropy difference of the two forms of acetylamino-acid *N*-methylamide, of which only one form has an internal hydrogen bond as mentioned below[70, 76], and, hence, of the value of the entropy change observed on denaturation of some proteins accompanied by an unfolding of the polypeptide chain.

## MICROWAVE SPECTRA AND OTHER EXPERIMENTS

The measurements of the dispersion and absorption of short electric waves described in the beginning of this paper were made in the liquid state. After the development of the microwave technique, the absorption measurements were made at shorter wavelengths (*e.g.* at about 3 cm)[3] and also in the gaseous state. In this state the fine structure of rotation spectra can be analysed on the basis of the theoretical treatment of energy levels, including both over-all and hindered internal rotations, and in some cases also the inversion doubling. The height of the potential barrier was found to be 1975 cal/mole for $CH_3NH_2$[109], 1066 cal/mole for $CH_3OH$[110], 3144 cal/mole for $NH_2NH_2$[112], 3140 cal/mole for $C_6H_5OH$[111], *etc.*

Investigations on electron spin resonance also provide us with information about the barrier to internal rotation. For example, from the change of spectra with temperature of an irradiated single crystal of alanine, the barrier height was found to be 3·6 kcal/mole[108].

The measurement of the dispersion and absorption of sound can be used for the determination of the energy difference between rotational isomers and the barrier height in the liquid state. Such a measurement was made on ethyl formate and ethyl acetate[107].

## n-PARAFFINS AND POLYETHYLENE

n-Paraffins contain only C—C bonds in the chain, and the unit structure may be considered to take either the *trans* or the *gauche* form. It is interesting to see that the molecules of n-paraffins in the solid state take the extended zigzag chain form: *i.e.* a form in which all the unit structures take only the *trans* form[27]. All the observed Raman and infra-red frequencies were in good agreement with those calculated for this extended chain[32]. This form is one of the stable configurations in the liquid state, so long as the number of carbon atoms is not large. However, in cetane (with sixteen carbon atoms) the Raman lines arising from the extended form are no longer detectable in the liquid state. This may have something to do with the theory of segments, in which the long chain molecules are considered to flow as segments, but not as single units[63]. The fact that n-paraffin molecules exist only in the extended form in the solid state, and in various forms in the liquid state, seems to be related to the alternation and convergence of melting points of n-paraffin series[62].

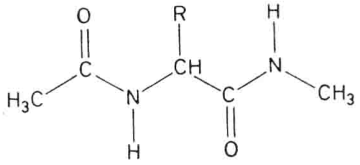
The substitution of some hydrogens or polyethylene by halogen or other groups yields various chain polymers of practical use. Polyvinyl chloride is one of the important polymers belonging to this category. The assignment of the observed frequencies was made by the calculation of normal vibrations of syndiotactic and threefold isotactic structures[88, 89], as well as of model compounds of simple structure[86]. This was also confirmed by the polarized infra-red measurements[87].

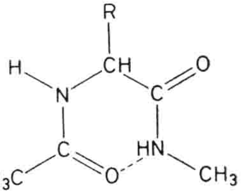
## POLYPEPTIDE CHAINS

So far polymers containing only equivalent bonds in the chain (or one atom chain) have been discussed. The internal rotation of two atom chains (*e.g.* polyoxymethylene) and three atom chains was also studied. A matrix method for the determination of chain configurations as a function of bond lengths, bond angles and internal rotation angles was proposed. From the values of these molecular constants obtained from the experimental results of simple molecules, the stable configurations of polymer chains have been determined[80].

In the case of polypeptide chains the calculation resulted in a few stable configurations, whereby the stability depends not only on the stable internal rotation angles but also on the internal hydrogen bonds. These include the extended chain proposed by Meyer and Mark, the folded chain proposed by us[66, 85], and the α-helices proposed by Pauling and Corey.

Of many simple molecules with structures of interest in the study of polymer chains, *N*-methylacetamide[69, 83] and acetylamino-acid *N*-methylamides[70–78, 81–85] have been studied by us from various angles. It is interesting that molecules of acetylamino-acid *N*-methylamides were shown to exist in the two forms shown in the following figure:





Each of these has stable internal rotational angles, and, therefore, all the atoms are not on the same plane. The equilibrium ratio of these two forms is different from one substance to another, and in the extreme case of acetylproline *N*-methylamide in carbon tetrachloride solution, all the molecules exist in folded forms[72, 73].

From these facts we may conclude that in natural polypeptides some amino-acid residues tend to adopt extended forms, and others folded or helical forms, and that a specific combination of these forms corresponds to the specificity of the protein[66, 85].

The order of the amino-acid residues has been determined in insulin and other hormonal proteins and in some of the enzymes. If an amino-acid residue controls the configuration of the main chain in its vicinity, each of the residues will adopt the complicated configuration characteristic of the chain. It is considered that the various interesting actions of proteins *in vivo* are explained primarily by the fact that each of the protein molecules has such a characteristic secondary structure.

Infra-red absorption studies indicate that a polypeptide chain with glycine and alanine linked alternately forms the main portion of silk fibroin. In such a case the regularity of the configuration can be understood from the same point of view. It seems natural that synthetic polypeptides form regular structures such as the $\alpha$-helix, because they are all built from the same amino-acid residues.

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# MOLECULAR VIBRATIONS AND PHYSICO-CHEMICAL PROBLEMS

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On an occasion of this sort, it is appropriate to assess the present position and draw attention to some main trends. I am concerned today with molecular vibrations, and therefore primarily with infra-red and Raman spectra. For physical chemistry, perhaps the most important of the early work was the determination and assignment of vibration frequencies of small molecules, especially those having some degree of symmetry; and through this to establish the molecular force field and obtain useful bond stretching and bending force constants. There was also the measurement of vibration–rotation bands of small molecules with high resolution, to determine the molecular rotational constants, moments of inertia, centrifugal stretching constants, and Coriolis coupling coefficients. Later, this was helped very much by the use of very sensitive photoconductive cells and other more sensitive detectors to get higher resolving power, and also by the application of isotope effects.

In both these directions, progress has been slower, as larger molecules have to be studied. The number of molecules for which a complete and unambiguous frequency assignment is known is still surprisingly small. The difficulties of getting a satisfactory potential energy function are well known. Automatic computors have been very useful for making rapid trial and error calculations, but there are inherent theoretical ambiguities and difficulties which these instruments alone cannot overcome. The recent marked progress of experimental technique in the far infra-red should provide much more information about low frequency vibrations, torsional and skeletal bending modes.

Microwave spectroscopy has of course given highly accurate structural data, better than that obtainable from vibration–rotation bands, but it is usually limited to the zeroth vibrational state, and is not always as conclusive as may be supposed[1]. More recent work on the fine structure of vibration–rotation bands is directed to the determination of the $\alpha$ values, which give us the variation of rotational constant $B$ with vibrational state, and through which we may hope to derive the equilibrium values of the rotational constants. Of course, with a larger molecule for which there may be many $\alpha$ values, this computation is still somewhat uncertain. Vibration–rotation bands are also useful in providing the Coriolis factors $\zeta$ which may be useful in connexion with the molecular force field.

With much larger molecules, with which chemistry is usually concerned, the main interest has of course been to discover absorption bands which are associated with localized vibrations and which can be used in structural