THE VIBRATIONAL SPECTRA OF CHLOROSUBSTITUTED HYDROCARBONS

by

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Chapter V.B is an extension of some work by D.A.C. Compton which was submitted for a Ph.D. degree in April, 1977. The interpretation of the additional data included in this section of the present thesis was jointly undertaken with Dr. Compton.

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ABSTRACT

Infrared spectra of saturated and unsaturated chlorinated hydrocarbons have been studied using low temperature techniques, including isolation in an inert matrix. The compounds were selected in relation to problems in the understanding of the properties of poly (vinyl chloride).

The physical properties of poly (vinyl chloride) and the capacity to fabricate various products depends on detailed structure and conformation of the polymer chain. Conformational content of model compounds by infrared spectroscopy has been shown to be very valuable in relation to the polymer. In particular, the C-Cl stretching frequency of poly (vinyl chloride) is sensitive to structure and conformation and correlations have been made with these model compounds.

In relation to the determination of the enthalpy difference between conformers ($\Delta H^{\ominus}$) by vibrational spectroscopy, a comprehensive review of existing literature is presented for conformational equilibria involving a wide range of compounds.

In the case of saturated chloro-hydrocarbons, vibrational assignments in relation to equilibria between conformers are presented for 2-chlorobutane, isomeric 2,4-dichloropentanes and isomeric 2,4,6-trichloroheptanes.

For unsaturated chloro-hydrocarbons more detailed structural and thermodynamic information has been determined in the case of allyl chloride and 2-chlorobuta-1,3-diene (chloroprene).

Information on these model compounds is critically considered in relation to similar information from poly (vinyl chloride). Some conclusions concerning the polymer are that there are present some conformations which are unfavourable to the structure of the polymer chain and which have previously tended to be ignored. Also some previous assumptions concerning the CH_2 deformation region of the poly (vinyl chloride) spectrum and mathematical resolution of peaks have been clarified.

CHAPTER I

Introduction

1. List of Compounds Studied
2. Saturated Compounds
3. Unsaturated Compounds
4. Calculation of Rotational Band Shapes in the Gas Phase

CHAPTER I

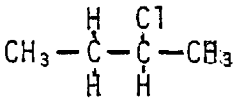
Introduction

The object of this work has been to employ various methods of vibrational spectroscopy, particularly at low temperatures, in order to obtain structural information relating to a series of chlorosubstituted hydrocarbons which has up to now been either missing altogether or else incomplete. This information is required in order to clarify the conformational behaviour of the compounds.

1. List of Compounds Studied

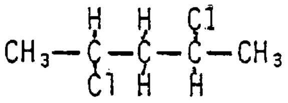
(a) Saturated

2-chlorobutane



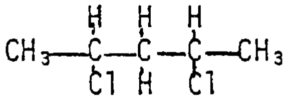
$CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3$

± -2,4-dichloropentane



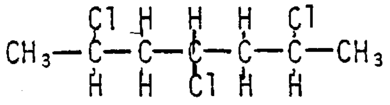
$CH_3-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3$

meso-2,4-dichloropentane



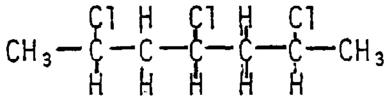
$CH_3-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-CH_3$

Syndiotactic 2 ,4,6-trichloroheptane



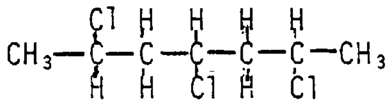
$CH_3-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3$

Isotactic 2 ,4,6-trichloroheptane



$CH_3-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3$

Heterotactic 2 ,4,6-trichloroheptane

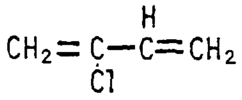


$CH_3-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-CH_3$

(b) Unsaturated

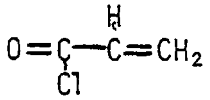
Allyl Chloride $CH_2{=}CH-CH_2-Cl$

2-chlorobuta-1,3-diene (chloroprene)



$CH_2{=}\underset{Cl}{C}{-}\overset{H}{C}{=}CH_2$

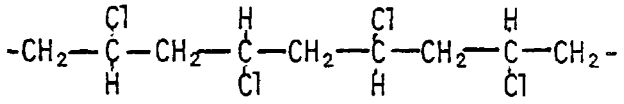
Propenoyl Chloride



$O{=}\underset{Cl}{C}{-}\overset{H}{C}{=}CH_2$

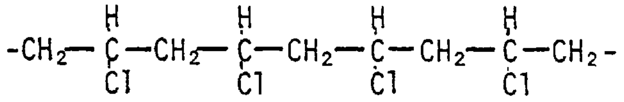
(c) Poly (vinyl chloride)

Syndiotactic



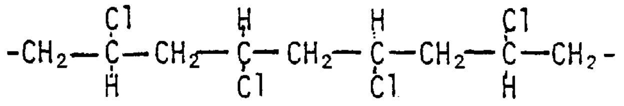
$-CH_2-\underset{H}{\overset{Cl}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-\underset{H}{\overset{Cl}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-$

Isotactic



$-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-$

Heterotactic



$-CH_2-\underset{H}{\overset{Cl}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-\underset{H}{\overset{Cl}{C}}-CH_2-$

2. Saturated Compounds

The saturated compounds have been selected because of their relevance as model compounds for the polymer poly (vinyl chloride) since a considerable amount of information concerning conformation has not yet been clarified for these compounds which could be of use in the determination of conformation for the polymer.

Matrix isolation techniques which involve isolation of a sample in a matrix of inert gas at very low temperatures have been employed, together with reexamination of spectra at high resolution since this method can yield considerable information relating to overlapping fundamental bands, isotope splitting, clarification of assignments and conformational equilibria; the latter being particularly important in relation to the compounds which serve as models for P.V.C.

Unsaturated chlorosubstituted hydrocarbons pose different problems to saturated systems because of the nature of barriers opposing internal rotation associated with π bonds of olefins. Comparative information between the two types of chlorinated hydrocarbons (including an analogous carbonyl compound) was therefore collected. This information enabled some detailed thermodynamic parameters to be determined.

Additionally a review was carried out in order to evaluate the usefulness of variable temperature infrared and Raman studies as a means of determining values of $\Delta H^{\ominus}$ for conformational equilibria and to collate such information which has been deduced for a wide range of compounds which bear some relation to those which have been studied in detail in this project.

It is necessary in order to explain the use of the saturated compounds in relation to P.V.C. in the present study, to give a brief resumé of the story of the use of infrared spectroscopy in the structural analysis of the polymer.

Grisenthwaite and Hunter (1,2) and Krimm et al (3) around 1958 were the first to indicate clearly that infrared spectroscopy was of value in configurational and conformational analysis of the P.V.C. chain. They also showed that polymerization conditions could make a difference to the structure of the polymer. Temperature differences were seen to have a marked effect on the spectra in the C-Cl stretching region.

From these studies a band at 605 cm^{-1} was assigned to syndiotactic sequences and two bands at 615 cm^{-1} and 692 cm^{-1} assigned to disordered portions of the chain.

There next followed a rapid breakthrough in qualitative understanding of the C-Cl stretching region of the spectrum relating frequencies of bands to configurational and conformational states. This determination had been achieved by several approaches to the problem but the key to the information came from studies of simple model compounds.

Studies of the spectra of (±) and meso-2,4-dichloropentanes were made by Shimanouchi and Tasumi (4) who then compared these with the spectra of P.V.C. The most interesting conclusion from this study was that the band at 690 cm^{-1} should be assigned to the C-Cl units of the isotactic configuration because the meso isomer which represents this configuration possesses a band around this value and the dl isomer which corresponds to the syndiotactic configuration does not.

Shipman et al (5) examined spectra of a range of secondary alkyl chlorides covering the energetically probable conformers likely to occur in low molecular weight model compounds and syndiotactic and isotactic configurations of P.V.C. They were able to give frequency ranges for the three types of conformations present in these compounds as,

S_{HH}	608 - 615 cm^{-1}
S_{HH}'	627 - 637 cm^{-1}
S_{CH}	655 - 674 cm^{-1}

An explanation of this notation is given in Chapter IV. The next important step forward in this type of study came from Krimm et al (6) who gave a much more comprehensive analysis of the C-Cl stretching region of P.V.C. The next step taken was the synthesis and spectral examination of 2,4,6-trichloroheptane as a model compound for P.V.C. (it was found that studies of this model (7,8) gave useful confirmatory evidence).

In the present study high resolution of all spectra has been used in order to determine whether or not any additional information can be obtained other than what has already been discussed and in order to clarify certain dubious assumptions, in particular concerning the CH_2 deformation region of the spectrum of P.V.C., extinction coefficients of conformer bands and also the Raman spectra of P.V.C.

3. Unsaturated Compounds

Moving on now to the unsaturated compounds, in the case of allyl chloride there are two possible conformations viz. cis and gauche. It was thought that matrix isolation spectra could provide improved vibrational assignments and that annealing of the spectra would help in determining conformer bands. Rotational structure determined from high resolution gas phase spectra has also been of help in determination of the major conformer population since previous workers (9) have assumed which isomer this is from electron diffraction studies. Calculations of rotational spacings for some of the compounds studied, including allyl chloride, are given at the end of this chapter.

The substituted butadiene 2-chlorobuta-1,3-diene (chloroprene) is a compound of commercial importance for which data relating to its conformational equilibrium has not yet been adequately determined. This compound has in this work been studied in some detail in order to obtain such information, along with the isoelectronic compound propenoyl chloride; as it was thought that a comparison of these two compounds would be of interest and also since values of parameters for propenoyl chloride so far published are dubious and hence require reexamination.

Comparison of the information from matrix isolation on conformational equilibria in saturated and unsaturated chloro compounds is likely to be useful since conformational equilibria are better characterised in unsaturated compounds.

4. Calculation of Rotational Band Shapes in the Gas Phase

For asymmetric rotors three types of band contours are recognized termed A, B or C bands depending on whether change in dipole moment occurs along the direction of the principal axis (10).

The separation between the maxima P, Q and R branch envelopes in the vibrational spectra will depend on the values of the three rotational constants which relate to the three moments of inertia

(I) about the respective principal axes;

$$A = \frac{h}{8\pi^2 I_A} \qquad B = \frac{h}{8\pi^2 I_B} \qquad C = \frac{h}{8\pi^2 I_C}$$

The molecules considered in this thesis have values of A, B and C which are different and are classified as asymmetric rotors. If two rotational constants are approximately equal, the molecules may be classed as an accidental symmetric rotor.

The degree of deviation from a symmetric top is defined as S, where

$$S = \frac{(2B-A-C)}{(A-C)}$$

This is a convenient term as it varies in value from +1.0 for an oblate rotor to -1.0 for a prolate rotor and 0.0 for a totally asymmetric molecule.

Calculations of the separation in cm^{-1} of the maxima of P and R branches and A and C bands follow in Table I.1 and Table I.2.

Values of $\rho = \frac{(A-C)}{B}$ are evaluated along with $\tilde{B}$, the average of the two rotational constants B and C which replace B in the case of an asymmetric top molecule. Values of $\tilde{\beta} = \frac{A}{2\tilde{B}} - 1$ can then be obtained and a simple mathematical derivation leads to the final equation for the value of the spacing in the case of A type and C type bands. The calculations are performed for the various conformers of 2-chlorobuta-1,3-diene, propenoyl chloride, allyl chloride and 2-chlorobutane.

In the case of chloroprene and propenoyl chloride the separations are found to be between 3 cm^{-1} and 4 cm^{-1}, larger for the trans isomer than for the cis for both C and A type bands. For 2-chlorobutane in the case of the S_{HH} and S_{HH}' conformations there is approximately 0.5 cm^{-1} difference in the separations for the two conformers, the S_{HH}' conformer having the larger value. Values of P and R separations for allyl chloride are very similar for both s-cis and s-gauche isomers, there being only

∿ 0.1 cm^{-1} difference in both the C type and A type bands.

When the values of the principal moments of inertia are sufficiently small, the vibrational-rotational transitions which make up the P, Q and R contours may be resolved into fine structure. The spacings of these bands which constitute the fine structure may be related to the principal moments of inertia of the molecule and in turn to the conformation for which these are calculated. The spacings for the bands with C contours of a symmetric rotor are 2 (A-B). In the case of an asymmetric rotor which accidentally approximates to a symmetric rotor the value $2\ (A - \frac{1}{2}\ (B + C))$ may be used.

The calculated values of spacings suggest that, at the maximum resolution available for the present work (0.5 - 0.6 cm^{-1}), it is not possible to resolve the fine structure of bands of the s-trans 2-chloro-1,3-butadiene and propenoyl chloride although it may be possible to resolve the corresponding bands of the s-cis conformers.

In the case of both conformers of 2-chlorobutane the separations are too small for resolution.

In the case of allyl chloride the calculated spacings are large enough for resolution and the spacings measured may be diagnostic for the conformer giving rise to the band, viz. s-cis 1.40 cm^{-1}, gauche 1.235 cm^{-1}.

Table I.1 Parameters Associated with P and R Contours and Rotational Spacings

	2-Chlorobuta-1,3-Diene		Propenoyl Chloride	
	$CH_2 = CH - CCl = CH_2$		$CH_2 = CH - CCl = O$	
	trans	cis	trans	cis
I_A	158.53	99.2	151.8	88.07
I_B	222.54	324.6	220.6	334.6
I_C	381.07	423.9	372.5	422.7
A cm^{-1}	0.1764	0.2819	0.184	0.318
B cm^{-1}	0.1257	0.0862	0.127	0.0836
C cm^{-1}	0.0734	0.0660	0.075	0.0662
(A - C)	0.1030	0.2159	0.109	0.252
(2 B-A-C)	0.0016	-0.1755	-0.005	-0.217
$S = \frac{(2\ B-A-C)}{(A-C)}$	0.0155	-0.812	-0.045	-0.861
$\rho = \frac{A-C}{B}$	0.819	2.505	0.858	3.014
$\tilde{B} = \frac{B\ C}{B + C}$	0.04634	0.03738	0.04715	0.03694
$\tilde{\beta} = \frac{A}{2\tilde{B}} - 1$	0.903	2.77	0.95	3.304
$\log (\tilde{\beta} + 4)$	0.6905	0.7973	0.6946	0.8637
$1.13 \log (\tilde{\beta} + 4)$	0.7803	0.9010	0.7849	0.9760
$(\tilde{\beta} + 4)^{1.13}$	6.030	2.962	6.094	9.462
$\frac{0.721}{(\tilde{\beta} + 4)^{1.13}}$	0.1144	0.0905	0.1183	0.0762
$S (\tilde{\beta})$	1.301	1.231	1.313	1.192
$\frac{(\tilde{\beta}\ T)^{\frac{1}{2}}}{9}$	1.243	1.116	1.254	1.110

Table I.1 continued

	2-Chlorobutane		Allyl Chloride	
	$CH_3 - CH_2 - CHCl - CH_3$		$CH_2 = CH - CH_2 - Cl$	
	S_{HH}	S_{HH}'	s-cis	s-gauche
I_A	186.9	173.2	35.4	39.4
I_B	255.2	272.2	296.7	297.7
I_C	406.7	351.1	306.9	307.8
A cm^{-1}	0.150	0.162	0.790	0.710
B cm^{-1}	0.110	0.103	0.094	0.094
C cm^{-1}	0.070	0.080	0.091	0.090
$(A - C)$	0.08	0.082	0.699	0.62
$(2\,B-A-C)$	0	-0.036	-0.699	-0.612
$S = \frac{(2\,B-A-C)}{(A-C)}$	0	-0.439	-0.991	-0.9871
$\rho \quad \frac{A-C}{B}$	0.7272	0.7961	7.436	6.596
$\tilde{B} = \frac{B\ C}{B + C}$	0.0427	0.0450	0.0459	0.0459
$\tilde{\beta} = \frac{A}{2\tilde{B}} - 1$	0.7564	0.80	7.606	6.734
$\log\,(\tilde{\beta} + 4)$	0.6773	0.6812	1.0647	1.0308
$1.13 \log\,(\tilde{\beta} + 4)$	0.7653	0.7697	1.2031	1.1648
$(\tilde{\beta} + 4)^{1.13}$	5.8254	5.8858	15.9621	14.6140
$\frac{0.721}{(\tilde{\beta} + 4)^{1.13}}$	0.1238	0.1225	0.0452	0.0493
$S\,(\tilde{\beta})$	1.3298	1.3259	1.109	1.120
$\frac{(\tilde{\beta}\ T)^{\frac{1}{2}}}{9}$	1.1930	1.2247	1.237	1.237

Table I.2 Values of P and R Spacings and Rotational Spacings

$$\Delta\nu_{PR}\ \text{A band} = 10\ S\ (\tilde{\beta})\ \left(\frac{\tilde{\beta}\ T}{9}\right)^{\frac{1}{2}}$$

$$\Delta\nu_{PR}\ \text{C band} = \tfrac{3}{2}\ \Delta\nu\ \text{A band}$$

Asymmetric Rotor-Prolate Molecule

	2-Chlorobuta-1,3-Diene		Propenoyl Chloride	
	trans	cis	trans	cis
$\Delta\nu_{PR}$ C bands	24.25	20.61	24.70	19.85
$\Delta\nu_{PR}$ A bands	16.17	13.74	16.47	13.23
$2\ (A - \frac{B + C}{2})$	0.15	0.41	0.17	0.49
2 (A-B)	0.10	0.39	0.14	0.47

	2-Chlorobutane		Allyl Chloride	
	S_{HH}	S_{HH}'	s-cis	gauche
$\Delta\nu_{PR}$ C bands	23.79	24.36	20.58	20.78
$\Delta\nu_{PR}$ A bands	15.86	16.24	13.72	13.85
2 (A - B)	0.08	0.12	1.40	1.235
$2\ (A - \frac{B+C}{2})$	0.12	0.14	1.395	1.235

CHAPTER II

Vibrational Spectra at Variable Temperature and the Determination of Energies Between Conformers

1. Introduction
2. Conformational Isomerism
3. Conformational Equilibrium
4. Vibrational Spectroscopic Methods and Conformational Isomerism
5. Sample Handling
6. Factors Governing Relative Stabilities Between Phases
7. Discussion of Data
8. Conclusion

CHAPTER II

Vibrational Spectra at Variable Temperature and the Determination of Energies Between Conformers

1. Introduction

This chapter describes experimental methods used to determine the energy differences between stable conformers and discusses the results. A number of physical methods permit these determinations but only results based on vibrational spectroscopy will be reviewed here to provide comparison of a wide range of compounds by those experimental methods which are based on molecular vibrations.

A proper understanding of conformational equilibria requires consideration of many physical and chemical techniques but such studies are best made on selected classes of compounds.

The energy difference is one of a number of thermodynamic parameters which may be determined, but a wider coverage of thermodynamic results would be too voluminous in other than a selected group of compounds.

The techniques of vibrational spectroscopy constitute the trinity, Infrared, Raman and Fourier Transform Infrared. They will be compared to make clear their complementary role, particularly in relation to variable temperature studies.

2. Conformational Isomerism

If one part of a molecule is rotated with respect to another part of the same molecule about a single chemical bond, one or more stable conformational isomers (or rotational isomers) may be formed corresponding to minimum potential energy states. These conformers (or rotamers) are rapidly interconvertible in the fluid phases and cannot be separated into chemically distinct forms (although it will be seen that they have some physically distinct properties). Their existence was established in the mid 1930's for a particularly simple molecule, ethane, by comparison (11) between the entropy, enthalpy and heat capacity values determined firstly by calorimetric methods and secondly by the methods of statistical thermodynamics.

Figure II.1 shows the variation of potential energy of ethane with rotation of the CC bond through 360^{o} (i.e. with change in the azimuthal angle). The minima correspond to staggered conformations in which the H atoms have greatest separations and least repulsive interaction energies. The maxima correspond to eclipsed conformations in which the H atoms have least separations and greatest repulsive interaction.

The potential energy function loses its three-fold periodic symmetry if the three-fold symmetry of the methyl is lost. Thus substitution of hydrogen by R (e.g. in n-butane) leads to two types of eclipsed conformers (R,H and R,R) and two kinds of staggered conformers (trans and gauche). The potential energy expression for n-butane is shown in Figure II.2. Consideration of the two types of staggered conformations reveals that the repulsive energies are greater in the gauche form than in the trans form. The difference between these two energy levels shown as minima in Figure II.2 is known as the enthalpy difference ($\Delta H^{\ominus}$) between the conformational isomers. The measurement of this difference in various systems is the subject of this chapter. The difference between neighbouring maxima and minima is termed the potential barrier hindering internal rotation. This barrier height may be determined in various ways but will not be considered here.

The penetrating insight provided by vibrational spectroscopy into conformational isomerism began to emerge very shortly after the discovery

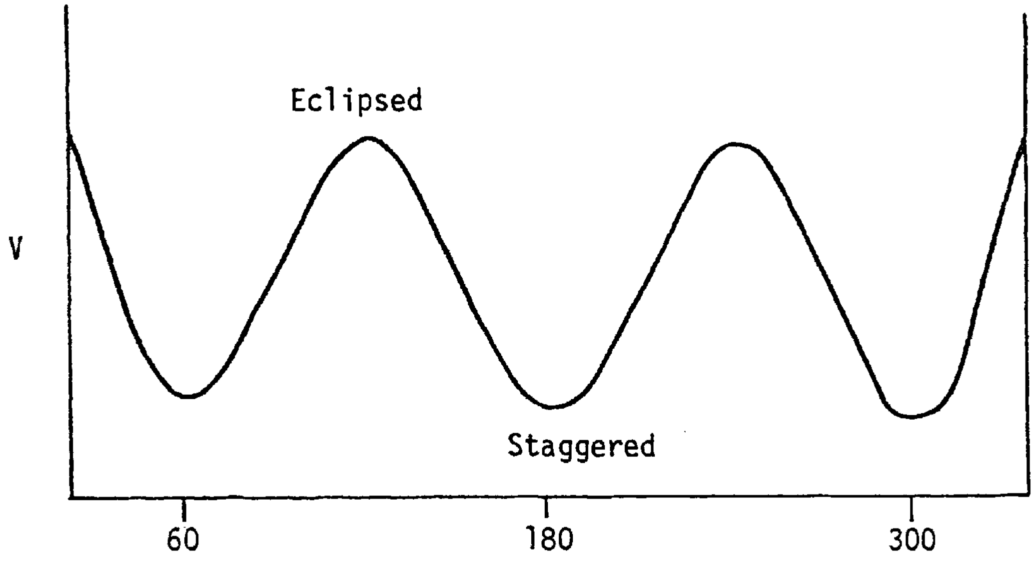


Fig. (II.1) Variation of potential energy of ethane with rotation of C-C bond between different conformers (3-fold barrier).

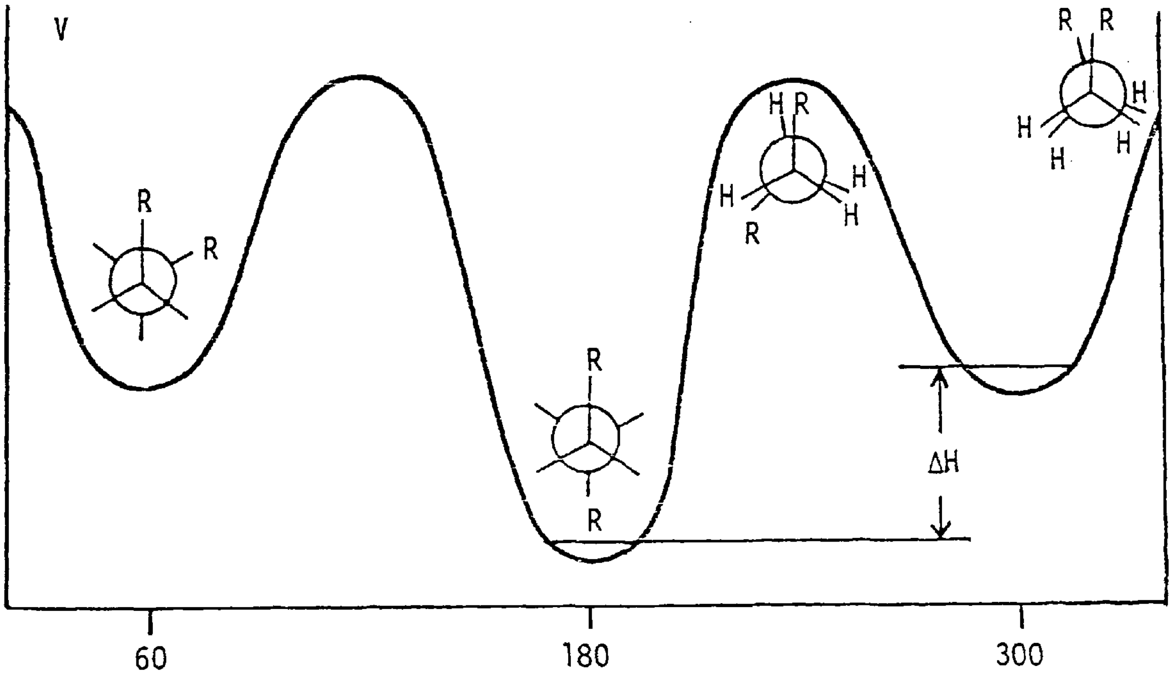


Fig. (II.2) Variation of potential energy of 1,2-disubstituted ethanes with angle of torsion.

in 1928 of the Raman effect. Kohlrausch (12,13) observed more lines in the Raman spectrum of n-propyl and n-butyl halides than would be expected on the basis of a single conformer and tentatively assigned these to isomerism. With rapid development of vibrational assignments Cabbanes (14) was able to identify and assign Raman bands to isomers of 1,2-dihaloethanes in terms of the symmetry of the s-trans form and less symmetrical conformational isomers.

Thus direct measurement was possible of components of a mixture of conformational isomers based on the vibrational molecular property. This provided confirmation for that evidence which was less direct and rested on measurement of bulk thermodynamic properties of the system.

3. Conformational Equilibria

The study of conformational equilibria requires a method with the following attributes.

(i) Ability to study a system in which the separate existence and structural features of each conformer may be identified qualitatively.

(ii) Ability to measure the concentration of each of two or more conformers quantitatively.

(iii) Ability to study compounds in solid, liquid and gas phases and in solution in a variety of solvents.

(iv) Ability to make measurements within the life-time of short-lived components of the system which may interconvert on a very rapid time-scale.

(v) Ability to make measurements on a system when the conditions affecting the position of equilibrium (e.g. temperature) can be varied and measured.

In principle the three principal methods of vibrational spectroscopy possess these various attributes. The vibrational spectra of an equilibrium (or non-equilibrium) mixture of conformers will contain bands arising from the molecular vibrations of all conformers. Practical limitations are set by the extent to which vibrational bands from conformers overlap. In extreme, the vibrational bands of each conformer may be observed separately. At the other extreme all vibrational bands of one conformer may be coincident with those of another. The normal pattern is that those vibrational modes which are essentially the same are not distinguishable, whereas other vibrational modes are dependent on the skeletal and stereo arrangements of bonds, and corresponding modes are different in each conformer. In some cases there may only be one pair of bands in this category. In the case of a molecule with a two-fold barrier opposing internal rotation by virtue of conjugation between two double bonds causing two planar stable forms, for example α, β saturated esters possessing s-_trans_ and s-_cis_ conformers (15) or t-_butyl_ formate possessing _cis_ and _trans_ conformers, a potential energy diagram may be described (Figure II.3) in terms of a low energy conformer A, and a high energy conformer B.

The criteria for identifying corresponding modes in the two conformers are as follows:

(i) As the temperature of a sample in the fluid form increases the relative intensity of bands due to high energy conformers increases (and that of bands due to low energy conformers decreases).

(ii) As the temperature of a sample in the fluid form decreases the relative intensity of bands due to low energy conformers increases (and that of high energy conformers decreases).

(iii) When the sample is cooled in such a way as to form a stable crystalline solid form, bands due to high energy conformers disappear.

(iv) The experimental information obtained for infrared, Raman or

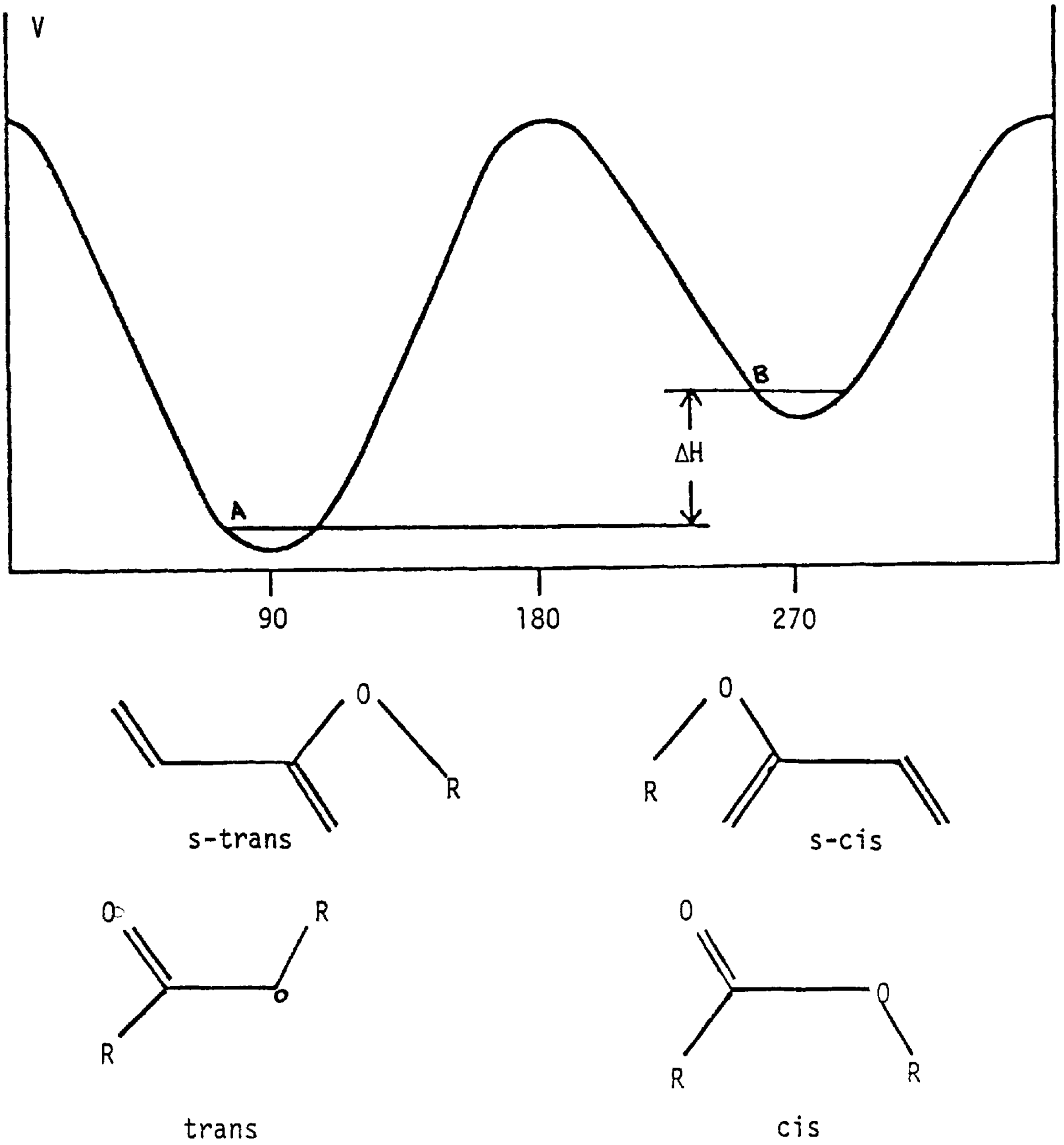


Fig. (II.3) Variation of potential energy for a system with two-fold barriers.

interferometry is consistent taking into account differences in selection rules, intensities and technical factors which influence limits of detection and spectroscopic range and states of matter.

(v) Conformer bands should be observed in pairs corresponding to modes of similar form but slightly different frequencies in the high energy conformer (B) and low energy conformer (A).

(vi) The concentration of A and B at the conditions of measurement must be sufficient for detection and measurement of the vibrational band under the conditions used (typically about 5% or more).

Consider the equilibrium $A \rightleftharpoons B$; the concentration of conformers in the high energy state, C_B, relative to that in the low energy state, C_A, is given by the Van't Hoff isotherm expression

$$\frac{C_B}{C_A} = e^{\frac{-\Delta G^\ominus}{RT}} \qquad \ldots \text{II.1}$$

Where $\Delta G^\ominus$ is the Gibbs free energy difference between the conformers and is given by the expression:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \qquad \ldots \text{II.2}$$

The standard enthalpy difference $\Delta H^\ominus$ may be taken as the difference in energy between the two minima. Strictly this assumes the pressure and volume dependence of concentration with temperature is negligible which is approximately true.

The vibrational band intensities of selected conformer bands may be related to the concentration of each conformer. In the case of absorbance (A) measurement by dispersive or Fourier transform methods, the Beer Lambert Law leads to the relationships

$$A_A = \varepsilon_A C_A \ell \qquad \ldots \text{II.3}$$

$$A_B = \varepsilon_B C_B \ell \qquad \ldots \text{II.4}$$

where ε and ℓ are extinction coefficients of particular conformer bands and the path-length respectively.

Substitution of 2, 3, and 4 into 1 leads to

$$\frac{A_B\ \varepsilon_A}{A_A\ \varepsilon_B} = e^{\frac{-\Delta H^\ominus}{RT}}\ e^{\frac{\Delta S^\ominus}{R}} \qquad \text{. . . II.5}$$

This may be more conveniently expressed as

$$\ln\frac{A_B}{A_A} = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R} - \ln\frac{\varepsilon_A}{\varepsilon_B} \qquad \text{. . . II.6}$$

If it is assumed that $\Delta S^\ominus$ and the ratio $\varepsilon_A/\varepsilon_B$ are constant with temperature it is possible to determine $\Delta H^\ominus$ by making a series of measurements of A_B/A_A at various accurately determined temperature values T.

From equation (6) further assumptions have led to the calculation of $\Delta S^\ominus$ either using measurements of a third band common to both conformers (16) or determining ε_A and ε_B by a simple graphical procedure (17).

For Raman spectra the intensity of a conformer band is linearly dependent on concentration and the corresponding equation to (6) differs by replacing the extinction coefficient by the corresponding Raman emission intensity coefficient.

The contribution of vibrational spectroscopy to the study of conformational isomerism has been reviewed by Mizushima (18), Sheppard (19) and Park, Pethrick and Thomas (20).

4. Vibrational Spectroscopic Methods and Conformational Isomerism

It has been noted that Raman spectroscopy was the initial method by which conformational isomerism was detected. This accords with the relative ease with which vibrational spectra could be obtained in the 1930's providing favourable samples were used which would scatter sufficient of the incident radiation from the mercury arc sources available at that time.

Raman spectra are measured in the visible region of the spectrum. The control of, and measurement of temperature of the sample over a wide range can be readily achieved using the appropriate optical materials subject to the collection of sufficient incident radiation by the sample.

The vibrations which are weak or inactive in the Raman are usually strong or active in the infrared. The i.r. region of the electromagnetic spectrum in which absorption of vibrational frequencies takes place posed technical difficulties of source, optics and detection until advances of electronics in the 1940's made the acquisition of infrared spectra easier than Raman for most samples, particularly if coloured or present in small quantities.

The early infrared spectrometers evolved from single beam to double beam utilizing an attenuator in the reference beam which was driven in and out by a servo mechanism to achieve a null balance in comparison with the sample beam. The absorbance measured as a function of wavenumber was proportional to this mechanical movement. Non-linear effects in this movement limited the accuracy of absorbance measurements further. Recent advances in electronics and instrumentation have led to several manufacturers producing instruments which measure the direct ratio of sample to reference beam with considerably more accuracy than is possible by a self-balancing servo mechanism and which is capable of scale expansion and computer enhancement with opportunities to measure bands at low absorbance or against strongly absorbing backgrounds. A further feature of several modern instruments is the ability to chop the radiation before and after the sample. This enables a true measure of absorption of radiation from the source by the sample to be made by isolating effects due to exchange of energy between sample and detector. These effects may be expected particularly when the sample is at a higher or lower temperature than the source. However, when a comparison was made (21) of the calculation of $\Delta H^{\ominus}$ for methyl crotonate using two infrared spectrometers with the different chopping modes no significant differences were obtained.

The advent of the Laser in the 1960's enabled Raman spectroscopic measurements to be made with similar ease to infrared. The two methods are complementary both in a fundamental way and in a technical way. Fundamental principles govern which method enables particular vibrational modes to be measured, but consequent technical considerations governing the condition or nature of the sample leads more favourably to one or another method.

The potential application to vibrational spectroscopy of the interferometer designed by Michelson in 1891 lay dormant until the 1960's. Early developments were directed to the measurement of far infrared spectra. The disadvantage of the computer stage to convert the interferogram into an absorption spectrum by Fourier transformation led to parallel developments in dispersive instruments for the far infrared region. This region is important in determining torsional frequencies and hence barrier heights opposing internal rotation.

Improvement in instrumentation led to interferometers for mid infrared spectroscopy. The precision needed for the collection of data and the computing of the Fourier transform stage resulted in the total process being more costly than dispersive methods for infrared. The spectra of conventional samples are essentially the same by interferometry and dispersion. The ability to accumulate interferometric data by rapid scanning of a sample many times leads to high sensitivity. Samples of very high absorbance and samples of very low absorbance may therefore be measured.

The method therefore provides the potential for making variable temperature measurements on samples inaccessible to conventional dispersive spectroscopy.

The ability to measure spectra by Raman, direct infrared absorption, or interferometry (followed by Fourier transformation leading to an infrared spectrum) has led to a healthy rivalry. Raman and infrared are not directly comparable. Raman spectroscopy is a light scattering phenomenon, in which shifts in visible radiation are a consequence of polarizability changes accompanying molecular vibrations. Infrared spectroscopy is an absorption of vibrational frequencies as a consequence of dipole moment changes accompanying molecular vibrations.

I.r. and F.T.-I.R. are directly comparable leading essentially to the same result. There is therefore scope for enthusiasts to develop each method to demonstrate achievements not possible by the other. Indications are so far that i.r. has the edge in cost and convenience. F.T.-I.R. has the edge in sensitivity and speed of obtaining spectra over a wide spectral range.

Figures II.4, II.5 and II.6 show the optics of typical modern infrared, Raman and Fourier transform infrared spectrometers respectively.

5. Sample Handling

The essential requirement in the determination of enthalpy difference between conformers by vibrational spectroscopy is to make accurate intensity measurements in the fluid phases at measured temperatures over temperature ranges as wide as possible.

Intensity measurement by infrared or Raman of samples at ambient temperatures are well established. The peak height of the band or the area measured by a planimeter can be related to concentration. Comparison of results using both methods tend to show similar final results, when bands overlap, computer methods aid the determination of the separate intensities.

There is much literature on measurement of absolute intensities in

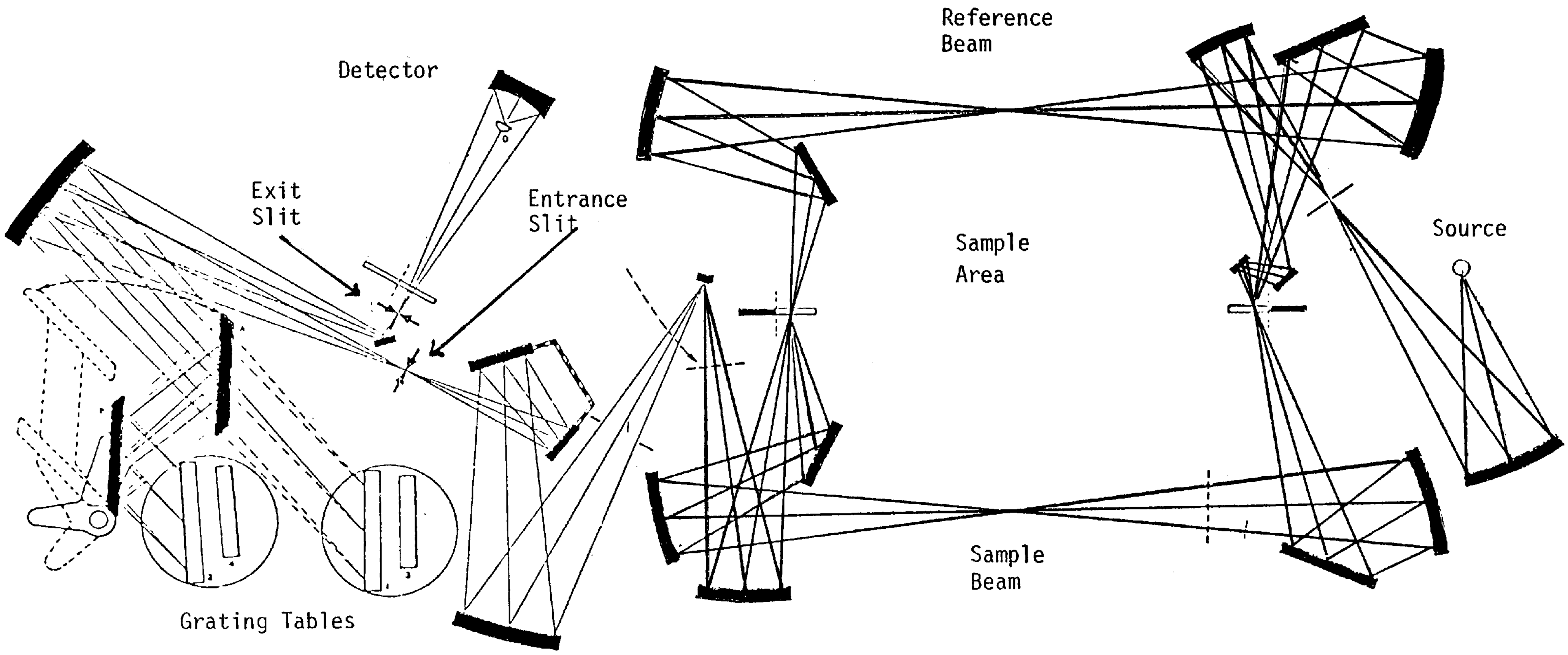


Fig. (II.4) Optics of ratio recording infrared spectrophotometer.

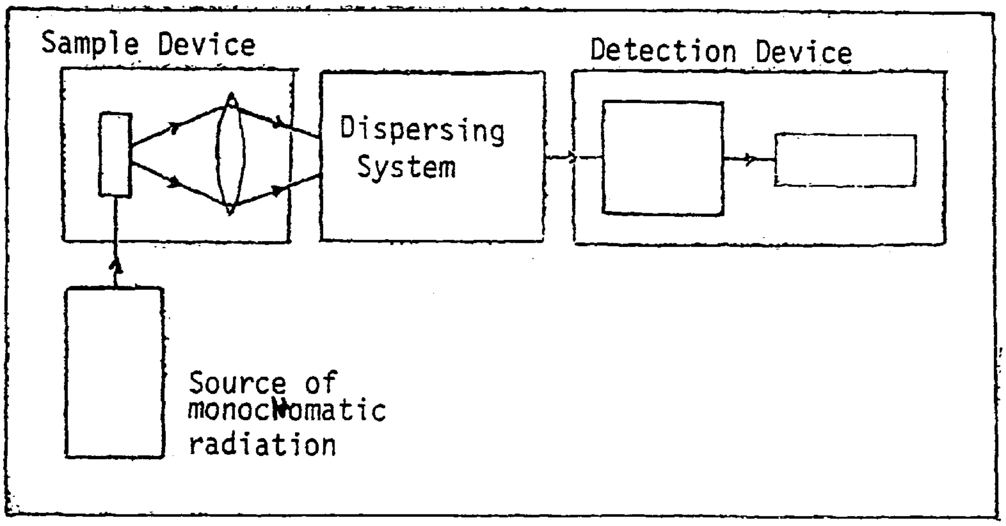


Figure II.5 Optics of Raman Spectrometer

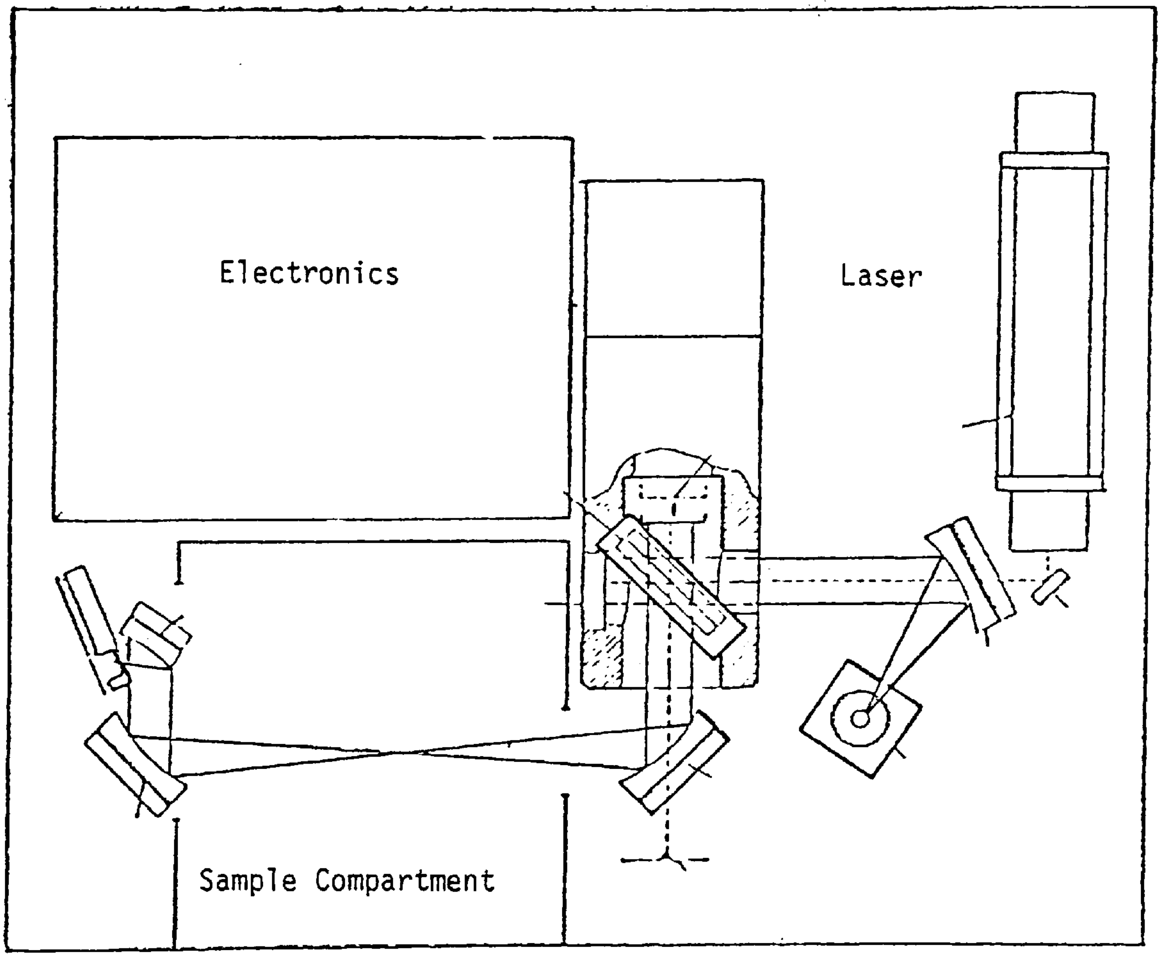


Fig. (II.6) Optics of Fourier Transform Infrared Spectrometer vibrational spectroscopy. For the determination of $\Delta H^{\ominus}$ values the relative intensities of two similar adjacent bands is required. Many of the errors of instrumentation and cell imperfections are fortunately cancelled out in the determination of the A_B/A_A term in Equation 6. The nature of these errors and their elimination need therefore not be pursued for the present purposes.

Cells for recording spectra at variable temperatures are shown in Figure II.7. Liquids for Raman study may sometimes, with advantage, be distilled into a capillary tube and sealed under vacuum. Small samples contained in this way can be mounted in a system described by Harney and Miller (22) in which a controlled flow of cold nitrogen or heated nitrogen takes the sample to each required temperature as measured by a thermocouple near the sample. Spectra recorded in this manner can give misleading band depolarization data because of multiple reflections from the walls which can change the polarization of a band. It is therefore desirable that any necessary depolarization measurements are taken in conventional cells.

The measurements of spectra in the infrared at variable temperature by either dispersive or interferometric methods require a vacuum tight cell mounted in a block which can be cooled by refrigeration or heated electrically in a controlled manner with temperature measurement from a thermocouple inserted in the cell near the sample.

The equipment shown in Figure II.7 can be readily mounted in the cell compartment of either a dispersive instrument or an interferometer. A double jacket enables the surroundings to the cell to be evacuated to minimize loss or gain of heat by the sample other than from the controlled source.

Most $\Delta H^{\ominus}$ measurements reported relate to samples in the liquid phase when Raman spectroscopy may be used or solution phase (usually CS_2)

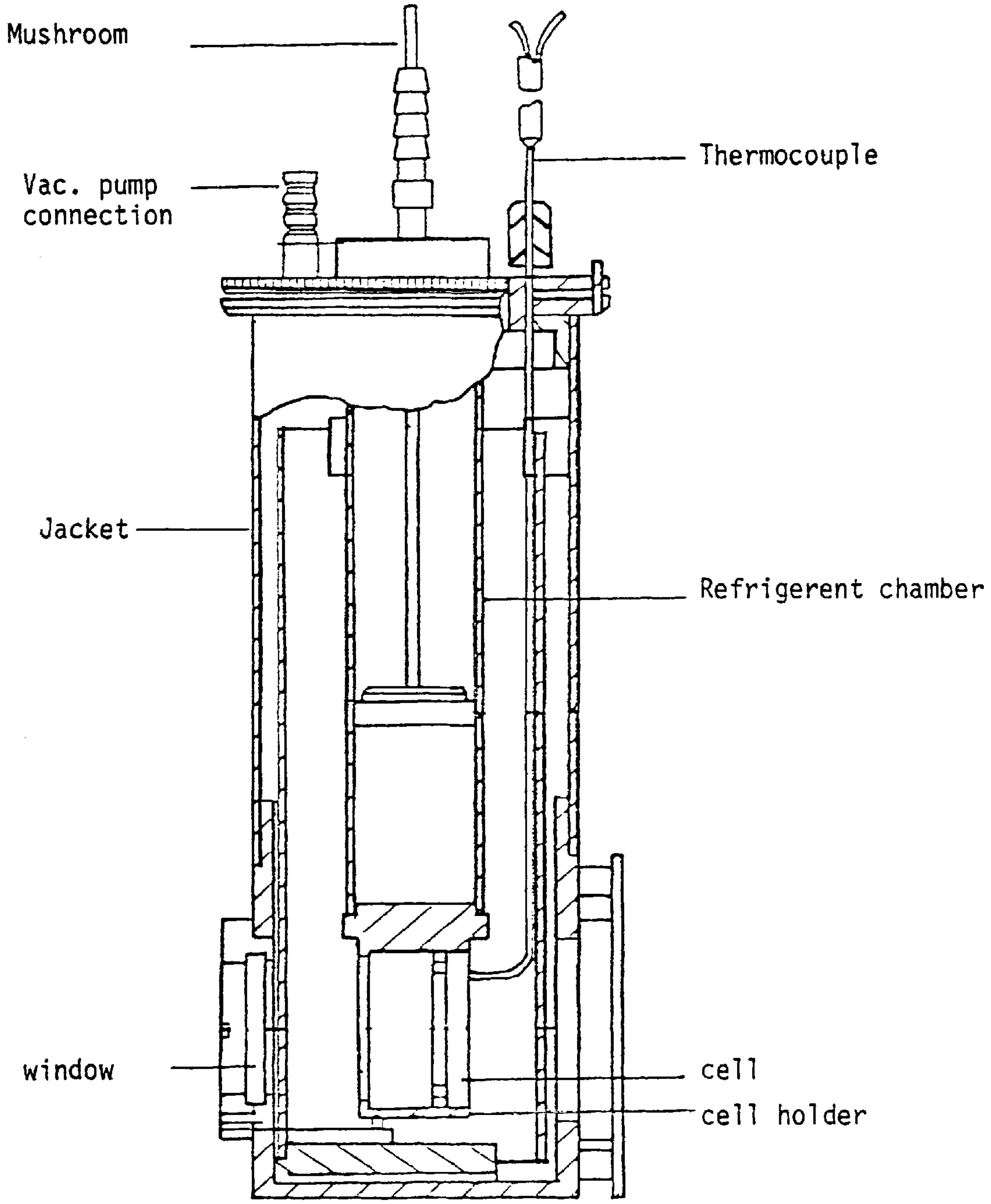


Fig. (II.7) A variable temperature cell for Raman, infrared and interferometry.

when infrared spectroscopy may be used. Annealing by controlled cooling can lead to stable solid forms. Gas cells which are heatable are readily available or easily constructed for infrared and can be constructed with more difficulty for Raman. If the cell in either technique is multipath via multiple internal reflection by mirrors, there are problems of changing alignments during heating.

The greater sensitivity of interferometry opens up the opportunity to make $\Delta H^{\ominus}$ measurements under conditions otherwise inaccessible and/or on pairs of bands normally too weak to be used. The remainder of this chapter will indicate the state of the art achieved largely by conventional Raman and i.r. and serves to point up problems partly or wholly unsolved for which the extra dimension promised by F.T.-I.R. would be an advantage.

6. Factors Governing Relative Stabilities Between Phases

The ability to determine $\Delta H^{\ominus}$ values in various phases has provided interesting differences. Thus in the 1,2-dihaloethanes a detailed study suggests that the s-*trans* form is the more stable in the gas phase, whereas the *gauche* form is the more stable in the liquid phase (23). These and other workers consider that the stability in the gas phase is determined by intramolecular steric interactions but that the stability in the liquid phase is determined by dipolar and quadrupolar interactions. Although some progress was made towards putting these ideas into a quantitative form it is apparent that the forces governing conformational isomerism are only imperfectly understood.

7. Discussion of Data

(i) Symmetrically 1,2-disubstituted Ethanes

These compounds may be rationalized in terms of an equilibrium between s-trans and gauche conformers as shown in Figure II.2. A negative value for $\Delta H^{\ominus}$ implies gauche has lower energy than the trans.

Table II.1 provides data on those compounds which have halogens, cyanide, methyl, ethyl or larger substituents. It is noted (24,26) that the value of $\Delta H^{\ominus}$ increases with size of halogen in the gas phase. Vibrational assignments reveal that for the gas phase, bands associated with the low energy form correspond to the trans conformer, whereas the bands associated with the high energy form correspond to the gauche conformer.

Furthermore, in Table II.1 it is noted that the $\Delta H^{\ominus}$ increases from 0.84, 4.58 to 7.4 for F, Cl and Br. This correlates with the sum of the Van der Waals radii of the two halogen atoms. So far it has not been possible to obtain $\Delta H^{\ominus}$ values for larger substituents in the gas phase.

Klaboe and Nielsen have demonstrated (24) that the trans and gauche forms of 1,2-difluoroethane are comparable in enthalpy in the gas phase, but that the gauche form is considerably more stable in the liquid phase. This change is not completely understood but is in accord with dielectric theory. The polar gauche isomer should have a lower potential energy in the liquid state than in the gas state while the non-polar trans isomer should have similar potential energies in the two states. The authors were able to correlate relative stabilities with dielectric constants of a range of solvents of increasing polarity (cyclohexane, carbon tetrachloride, chloroform, acetonitrile and nitromethane).

Succinonitrile (31) shows unusual behaviour in the solid state in that bands are observed corresponding to two isomers until the temperature is reduced below - 44°C, when bands are only observed corresponding to the low energy conformer.

A vibrational study of 1,2-diiodoethane by Tanabe (30) in solution and the solid enabled the $\Delta H^{\ominus}$ value between the trans and gauche forms to be estimated as 5.77 ± 0.42 by variable temperature. This result is considered more accurate than several previous ones by virtue of the double chopping mode discussed earlier. A method based on measurement of absolute intensities is described which leads to a $\Delta H^{\ominus}$ value of 5.43 ± 0.42 which is in excellent agreement. Additionally, by computing normal frequencies as a function of the dihedral angle of the gauche conformer and comparing with observed values the author was able to determine a value of $85^{\circ} \pm 5^{\circ}$ for the dihedral angle. These parameters have been compared with values determined by calculations based on atomic Van der Waals forces and residual electrical charges in the iodine atoms and from ^{13}C n.m.r. data.

A method based on absorbance, measured as a function of differing solvent polarities by Powling and Bernstein (35), enabled comparison of $\Delta H^{\ominus}$ values of 1,2-dihalogenated ethanes with temperature measurements in the gas phase. It was argued that the solvent effect was eliminated in the method and shown that these values correlated better with the gas than the liquid values. This approach to $\Delta H^{\ominus}$ measurements appears to be little developed in other systems.

(ii) Asymmetrically 1,2-disubstituted Ethanes

These are also understood in terms of trans and gauche conformers as in Figure II.2, although the substituents differ.

Table II.2 consists of mixed 1,2-disubstituents of ethane. The halogen compounds reveal $\Delta H^{\ominus}$ values generally consistent with the symmetrical disubstituted compounds (Table II.1). Thus the value of

1-bromo-2-chloroethane (35), $\Delta H^{\ominus}$ = 6.0 ± 0.4, is intermediate between that of 1,2-dichloroethane, (4.88 ± 0.4) and that of 1,2-dibromoethane (7.4 ± 0.83) for measurements in the gas phase. These may be correlated with steric interactions as measured by Van der Waals radii.

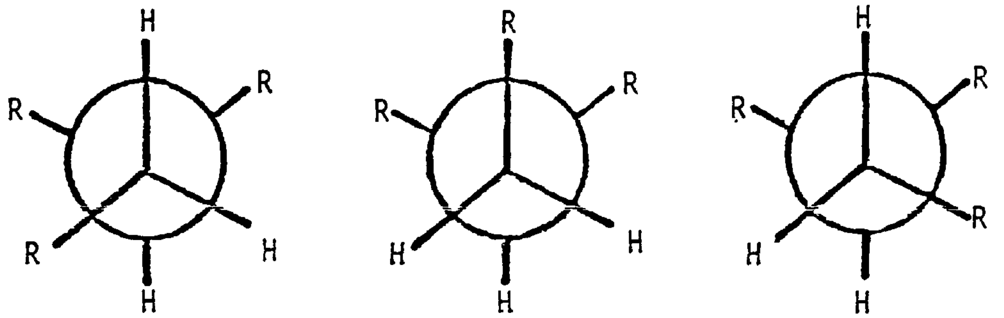
In the case of 1-fluoro-2-halogenoethanes (37) reversal in stability occurs on passing through the liquid gas phase boundary. The trans form is again more stable in the gas state, whereas the gauche form is more stable in the liquid state.

The infrared and Raman spectra of the halogenated compounds X CH_2CH_2CN have been studied in the liquid state (38,42) and the gauche form is found to be the low energy form, the difference from the trans increasing with X = F, Cl and Br. The effect noted in FCH_2CH_2F and $CNCH_2CH_2CN$, namely persistence of a conformer mixture until the temperature is lowered to -44°C, is also observed in FCH_2CH_2CN.

The infrared and Raman spectra of 2-chloroethanol (43), 2-fluoroethanol (44), 2-bromoethanol (44) and 2-iodoethanol (44) show the gauche form to be relatively more stable because a strong intramolecular hydrogen bond is favoured. In the case of the most polar fluorine compound the $\Delta H^{\ominus}$ value is largest (8.7 ± 2.2) which correlated with the absence of the unbonded OH stretching mode in solution in carbon tetrachloride and the high stability of the gauche conformer with strong intramolecular hydrogen bonding between OH and F. Conformational equilibria have also been established in compounds with aromatic substituents (45).

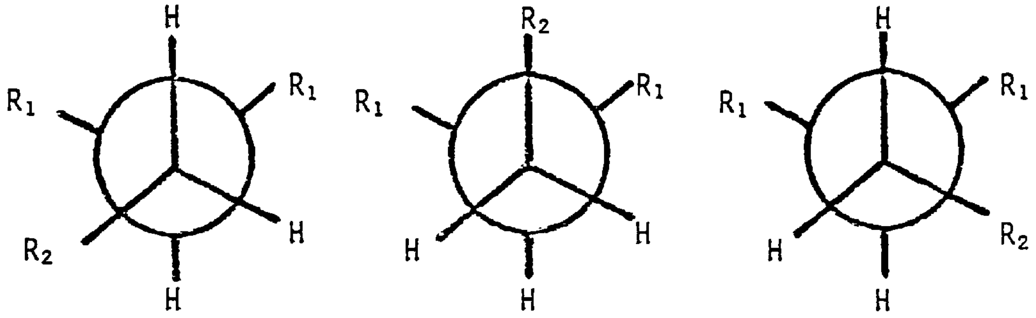
(iii) 1,1,2-trisubstituted Ethanes

This constitutes a class of compounds with structures likely to be as indicated in Figure II.8. One nomenclature commonly used is to specify the single substituent as trans and gauche to the two 1-substituents (tg) as in Figure II.8 or as gauche to both substituents (gg).



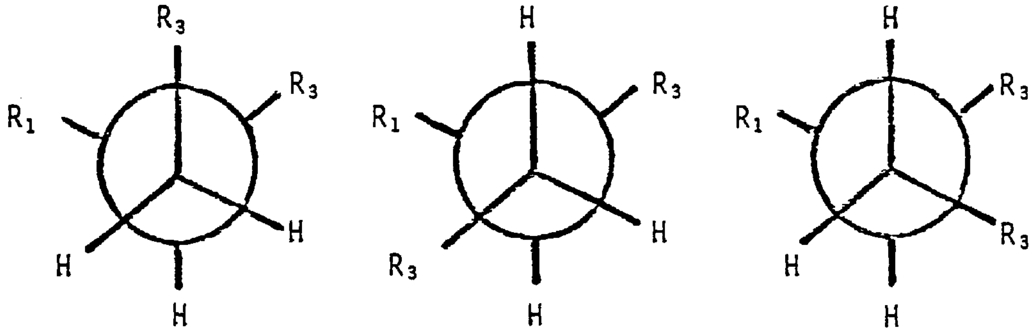
tg gg tg

1,1,2-trisubstituted ethanes



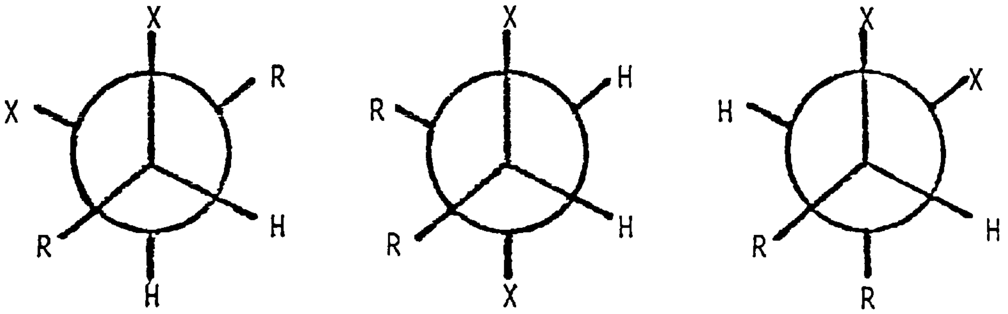
tg gg tg

Isobutyl Halides (R_1 = Me, R_2 = Halogen)



A B C

Sec. Butyl Halides (R_3 = Me, R_1 = Halogen)



S_{HH} S_{HHAL} S_{HR}

Forms of Tetra Substituted Ethanes

Fig. (II.8) Substituted ethanes as described in Table (II.3) and (II.4)

The simplest molecule within this category may be taken as 1,1,2-trichloroethane. This comparison of gaseous liquid and solid spectra at variable temperatures (46) suggests the less polar form (tg) has less energy than the more polAR form (gg). The ΔH^{Θ} values reported for measurements on several pairs of bands averages to 1.10± 0.12 kJmol^{-1} for the liquid and 12.0 ± 0.5 kJmol^{-1} for the gaseous state. The large difference between the vapour and liquid state can be related to the very high polarity of this molecule. Following n.m.r. studies, Sheppard and Turner (27) utilize these values to determine various coupling constants in the different conformers.

Studies of the isobutyl halides (47) and cyanide (48) reveal the influence of methyl substituents on the configuration in question.

Isobutyl halides (47) have been shown to exist in low energy (tg) forms for which two equivalent possibilities occur and in a high energy (gg) form. The ΔH^{Θ} values for isobutyl chloride and bromide (Table II.3) are given for vapour and liquid states. The latter are not in very good agreement with those derived by ultrasonics (47). The discrepancies were attributed to an accumulation of errors from assumptions made in the ultrasonic method. The ΔH^{Θ} value for isobutyl cyanide was determined for the liquid phase by Raman (48) but the assignments suggest that the (gg) form is more stable than the (tg) form.

In view of the similarity in polarity and other properties between the halogen and cyanide substituents, the conflict in relative stabilities between the (gg) and (tg) conformers is likely to be more apparent than real and a detailed reexamination of assignments would seem desirable.

An example of a similar configuration is 2,2-dichloroethanol (51). Here the stable predominant form is the (gg) by virtue of intramolecular hydrogen bonding, but i.r. and Raman spectra suggest the (tg) form also exists in the solid, liquid and gaseous states.

Secondary butyl halides differ from isobutyl halides by permitting three rather than two conformers with different energy. Pentin and co-workers (49) have shown that the relative enrgies can be determined as B < C < A (Figure II.8) and then the $\Delta H^{\ominus}$ values can be determined between each two states, (Table II.3) for secondary butyl chloride and bromide.

Some rationalization to the values of $\Delta H^{\ominus}$ was provided (47) based on Sheppard's rules (19). The $\Delta H^{\ominus}$ is considered in terms of contributions of interactions between non-bonded groups of the same kind and non-bonded groups of a different kind. Comparison of results calculated from these results with those shown in Table II.3 are in reasonable agreement and suggest that non-bonded interactions between similar groups do not change from molecule to molecule.

(iv) 1,1,2,2-tetrasubstituted Ethanes

The 1,1,2,2-tetrahalogeno-ethanes (Table II.4) have possibilities of existing in trans and gauche forms (Figure II.2). In tetrafluoroethane, i.r. and Raman studies (25) suggested the trans was more stable by 4.85 kJ mol^{-1} compared to the gauche in the vapour state. Intramolecular HF bonding is considered to stabilize this form. Tetrachloroethane results have been attributed to Berstein and Powling (35) using solvent rather than temperature variation. Results for this compound in liquid and solution given in Table II.4 are quoted by Sheppard and Turner (27) but taken from earlier work. Tetrabromoethane has been reported (51) as showing total reversal in relative energy between gas and liquid states for the trans and gauche forms, i.e. gauche is the low energy form in the liquid.

In the case of the mixed tetrasubstituted compound, 1,1-dichloro-2,2-difluoroethane, the $\Delta H^{\ominus}$ value in the liquid state also follows the trend of revealing a higher energy for the trans conformer than for the gauche.

(v) Unsymmetrical - tetrasubstituted ethanes

Table II.5 contains compounds in which two substituents R^2 and one substituent R^1 are attached to the same carbon. In the case of 1,2-dibromo-1,1-difluoroethane, the ΔH^{Θ} value between the less stable and more stable conformer has the same sign in the gas and liquid phase. The spectroscopic data did not permit the identification of the more stable conformer as trans or gauche.

In the case of the 2-halogeno-2-methylbutanes (54), the ΔH^{Θ} values are determined in the liquid and gas states (except for the iodo compound). Simple models based on steric repulsive forces and Van der Waals radii suggest the ΔH^{Θ} values should decrease from the chloride to the iodide. The probable trend is in the other direction which suggests other interactions additional to steric repulsive forces must occur.

(vi) Diastereo Forms of Tetrasubstituted Ethanes

The 2,3-dihalogenobutanes listed in Table II.6 possess asymmetry at the C-2 and C-3 carbons which enables the molecules to exist in the meso form and the dl form. Conformational possibilities are different in the two diastereo isomers. In the meso form the low energy form is found to be trans in the vapour state in all cases listed. In the case of 2,3-dibromobutane, for the liquid phase the low energy state is gauche. The difference between liquid and gas phase enthalpies is explained by dielectric theory. In the dl form there are two different energy levels corresponding to two identical gauche conformers in the meso form. The three conformers are shown in Figure II.8 using a nomenclature put forward in earlier references. Careful assignment permits the identity of the two levels corresponding to each ΔH^{Θ} value (Table II.6). In the gas state the ΔH^{Θ} values reveal a definite pattern. For the dl form the relative energies are found to be

$S_{HH} \approx S_{HHal} > S_{HCH_3}$. This is consistent with the large steric repulsion arising from the four large substituents in gauche positions in the S_{HH} and S_{HHal} but much less steric crowding in the S_{HCH_3} form.

1,2,3,4-tetrachlorobutane has, in principle, fifteen meso conformers and eighteen dl conformers. To a reasonable approximation many of these are similar and only three spectroscopically distinguishable conformers need to be considered for each form (56). Although it is not feasible to report $\Delta H^{\ominus}$ values, the stable forms have been identified by vibrational spectroscopy and n.m.r. studies.

(vii) Hexasubstituted Ethanes

Table II.7 consists of ethane-type compounds where all the hydrogens have been replaced by one or another of the halogens. Considering the 1,2-dihalotetrafluoroethanes, we see that for the gas phase, $\Delta H^{\ominus}$ increases with the size of the halogen in the 1,2 position, i.e. in the order Cl, Br, I. As would be expected, the value for 1-bromo-2-chlorotetrafluoroethane lies between the values for the dichloro compounds and the dibromo compounds and the value for trifluoro compounds is slightly smaller than that of the dichloro compounds. All the gas phase values in this table therefore follow the expected trends of the earlier tables.

The trans isomer is the more stable form in both liquid and gaseous phases for each of the compounds included in the table except 1-fluoro-1,1,2,2-tetrachloroethane in which the equilibrium is reversed to favour the gauche isomer in the liquid phase.

(viii) Ethers

Rotation of one or both of the R-O bonds in ethers may be expected to follow similar patterns as in corresponding C-C bonds with additional features arising from the electronic properties of the oxygen. Vibrational consequences of conformational changes are more readily detected when the R group has marked polarity or lack of symmetry. In other cases conformational equilibria takes place but may be difficult to detect (Table II.8).

A number of studies have been made in which a vinyl group is directly attached to an ether oxygen. In the simplest case of methyl vinyl ether, two conformers were shown to exist in liquid and vapour (66). Rotational structure of bands due to the low energy form indicated this was in planar *cis* conformation (Figure II.9 (ii)), whereas the high energy form was *gauche* rather than the *trans* form (Figure II.9 (i)) unless the *trans* (Figure II. 9 (i)) is stabilized by a particularly bulky substituent.

The larger value of $\Delta H^{\ominus}$ in the gas compared to the solution state is consistent with results described previously for halogenated ethanes. The stability of the *cis* form is attributed to electrostatic attraction between the polar O-CH group and the polarizable C=C group and between the α vinyl C-H bond and the oppositely orientated dipole of the oxygen lone pair orbitals. Both of these interactions would be a maximum in the *cis* structure (Figure II.9 (ii)). Higher alkyl vinyl ethers exist in similar equilibria, the low conformer of ethyl vinyl ether is considered 'sickle' shaped (64) as in Figure II.9 (iii). High energy conformers are judged to be non-planar from the poorly defined contours of bands. In both compounds the proportion of the high energy conformers increases in solvents of increasing polarity which suggest it is the C-O bond which is rotated out of the plane of the vinyl group. Furthermore vibrational analysis (63) of alkyl vinyl ether supports the conclusions that the stable form is *cis* and that the case of ethyl vinyl ether, two skew high energy forms ~~high energy forms~~ exist in the liquid and gaseous states.

In this more recent work the $\Delta H^{\ominus}$ values for alkyl vinyl ethers in the liquid state, determined by Raman, appear significantly greater than the values determined in the vapour or solution state by infrared methods, although the authors claim they are consistent within experimental error Conformations of n-butyl vinyl ether were suggested (63) but no quantitative measurements were possible.

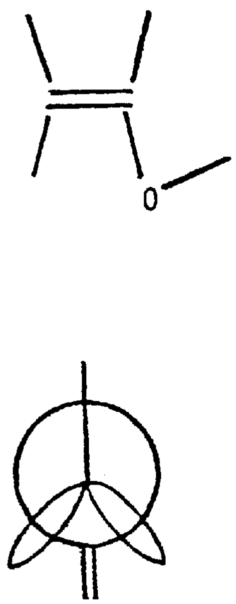
The general conclusions are further supported by studies of 2,2,2-trifluoroethyl vinyl ether (69), in which the rotation was found to take place at the bond between the oxygen and the vinyl group rather than between the oxygen and the ethyl group.

In the case of divinyl ether (65), two isomers are indicated by Raman and infrared. Observed spectra indicate from symmetry consideration that the more stable form is planar trans-trans (Figure II.9 (v)), whereas the less stable form is non-planar. The results were supported qualitatively by Molecular Orbital calculations, although a somewhat higher value for the $\Delta H^{\ominus}$ value between the conformers was indicated.

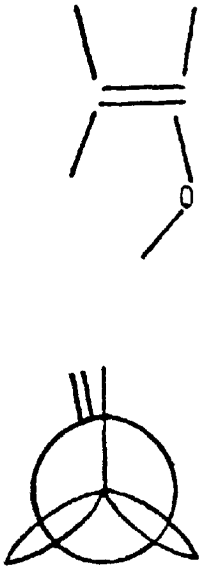
Ethers with other groups bonded to oxygen have been shown to exhibit conformational isomerism. In the case of the groups propargyl (70), acetonitrile (70) and halosubstituted dialkyl ethers, the stable conformer may be determined in each case, but the nature of the spectra render the enthalpy determination difficult.

(ix) Esters

The OR^2 group of esters is likely to generate features in common with ethers and additional features stemming from the R^1CO group. The former features are isolated in formates ($R^1 = H$). Methyl and ethyl formates are isoelectronic with methyl (66) and ethyl (64) vinyl ether. Spectroscopic evidence suggests a cis skeletal form (Figure II.10 (i)) unless the trans (Figure II.10 (ii)) is stabilized by a particularly bulky substituent (e.g. R^2 = t-butyl (78) or R^2 = propargyl (76)) which leads to steric repulsive forces between lone pair electrons on the carbonyl and R^2. These forces result in an equilibrium between I and II. Evidence based on vibrational

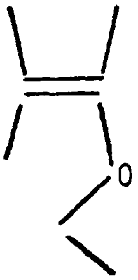


trans I

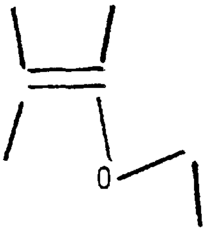


cis II

Methyl Vinyl Ether

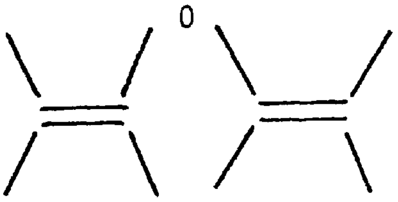


III



IV

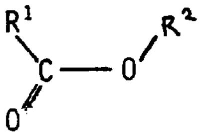
Ethyl Vinyl Ether



V

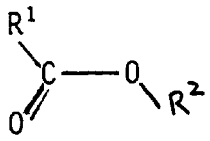
Divinyl Ether

Fig. (II.9) Ethers as described in Table (II.9)



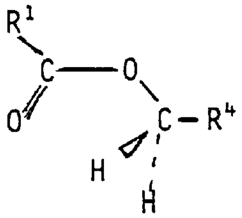
I

cis

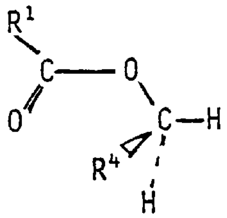


II

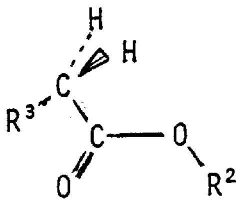
trans



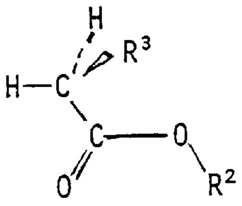
III



IV



V



VI

Fig. (II.10) Esters as described in Table (II.10) spectroscopy (78) suggests conformers arise from rotation about the HCO-O bond in t-butyl formate for which $\Delta H^{\ominus}$ has been estimated as 0.63 ± 0.08 kJmol^{-1} and from rotation about the HCOO-R group in isobutyl formate for which $\Delta H^{\ominus}$ was estimated as 3.1 ± 0.2 kJmol. This latter rotation is also considered present in a series of ethyl esters and $^{2}H_{5}$ ethyl esters of saturated acids (73). The $\Delta H^{\ominus}$ values provided in Table II.9 are attributed to the equilibrium III$\rightleftharpoons$IV in Figure II.10.

Studies of alkyl n-butyrate (73) suggested equilibria of the type V $\rightleftharpoons$ VI. For methyl propionate some comparative evidence (79) supports the more stable conformer as being cis V, in which the methyl group eclipses the carbonyl and the less stable conformer as gauche where equivalent forms provide a favourable entropy factor. A more sensitive compound for detecting this equilibrium is methyl chloracetate (77) because the polar chlorine group can exert interactions through space which split the carbonyl according to whether the chlorine group is cis or gauche. Raman and infrared studies (75) also enable conformations of dimethyl carbonate to be deduced.

(x) Ketones and Aldehydes

The conformers which exist in esters from rotation of the group bonded to the carbonyl may be expected also in ketones. Conformers are detected in butanone (81) and in diethyl ketone (82), but the lack of difference in polarity between conformers results in lack of sufficient resolution between bands belonging to different conformers for quantitative measurements. In chloroacetone (83) the $\Delta H^{\ominus}$ value has been obtained both by the temperature variation method and by the absolute intensity method which enables the dihedral angle of the gauche form to be determined as $150^{\circ} \pm 10^{\circ}$. The two conformers have well resolved carbonyl bands as in esters with similar substituents (77). The stable conformer being trans in which the chlorine eclipses the carbonyl in each case.

A detailed study of propanal revealed confirmation of the greater stability of the cis form compared to the skew (84). (See Table II.10).

(xi) Substituted Propenes

These compounds bear a formal resemblance to ketones and aldehydes by virtue of the similarity between the methylene and carbonyl groups. A number of monohalomethyl propenes have been studied (Table II.11). The general pattern would appear to show that the more polar gauche form was the lower energy form which may be isolated in the solid, whereas the less polar cis form was the higher energy form which was present to an increasing extent at higher temperatures in liquid and gas state. The $\Delta H^{\ominus}$ values have not been reported. Studies of allyl chloride (88) and cyanide favour a gauche stable conformer.

(xii) Substituted 1,3-butadienes

1,3-butadiene has been shown to be predominantly in the s-trans form. High temperature vapour studies (89) led to changes attributed to s-trans and s-cis equilibria and from intensity measurement of infrared bands a $\Delta H^{\ominus}$ value was calculated (Table II.12). These changes could not be confirmed by low temperature studies in solution (90) but under these conditions 2-methyl-1,3-butadiene revealed spectral changes in the Raman leading to the determination of $\Delta H^{\ominus}$ and to the estimation of a concentration of s-cis of 11% at normal temperature (Figure II.11).

The 1,1-dibromo-3-fluoro-1,3-butadiene and the corresponding 1,1-dichloro compounds have been shown (17) to possess a higher proportion of the s-cis conformer leading to $\Delta H^{\ominus}$ values which were also obtained by n.m.r in $CFCl_3$ as solvent to give similar values to those determined by infrared in CS_2.

Molecular models suggest 2,3 steric interactions in butadiene inhibit

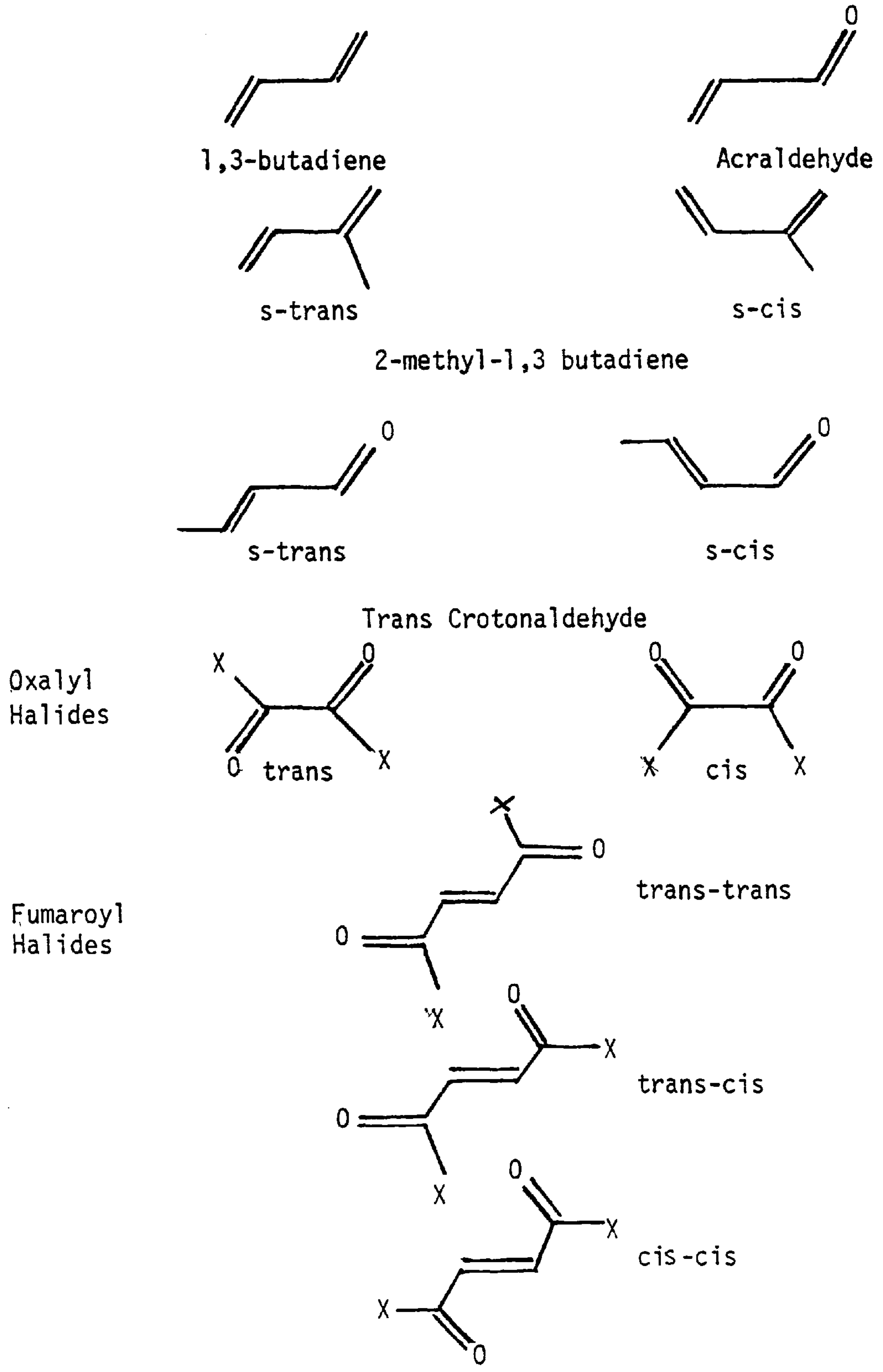


Fig. (II.11) Conjugated systems as described in Tables (II.12) and (II.13) the formation of the s-*cis* form. When there is a substituent at the 2-position, the s-*trans* form becomes less stable because of interactions between the 2 substituent and the nearest vinylic hydrogen (2,4 interactions). The substitution of a halogen atom in the terminal position further reduces the stability leading to an increase in the energy towards that of the s-*cis* conformer and a consequent smaller ΔH^{Θ} value. The possibility of *gauche* non-planar forms of conjugated compounds has also been considered.

(xiii) α, β Unsaturated Carbonyl Compounds

It is useful to regard acraldehyde as the parent of a wide range of substituted α, β unsaturated carbonyl compounds. Evidence based on rotational and vibrational-rotational structure has shown that acraldehyde is predominantly s-*trans* and ultrasonic relaxation studies indicate the ΔH^{Θ} value is very high and corresponds to very low concentration of s-*cis* conformer. A vibrational study of *trans* crotonaldehyde enabled an estimate (91) of 7.1 kJ mol^{-1} to be made for the ΔH^{Θ} value between the s-*trans* and s-*cis* forms (Figure II.11).

Substitution of methyl, halogen and alkoxy in the 2-position to form ketones, acryloyl (crotonoyl) halides and esters, respectively, reduces the value of ΔH^{Θ} considerably. This is attributed to a rise in the energy of the s-*trans* conformer relative to the higher energy s-*cis* conformer and to thereby lessen their energy difference. The ΔH^{Θ} values in Table II.13 are of similar magnitude but smaller than in the corresponding skeleton. These studies provide a basis for understanding the conformational equilibria in more complicated α, β unsaturated carbonyls. For example, various conformers of fumaroyl and maleoyl halides (94) and alkyl fumarates and maleates (95) have very different symmetries. In the case of fumaroyl halides, vibrational spectra support at least two forms of approximately equal energies having C_s (cis - trans) and C_{2h} (trans - trans) symmetries in solution in CS_2. In the case of fumaroyl fluoride, ^{19}F n.m.r. provides evidence for the three isomers shown in Figure II.11, but it was not possible to determine the relative energies of ΔH^Θ values. Similar results were obtained in the maleoyl halides.

Dialkyl fumarates were considered (95) to exist in equilibrium between trans - trans and trans - cis; the latter being the high energy form. The ΔH^Θ value for the dibutyl fumarate was found to be 1.55 ± 0.08 kJ mol^{-1} in CS_2 solution by infrared measurements and 1.66 ± 0.17 kJ mol^{-1} by Raman measurements. The corresponding values for the diethyl and dimethyl fumarates by Raman were somewhat lower and higher, respectively. The stabilizing features which cause this ester to exist as a solid at room temperature may also perturb the relative conformational energies. The Raman and infrared studies of alkyl maleates suggested (95) only one conformer, but a later study (96) supported at least two conformers.

(xiv) Oxalyl Halides

These represent the extension of the trend of compounds in Figure II.11 and provide opportunities to obtain wide general comparisons in conjugated systems.

The compounds studied are oxalyl chloride and bromide (98) shown to be more stable in the trans than cis by 9.2 and 12.1 ± 0.4 kJ mol^{-1}, respectively, based on low and high temperature Raman studies of liquids.

(xv) Ring Compounds

Table II.14 is made up of ring compounds, mainly substituted cyclohexanes and cyclohexenes. The energy values for cis and trans 2-chloromethylcyclohexanes are just about equal and are opposite in size. The cis favours the equatorial methyl conformer and the trans favours the diequatorial conformation.

The most stable conformer of cis or trans 1-chloro-4-methylcyclohexane is the conformer in which the Me group is in equatorial conformations.

The energy differences for iodo conformations of cyclohexene and 1-iodo-1-methylcyclohexane are 1.67 and 2.80 kJ mol^{-1}, respectively, in the former case favouring the equatorial conformer and in the latter favouring the axial conformer. Dilution of either compound with polor or non-polar solvents does not change the energy difference appreciably.

4-methylcyclohexene exists mainly as the equatorial conformer in the liquid state with energy difference of ∿ 1.59 kJ mol^{-1}; and 4-bromocyclohexene also exists mainly as the equatorial conformer in the liquid state, the energy difference in this case is 3.59 kJ mol^{-1}; in both cases the equatorial form only was present in the solid phase.

(xvi) Miscellaneous

In Table II.15 there is no structural similarity between the compounds considered. Considering conformations of dialkyl disulphides, for ethyl methyl disulphide, the gauche - gauche isomer was found to be more stable than the trans - gauche isomer by ∿ 3.76 kJ mol^{-1} and for the diethyl disulphide the (ggg) was found to be more stable than the (tgg) conformer by about 2.5 kJ mol^{-1} in the liquid state.

Of the three types of ring sulphite molecules considered, form I exists mainly as the chair conformation, form II as the twist conformation and form III as the chair twist conformation.

In the case of dichlorophenoxysilane the gauche conformer is predominant in the liquid phase while the anti-conformer is favoured in the crystalline phase, the energy difference of the two conformers is ∿ 3.34 kJ mol^{-1}.

8. Conclusion

The measurement of the energy difference between conformers, $\Delta H^{\ominus}$, and other thermodynamic parameters is a fundamental probe into chemical and physical behaviour. Rotation of a chemical bond leads to chemical and physical change in the same way as the breaking of a chemical bond. Vibrational spectroscopy serves as an analytical method to determine the way proportions of the components change with temperature or other constraints. The factors which determine change and the position at which equilibrium takes place are two-fold: tendency to achieve greater stability or lower energy and a tendency to increase the entropy of the system. This statement is represented by Equation 2.

This chapter surveys results obtained by vibrational spectroscopy. Within the various classes of compounds studied it is possible to examine the structural factors which influence equilibrium and change.

Many of the results were measured many years ago when instrumentation was not adequate for accuracy. Improvements have been made in recent times in sensitivity, accuracy, resolution and speed in dispersive infrared, Raman and Fourier transform infrared following interferometry measurements. Additionally, advances have been made in the determination of intensities of bands which are partially overlapped and in computer handling of data. Using faster automated methods, it is likely that the $\Delta H^{\ominus}$ values in families of compounds can be measured rapidly and accurately leading to improved correlations with structural factors and a better understanding of the process of chemical and physical change.

Table II.1 RCH_2-CH_2R Enthalpy Differences

Compounds	Substituents R	$\Delta H^{\ominus}$ (kJ mol^{-1})	Phase	Method	Refs.
1,2-difluoroethane	F	0·89	Gas	I.r.	24
		−3.8	Liquid	I.r.	24
				Raman	25
1,2-dichloroethane	Cl	4.58 ± 0.4	Gas	I.r.	26
		0.00	Liquid	I.r.	
				Raman	26
		1.67	Soln. in Hexane	I.r.	27
			Liquid	I.r.	28
1,2-dibromoethane	Br	7.4 ± 0.63	Gas	I.r.	26
		3.1 ± 0.5	Liquid	Raman	28
				I.r.	29
		3.95	Soln. in Hexane	I.r.	27
		1.67	Soln. in CH_3NO_2	I.r.	27
1,2-diiodoethane	I	5.77 ± 0.42	Soln.	I.r. Raman	30
Succinonitrile	CN	-1.5 ± 0.20	Liquid	I.r.	31
n-butane	Me	3.18 ± 0.4	Liquid	Raman	32
n-hexane	Et	2.1 ± 0.4	Liquid	Raman	32
1,6-dibromobipropargyl	$C{\equiv}CBr$		Liquid	I.r.	33
1,4-dibromo butane	CH_2Br	-2.1 ± 0.4	Liquid	I.r.	34

Table II.2 R^1CH_2-CH_2R^2 Enthalpy Differences

Compounds	Substituents		$\Delta H^\ominus$	Phase	Method	Refs.
	R^1	R^2	(kJ mol^{-1})			
1-bromo-2-chloroethane	Br	Cl	6.0 ± 0.4	Gas	I.r.	35
			2.05 ± 0.4	Liquid	Raman	35, 36
1-bromo-2-fluoroethane	Br	F	1,25 ± 0.32	Gas	I.r.	37
			-3.4 ± 0.8	Liquid	I.r.	37
1-iodo-2-fluoroethane	I	F	6.30	Gas	I.r.	37
			-2.5	Liquid	I.r.	37
β-bromo-propionitrile	Br	CN	-2.26 ± 0.22	Liquid	I.r.	38
β-bromo-propionitrile	Br	CN	-2,38	Liquid	I.r.	39
β-chloro-propionitrile	Cl	CN	-1.85 ± 0.18	Liquid	I.r.	38
β-chloro-propionitrile	Cl	CN	-1.55	Liquid	I.r.	40
β-fluoro-propionitrile	F	CN	0.0	Liquid	I.r.	38
β-iodo-propionitrile	I	CN	-1.59 ± 0.15	Liquid	I.r.	41, 42
2-chloro-ethanol	Cl	OH	4.0 ± 0.38	Gas	I.r.	43
			5.0 ± 0.80	Soln. in CCl_4	I.r.	44
2-fluoro-ethanol	F	OH	8.7 ± 2.2	Soln. in CCl_4	I.r.	44

Table II.3 $R^1R^2CH\text{-}CH_2R^3$ Enthalpy Differences

Compounds	Substituents			$\Delta H^{\ominus}$	Phase	Method	Refs.
	R^1	R^2	R^3	(kJ mol^{-1})			
1,1,2-trichloroethane	Cl	Cl	Cl	12.0 ± 0.5	Gas	I.r.	46
				1.1 ± 0.12	Liquid	I.r.	46
				1.6	(1:1) Soln. in CCl_4	I.r.	46
				0.0	(1:1) Soln. in CH_3CN		
Isobutyl chloride	Me	Me	Cl	0.96 ± 0.08	Gas	I.r.	47
				1.55 ± 0.6	Liquid	I.r.	47
Isobutyl bromide	Me	Me	Br	1.25 ± 0.12	Gas	I.r.	47
				1.10 ± 0.50	Liquid	I.r.	47
Isobutyl cyanide	Me	Me	CN	3.0 ± 0.2	Liquid	Raman	48
2,2-dichloroethanol	Cl	Cl	OH		Liquid	I.r.	50
2-chlorobutane	Cl	Me	Me	(A - B) 2.5 ± 1.2	Liquid	I.r.	49
				(C - B) 1.6 ± 1.2	Liquid	I.r.	49
				(A - C) 1.0 ± 0.4	Liquid	I.r.	49
2-bromobutane	Br	Me	Me	(A - B) 2.5 ± 1.2	Liquid	I.r.	49
				(C - B) 2.1 ± 1.0	Liquid	I.r.	49
				(A - C) 0.4 ± 0.4	Liquid	I.r.	49

Table II.4 $R^1R^1CH\text{-}CHR^2R^2$ Enthalpy Differences

Compounds	Substituents R^1 R^1 R^2 R^2	$\Delta H^\ominus$ (kJ mol^{-1})	Phase	Method	Refs.
1,1,2,2-tetrafluoroethane	F F F F	4.85 ± 0.4	Gas	I.r.	25
			Liquid	I.r.	25
1,1,2,2-tetrachloroethane	Cl Cl Cl Cl	1.2 ± 0.8	Soln.	I.r.	35
		-4.6 ± 0.4	Liquid	I.r.	27
		-3.76	Soln. in Heptane	I.r.	27
		-5.86	Soln. in CH_3NO_2	I.r.	27
1,1,2,2-tetrabromoethane	Br Br Br Br	2.85	Gas	I.r.	51
		-3.2	Liquid	I.r.	
1,1-dichloro-2,2-difluoroethane	Cl Cl F F	-1.47	Liquid	I.r.	52

Table II.5 $R^1R^2R^2C-CH_2R^3$ Enthalpy Differences

Compounds	Substituents	$\Delta H^\ominus$ (kJ mol^{-1})	Phase	Method	Refs.
1,2-dichloro-1,1-difluoro-ethane	Cl F F Cl	1.8 ± 0.4	Gas	I.r.	52
			Liquid	Raman	52
1,2-dibromo 1,1-difluoro ethane	Br F F Br	3.0 ± 0.2	Gas	I.r.	53
		4.3 ± 0.2	Liquid	Raman	53
2-chloro-2-methyl-butane	Cl Me Me Me	4.6	Gas	I.r.	54
		1.5	Liquid	I.r.	
2-bromo-2-methyl-butane	Br Me Me Me	5.9	Gas	I.r.	54
		1.6	Liquid	I.r.	
2-iodo-2-methyl-butane	Me Me I Me	2.6	Liquid	I.r.	54

Table II.6 $R^1R^2CH-CHR^1R^2$ (meso and dl) Enthalpy Differences

Compounds	Substituents R^1 R^2 R^1 R^2	$\Delta H^\ominus$ ($kJ\ mol^{-1}$)	Phase	Method	Refs.
Meso-2,3-dichlorobutane	Me Cl Me Cl	5.4 ± 1.2	Gas	I.r.	55
		2.7 ± 0.4	Liquid	I.r.	55
Meso-2,3-dibromobutane	Me Br Me Br	6.0 ± 0.88	Gas	I.r.	55
		-1.82 ± 0.28	Liquid	I.r.	55
dl-2,3-dichlorobutane	Me Cl Me Cl				
$S_{HCl}-S_{HH}$		0.18	Gas	I.r.	55
		-0.29 ± 0.9	Liquid	I.r.	55
$S_{HH}-S_{HCH_3}$		6.7 ± 0.8	Gas	I.r.	55
		-1.63 ± 0.36	Liquid	I.r.	55
$S_{HCl}-S_{HCH_3}$		6.9 ± 0.6	Gas	I.r.	55
		1.75 ± 0.24	Liquid	I.r.	55
dl-2,3-dibromobutane	Me Br Me Br				
$S_{HH}-S_{HCH_3}$		6.6 ± 0.5	Gas	I.r.	55
		-1.8 ± 0.5	Liquid	I.r.	55
$S_{HBr}-S_{HCH_3}$		7.5 ± 1.2	Gas	I.r.	55
		1.9 ± 0.24	Liquid	I.r.	55
$S_{HBr}-S_{HH}$		0.75 ± 1.5	Gas	I.r.	55
		3.1 ± 0.50	Liquid	I.r.	55
1,2,3,4-tetrachlorobutane	CH_2Cl,Cl,CH_2Cl,Cl		Liquid	I.r.	56
				Raman	56

Table II.7 $R^1R^2R^3C\text{-}CR^4R^5R^6$ Enthalpy Differences

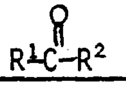
Compounds	Substituents						$\Delta H^{\ominus}$	Phase	Method	Refs.
	R^1	R^2	R^3	R^4	R^5	R^6	($kJ\ mol^{-1}$)			
1,2-dibromotetrafluoroethane	Br	F	F	Br	F	F	3.92 ± 0.2	Gas	I.r. Raman	57
							3.85 ± 0.2	Liquid	I.r. Raman	57
							3.90 ± 0.3	Liquid	I.r. Raman	58
1-bromo-2-chlorotetrafluoroethane	Br	F	F	Cl	F	F	2.5 ± 0.8	Gas	I.r.	59
							2.18 ± 0.8	Liquid	I.r.	59
1,2-dichloro tetrafluoroethane	Cl	F	F	Cl	F	F	2.1 ± 0.8	Gas	I.r.	59
1,1,2-trichlorotrifluoroethane	Cl	Cl	F	Cl	F	F	1.47 ± 0.63	Gas	I.r. Raman	60
1,2-diiodotetrafluoroethane	I	F	F	I	F	F	7.70 ± 0.4	Gas	I.r.	61
1,2-diiodotetrafluoroethane	I	F	F	I	F	F			Raman	62
1-fluoro-1,1,2,2-tetrachloroethane	F	Cl	Cl	Cl	Cl	H	3.35 ± 0.4	Gas	I.r.	59
							-1.60	Liquid	I.r.	60

Table II.8 R^1-O-R^2 Enthalpy Differences

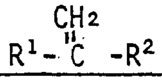
Compounds	Substituents		$\Delta H^\ominus$	Phase	Method	Refs
	R^1	R^2	(kJ mol^{-1})			
Methyl vinyl ether	$CH_2=CH$	Me	4.81 ± 1.0	Gas	I.r.	67, 66
			2.76 ± 0.84	Soln. in 1,1,2-trichloroethane	I.r.	68, 66
Ethyl vinyl ether	$CH_2=CH$	Et	3.3 ± 0.8	Soln. in 1,1,2-trichloroethane	I.r.	64
Alkyl vinyl ether	$CH_2=CH$	Me	6.02 ± 0.67	Liquid	Raman	63
	$CH_2=CH$	Et	6.53 ± 0.41	Liquid	Raman	63
2,2,2-trifluoroethyl vinyl ether	$CH_2=CH$	CH_2CF_3		Gas Liquid	I.r. I.r.	69 69
Divinyl ether	$CH_2=CH$	$CH_2=CH$	2.51	Liquid	I.r. Raman	65 65
Propargyl methyl ether	$HC\equiv CCH_2$	Me		Liquid	I.r.	70
Methoxy acetonitrile	$N\equiv CCH_2$	Me		Liquid	I.r.	70
Bischloro methyl ether	$ClCH_2$	$ClCH_2$		Liquid	I.r.	71
2-haloethyl alkyl ether	CH_2CH_2	R		Liquid	Raman	72

Table II.9 R^1COOR^2 Enthalpy Differences

Compounds	Substituents		$\Delta H^{\ominus}$ (kJ mol^{-1})	Phase	Method	Refs.
	$R^1CO\text{-}OR^2$					
Methyl acetate	CH_3	CH_3				80
Propargyl formate	H	$CH_2C{\equiv}CH$		Liquid, Gas	I.r.	76
t-butyl formate	H	$C(CH_3)_3$	0.63 ± 0.08	Soln. in CS_2	I.r.	78
	$R^1COO\text{-}R^2$					
	R^1	R^2				
Ethyl acetate	CH_3	C_2H_5	1.32 ± 0.06	Soln. in CS_2	I.r.	73
Isobutyl formate	H	$CH(CH_3)_2$	3.12 ± 0.17	Soln. in CS_2	I.r.	78
	$R^1\text{-}COOR^2$					
	R^1	R^2				
Methyl propionate	C_2H_5	CH_3	4.6 ± 1.25		I.r.	79
Methyl chloroacetate	$ClCH_2$	CH_3			I.r.	77
	$R^1O\text{-}COOR^2$					
	R^1	R^2				
Dimethyl carbonate	OCH_3	CH_3	10.9 ± 2.1	Liquid	I.r. Raman	75

Table II.10  $R^1\overset{O}{\overset{\|}{C}}-R^2$ Enthalpy Differences

Compounds	Substituents		$\Delta H^\ominus$	Phase	Method	Refs.
	R^1	R^2	(kJ mol^{-1})			
Methyl Ethyl Ketone	Et	Me		Liquid	Raman	81
Diethyl Ketone	Et	Et		Liquid Soln. in CCl_4 Soln. in CS_2	I.r. Raman	82
Chloroacetone	CH_2Cl	Me	1.84 ± 0.42	Soln. in CS_2	I.r.	83
Propanal	Et	H		Gas Liquid	Raman Raman	81
Propanal	Et	H	4.9 ± 1.0	Gas	I.r.	84
Propanal	Et	H	4.9 ± 0.5	Liquid	Raman	84

Table II.11  $R^1-\overset{CH_2}{\overset{\|}{C}}-R^2$ Enthalpy Differences

Compounds	Substituents		$\Delta H^\ominus$	Phase	Method	Refs.
	R^1	R^2	(kJ mol^{-1})			
2,3-dichloro and 2,3-dibromo-1-propene	CH_2Cl CH_2Br CH_2Cl	Cl Br Cl		Soln.	I.r. Raman	85 85
2,3-dichloro propene	CH_2Cl	Cl		Soln.	I.r.	86
2-chloro-3-fluoro-1-propene	CH_2F	Cl		Liquid	I.r. Raman	81
and 2-bromo 3-fluoro-1-propene	CH_2F	Br		Liquid	I.r. Raman	87
Allyl chloride	CH_2Cl	H	2.1 ± 0.2	Liquid	I.r.	88
Allyl Chloride	CH_2CN	H	1.9	Liquid	I.r.	88

Table II.12 substituted 1,3-butadienes Enthalpy Differences

Compounds	Substituents	$\Delta H^{\ominus}$ (kJ mol^{-1})	Phase	Method	Refs.
1,3-butadiene	H	7.1 ± 0.8	Gas	I.r.	89
2-methyl-1,3-butadiene	Me	4.59 ± 0.6	Liquid	Raman	90
1,1-dibromo 3-fluoro-1,3-butadiene	F	3.53	Soln. in CS_2	I.r.	88
1,1-dichloro 3-fluoro-1,3-butadiene	F	2.95	Soln. in CS_2	I.r.	88

Table II.13 substituted acraldehydes and 2-substituted trans crotonaldehyde

Compounds	Substituent	$\Delta H^{\ominus}$ (kJ mol^{-1})	Phase	Method	Refs.
trans-crotonaldehyde	H	7.1	Liquid	Raman	91
Methyl vinyl ketone	CH_3	1.93 ± 0.10	Soln. in CS_2	I.r.	92
		2.36 ± 0.21	Gas	I.r.	
Ethylidene acetone	CH_3	2.14 ± 0.21	Soln. in CS_2	I.r.	92
		2.45 ± 0.19	Gas	I.r.	
Acryloyl fluoride	F	0.63	Soln. in CS_2	I.r.	
Acryloyl chloride	Cl	2.50	Gas	I.r.	93
Methyl acrylate	OMe	1.36 ± 0.08	Soln. in CS_2	I.r.	21
Methyl *trans* Crotonate	OMe	1.27 ± 0.12	Soln. in CS_2	I.r.	21
		1.58 ± 0.23	Liquid	Raman	15

Table II.14 Ring Compounds

Compounds	$\Delta H^{\ominus}$ (kJ mol^{-1})	Phase	Method	Refs.
cis-	3.34			
trans 2-chloromethylcyclohexanes	-3.55		I.r.	98
cis and *trans* 4-chloromethylcyclohexanes			I.r.	99
Iodocyclohexane	1.67	Liquid	I.r.	100
1-iodo-1-methyl cyclohexane	2.80	Liquid	I.r.	100
4-methylcyclohexane	1.6	Liquid	I.r., Raman	101
4-bromocyclohexene	3.59	Liquid	I.r.	102

Table II.15 Miscellaneous

Compounds	$\Delta H^\ominus$ (kJ mol^{-1})	Phase	Method	Refs.
Dialkyl disulphide	3.76 2.50	Liquid	I.r., Raman	103
Isobutyl methyl sulphide		Liquid	I.r., Raman	104
Bis (alkylthio) methane		Liquid	I.r.	105
Ring sulphites	2.42		I.r.	106
Alkyl sulphides		Liquid	I.r.	107
Chlorophosphines		Liquid	I.r.	108
Dichlorophenoxy silane	3.34	Liquid	I.r.	109
Ethylchloro-silanes	1.67 1.17	Liquid	I.r., Raman	110
Methylvinyl-silane	2.76 ± 0.21	Liquid	I.r. Raman	111

CHAPTER III

Experimental Procedures

1. Infrared Spectra
2. Raman Spectra
3. Matrix Isolation Apparatus
4. Synthesis and Separation of ±- and meso-2,4-Dichloropentanes and Isomers of 2,4,6-Trichloroheptane

CHAPTER III

Experimental Procedures

1. Infrared Spectra – RECORDED AT POLYTECHNIC OF WALES.

Spectra of all compounds were recorded on the Perkin-Elmer model 580 spectrophotometer, also, in the case of 2-chlorobutane, spectra were recorded on the Digilab F.T.-15C Fourier transform infrared spectrometer in order to perform a variable temperature study of 2-chlorobutane in an exercise designed to compare the two techniques of using a normal dispersive spectrometer and a Fourier transform infrared instrument for variable temperature measurements.

Solutions of all samples were run in carbon disulphide or carbon tetrachloride at various concentrations and cell thicknesses. Liquid cells were used with various window materials, e.g. CsI or KBr and for variable temperature work cells were used which were specifically designed for use with the Specac 20.1000 variable temperature unit using liquid nitrogen as coolant. The same bariable temperature studies were performed on the Digilab Fourier transform infrared instrument.

Gas spectra were obtained at various pressures by using either a 10 cm cell with KBr windows or a Wilks long path gas cell with a variable path-length facility of 0.75 m to 22.75 m, again fitted with KBr windows. The wavenumber calibration was checked periodically.

2. Raman Spectra – RECORDED AT B.P. SUNBURY.

All Raman spectra were recorded on an Anaspec Model 33 Laser Raman spectrometer using an Argon ion laser and laser line 5145 Å giving up to 100 mw power. Samples were held in sealed capillary tubes.

Variable temperature studies were performed on the instrument using an Oxford instruments DN 704 accessory using liquid nitrogen as coolant. Studies were carried out at low temperatures and elevated temperatures over a temperature range from 100K to 373K at scan speeds of 100 cm^{-1} min^{-1} and 50 cm^{-1} min^{-1}.

3. Matrix Isolation Apparatus

All compounds have been studied using matrix isolation techniques in view of the fact that the technique can help to obtain considerable information relating to conformational equilibria, isotope splittings, overlapping fundamental or combination bands. This information in turn clarifies assignments, conformational equilibria and thermodynamic parameters. This occurs by virtue of the fact that matrix isolation of a species results in isolation of single molecules, if the technique is carried out correctly, which greatly simplifies the spectra obtained.

Simply, matrix isolation involves diluting the samples with an inert gas and freezing this into a solid at very low temperatures. The basis of the utility of the technique lies in the fact that the infrared spectrum of a matrix isolated molecule at cryogenic temperature consists of sharp purely vibrational absorptions, thus it is possible to resolve features separated by as little as 1 cm^{-1} and to measure the frequency of the absorption with a precision of the order of 0.1 cm^{-1}. In practice, a gaseous mixture of the absorbing species and the inert gas is rapidly cooled to form a solid matrix at a temperature sufficiently low to prevent diffusion of the absorber. With high matrix: absorber ratio the solutes may be expected to be "isolated" in the rigid matrix, and provided the low temperature is maintained, it can be examined at will by infrared spectroscopy. The success of the technique depends upon the rigidity of the matrix and it is essential to operate at the lowest temperature available.

Two types of systems have been used to carry out these studies, initially an Air Products AC2L cryogenic system using liquid nitrogen to precool hydrogen on a two stage cascade system was donated by Newcastle University; the other, The Air Products CS-202 Displex closed-cycle cryogenic system employing commercial grade helium as refrigerant which was purchased for the later stages of the work from University College, Swansea.

The first type of system mentioned above had a minimum cooling temperature of 20K, while the closed-cycle system had a minimum cooling temperature of 8K.

The AC2L apparatus consists basically of three sections, the cryotip, a vacuum line for handling gaseous samples and a service trolley which has been designed to handle the evacuation of the cryotip shroud and delivery of hydrogen coolant to the cryotip.

The trolley delivers hydrogen by means of four hydrogen cylinders and it is attached to these and to the vacuum line by moderately flexible couplings. The trolley is on wheels, as is the spectrometer, and each can be moved independantly to bring the cryotip into the infrared beam. The cryotip can be altered to suit different spectrometers since it is mounted on the service trolley by a horizontally extendable arm on a vertically raseable platform. The framework of the trolley is constructed of Dexion with a single 5/16" aluminium sheet floor, and all pumps and the pillar are bolted directly onto the floor of the trolley.

Commercial grade hydrogen is used as coolant and hence must be purified before use to remove any gases which would freeze and block the cryotip nozzle. The purification is carried out in two stages. A liquid nitrogen trap removes water vapour and carbon dioxide, and a warm absorber then removes nitrogen and oxygen.

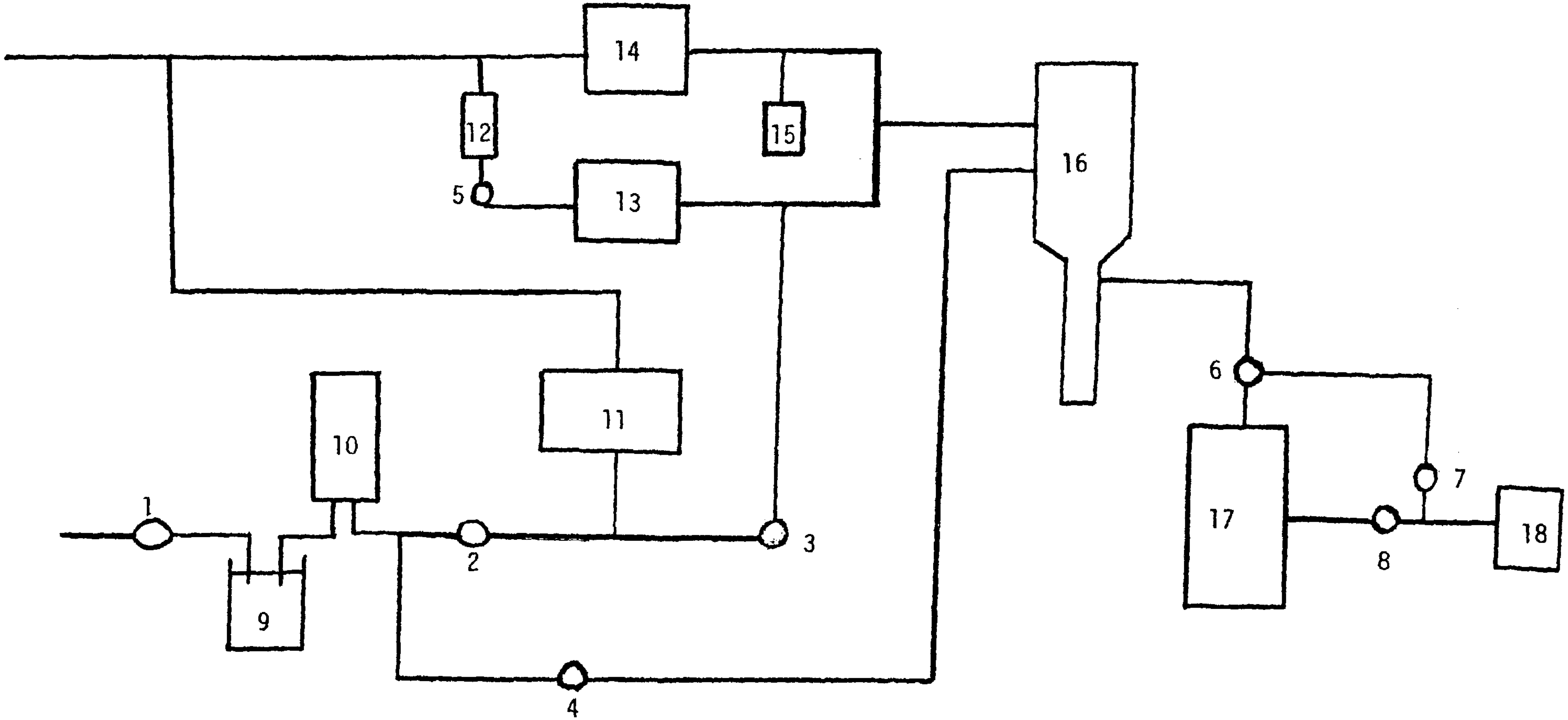
The hydrogen lines, the trap and absorber are pumped at room temperature before and after use to remove any free gas.

Regeneration of the absorber can be achieved by pumping whilst heating for 24 hours. A variac is fitted on the trolley to provide the 50 Volts maximum voltage used. It is necessary to regenerate the ABSORBANT after several months use.

Once a low temperature has been achieved the temperature of the sample is controlled by altering the rate of the hydrogen flow through the cryotip. This can be done either by altering the pressure of the incoming hydrogen using the pressure regulator on the cylinder bank, or by building up a back pressure on the exhaust hydrogen using the back pressure regulator. By this means annealing of a matrix can be carried out, i.e. raising the temperature of the matrix until is it just mobile, higher temperature results in matrix degradation.

A schematic exploded view of all the equipment on the trolley except electrical components and the cryotip mounting is shown in Figure III.1. The diagram depicts hydrogen being delivered (from a bank of four cylinders fitted with a pressure regulator) to the cryotip assembly, P, via a hydrogen handling system which is shown to the left of the cryotip. The cryotip shroud is evacuated by an Edwards E02 Diffusion pump and Penning gauges are used to measure the cryotip vacuum, and the normal room temperature vacuum achieved is 10^{-5} Torr and 10^{-6} Torr on cooling.

The apparatus controls are sited on a console on the trolley with the gauges and a Doric APD-T1 temperature readout, which monitors the temperature at the cold tip by means of the thermocouple. The diffusion pump cannot be operated unless both the rotary pump and the diffusion pump fans are running.



1-8	Valves	11	Backing Pump	14	Safety Valve	17	Diffusion Pump
9	Liquid N_2 trap	12	Flowmeter	15	Backing Pressure Gauge	18	Rotary Pump
10	Warm Absorber	13	Back Pressure Regulator	16	Cryotip Assembly		

Figure III.1 Diagrammatic representation of Apparatus Mounted on Service Trolley for AC2L system.

1 Glass Vacuum Shroud
2 Metal Outer Case
3 Cryotip Cooling Column
4 Heat Shield (with cutaway Section)
5 Thermocouple Mounting
6 Turned Brassed Nozzle

7 Ground Glass Socket
8 Cryotip Assembly
9 Caesium Iodide Window
10 Gas Input Tube
11 Potassium Bromide Outer Window
12 Thermocouple Lead

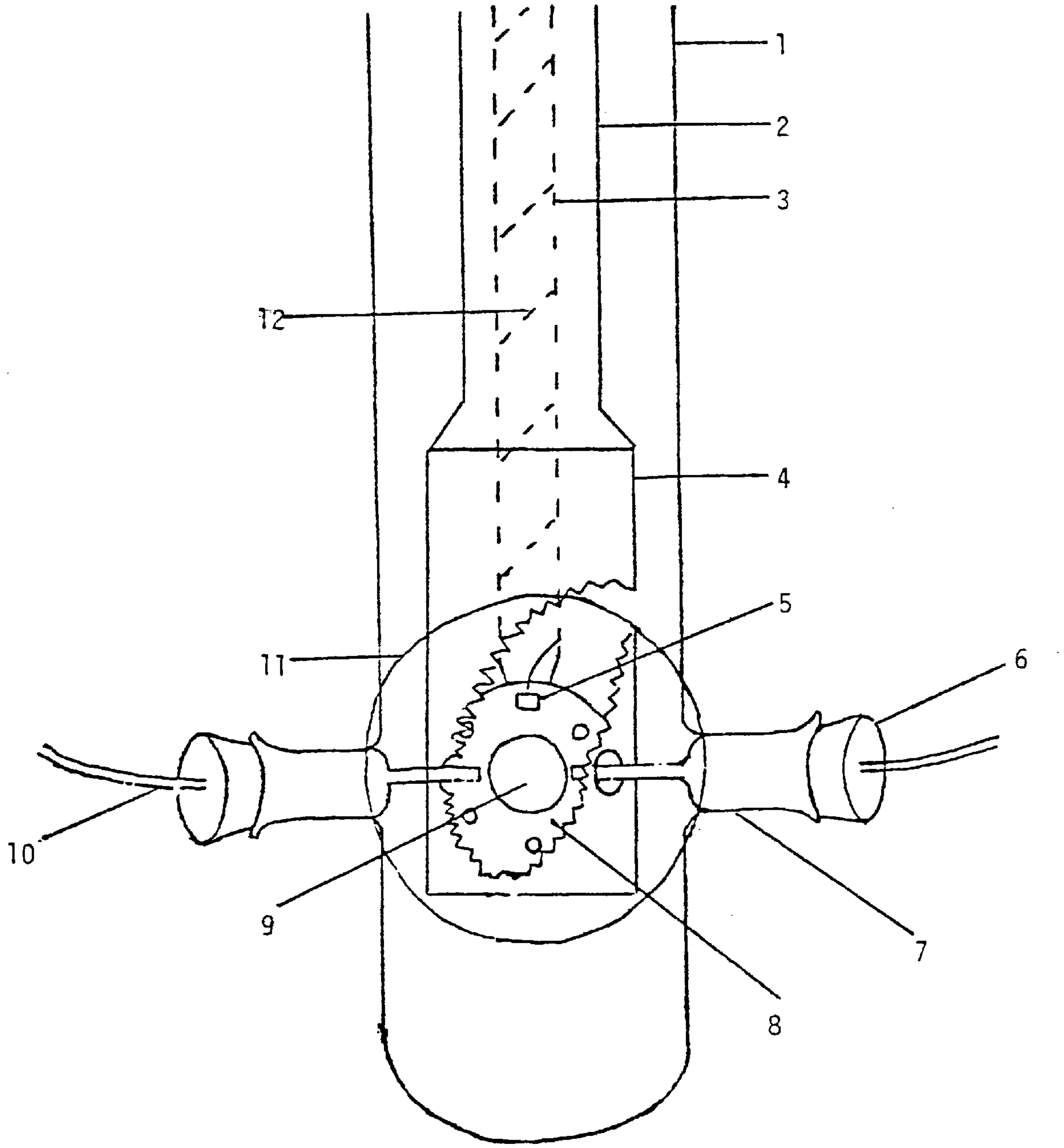


Figure III.2 Cryotip Assembly for AC2L System

The cryotip is capable of cooling a sample to approximately 19K by a two stage cascade process, (Figure III.2). Purified hydrogen gas is input from the service trolley and passes through liquid nitrogen to cool the gas to 77K. The cold gas cools the cryotip to the same temperature and exhaust hydrogen cools the incoming hydrogen in a heat exchanger. Once the inversion temperature is reached, cooling is accelerated by increasing pressure to 600 psi when Joule Thompson cooling occurs and a running temperature of about 23K is attained.

The cryotip temperature can only be maintained if thermal energy is stopped from reaching the tip. A glass shroud with KBr windows and sample input port encloses the cryotip and by holding this in a vacuum of at least 10^{-5} Torr convection and conduction by air is stopped. By placing the tip on the end of the long column which also acts as a hydrogen heat exchanger, conduction from the rest of the assembly is minimised. A heat radiation shield surrounds the tip and holes are cut into this for sample spray-on and spectroscopic examination.

The multipurpose vacuum gas handling line is shown as a diagrammatic representation in Figure III.4. Pumping is performed by an NGN PSR12 backing pump and an NGN diffusion pump. These pumps give vacuums of 2×10^{-5} Torr with and 10^{-2} Torr without the diffusion pump. One half of the line is installed with greaseless Teflon taps because some samples studied could interfere with grease seals and thus cause leaks.

Three, two or one litre bulbs are fitted so that a range of volumes can be mixed for matrix isolation work. For very low concentrations of samples the line "dead space" is about 220 cm^3. The matrix : sample ratios quoted are approximate, as accurate measurement of volumes and pressures is not easy, especially at low pressure.

The inert gas is introduced onto the line from a cylinder via a

1. Exhaust Valve
2. Inlet Valve
3. Surge Volume
4. Orifice
5. Warm End Displaced Volume
6. Seal
7. Displacer
8. Displacer Cylinder
9. Cold End Displaced Volume
10. Regenerator
11. Pressure Control Tube

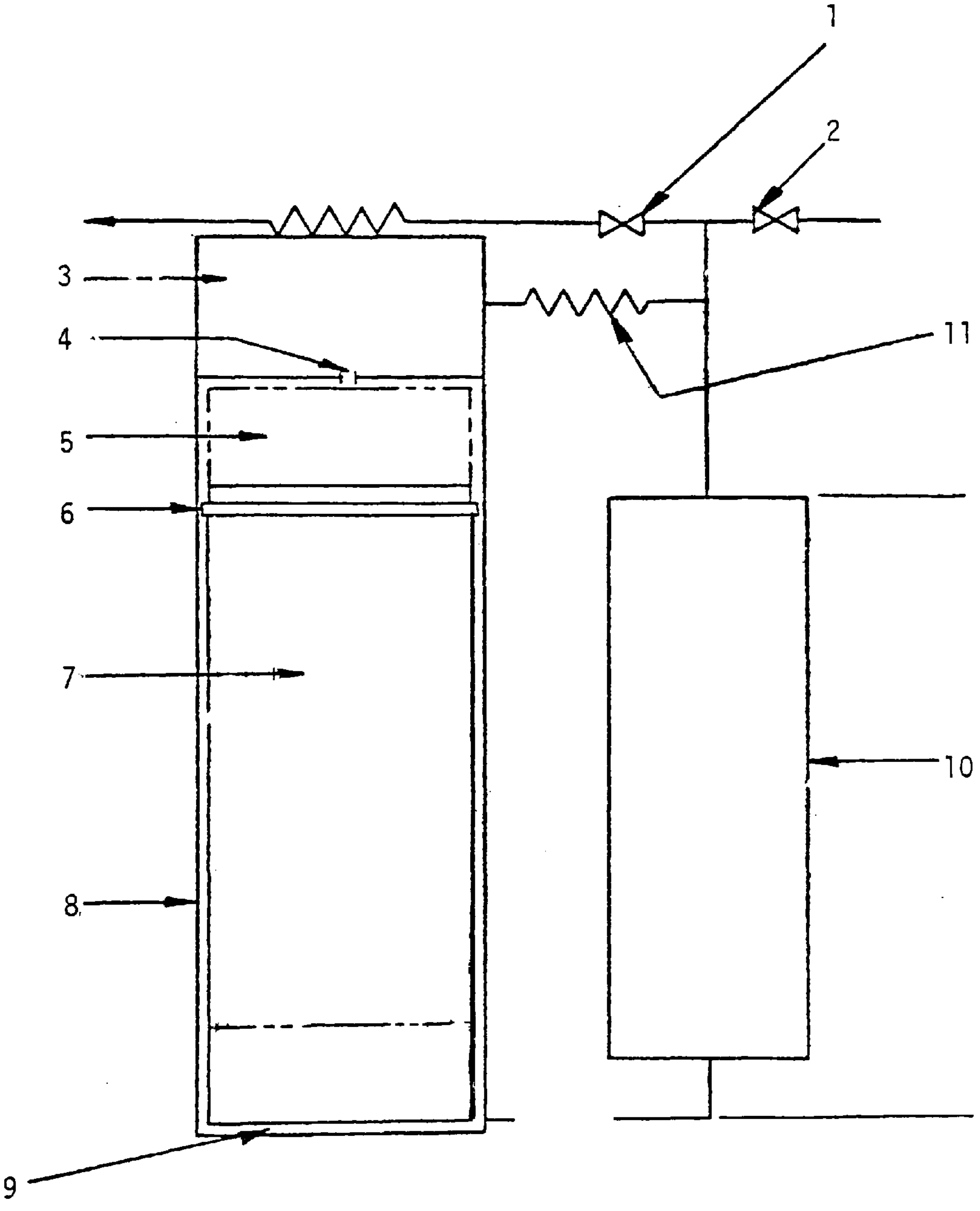


Figure III.3 Air Product CS-202 Helium System

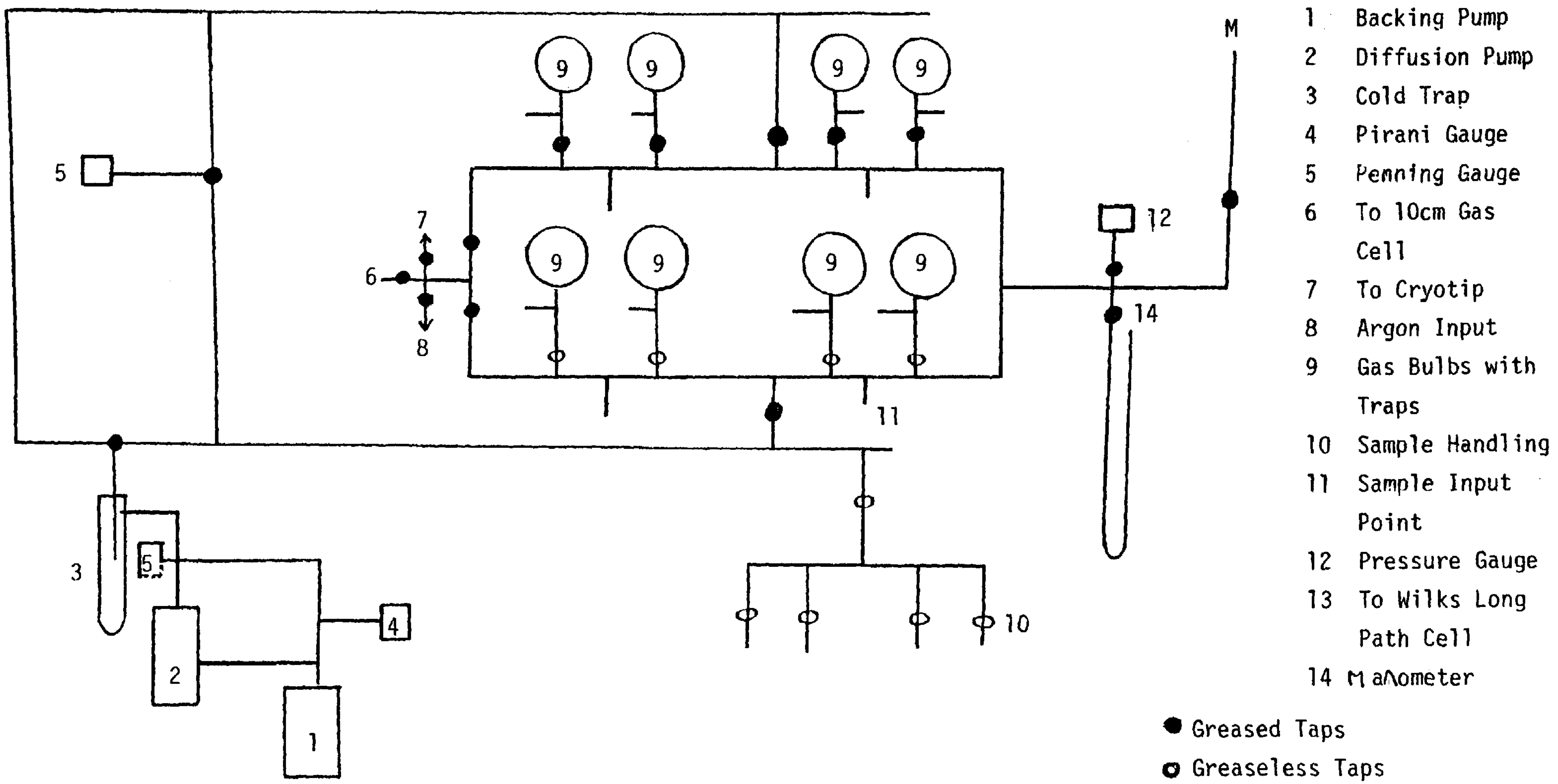


Figure III.4 Diagrammatic representation of multipurpose vacuum gas handling line pressure regulator and needle valve to ensure excess pressures do not build up quickly in the line.

A needle valve is fitted on the line to control the rate of flow of deposition of the sample/argon mixture which is sprayed onto the cryotip window. No quantitative estimate of rate of flow is made, as during spray-on the pressure drop in the line means that constant alteration to the needle valve setting is necessary.

The other system, i.e. the Air Product CS-202 helium system, provides a lower minimum temperature of cooling. The system basically consists of a two stage cryogenic cooler, a compact air-cooled, oil lubricated compressor and an electrical control panel. This system is based on the Stirling refrigeration cycle (Figure III.3).

What follows is a step-by-step description of one complete cycle. Since the process is repeated in both stages only one stage of the operation is described.

The gas is first of all compressed and then the high pressure gas flows down through the regenerator where it is cooled to the refrigeration temperature. The displacer then moves towards the warm end as gas bleeds out of the orifice into the surge volume (Figure III.3). Before it reaches the warm end the inlet valve is closed and the gas in the cold volume expands; the exhaust valve is now opened and the expanding gas in the cold volume leaves at a lower temperature than the entering temperature providing refrigeration and cooling the regenerator matrix as it flows back out.

During this phase the warm volume pressure drops and the displacer moves toward the cold end, gas beginning to flow back through the orifice from the surge volume and cold gas flowing out through the regenerator.

Before the displacer hits bottom, the exhaust valve is shut which produces partial recompression of the gas. The displacer remains briefly at the cold end while the gas pressure in the warm volume increases and the cycle then recommences.

More simply, the first step is that the compressor supplies a stream of purified helium gas to the cold head through an interconnecting line. The cold end serves as a small, high efficiency expansion engine in order to produce a quantity of refrigeration at the cold tip. A regenerative heat exchanger which is contained within the reciprocating piston of the expansion engine is used to produce refrigeration. Helium gas is admitted to the heat exchanger via a rotary valve whereupon it is cooled to minimum temperature prior to expansion. After expansion the helium flows out through the heat exchanger and returns to the compressor through a second line.

At the cold end, the cylinder assembly is constructed of stainless steel and together with the sample holder is surrounded by a vacuum shroud and a radiation shield (Figure III.5). The shroud is fitted with two KBr windows and two $\frac{1}{16}$" diameter vacuum quick-connect fittings at 45^{0} to the windows. These fittings allow the direct introduction of gaseous samples for deposition onto the cold CsI window at the end of the refrigerator.

Pirani and Penning gauges have again been used as in the case of the AC2L system for cold end vacuum readings. The temperature of the cold end is monitored by use of an iron doped gold vs chromel thermocouple wound around the cold end and attached to the sample holder.

Sample spray-on takes place in the same way using either the AC2L system or the Displex closed cycle system.

The first step is to move the spectrometer so that the cold tip lies in the path of the beam and the mixture is then sprayed onto the window slowly using the needle valve provided on the vacuum line. A suitable

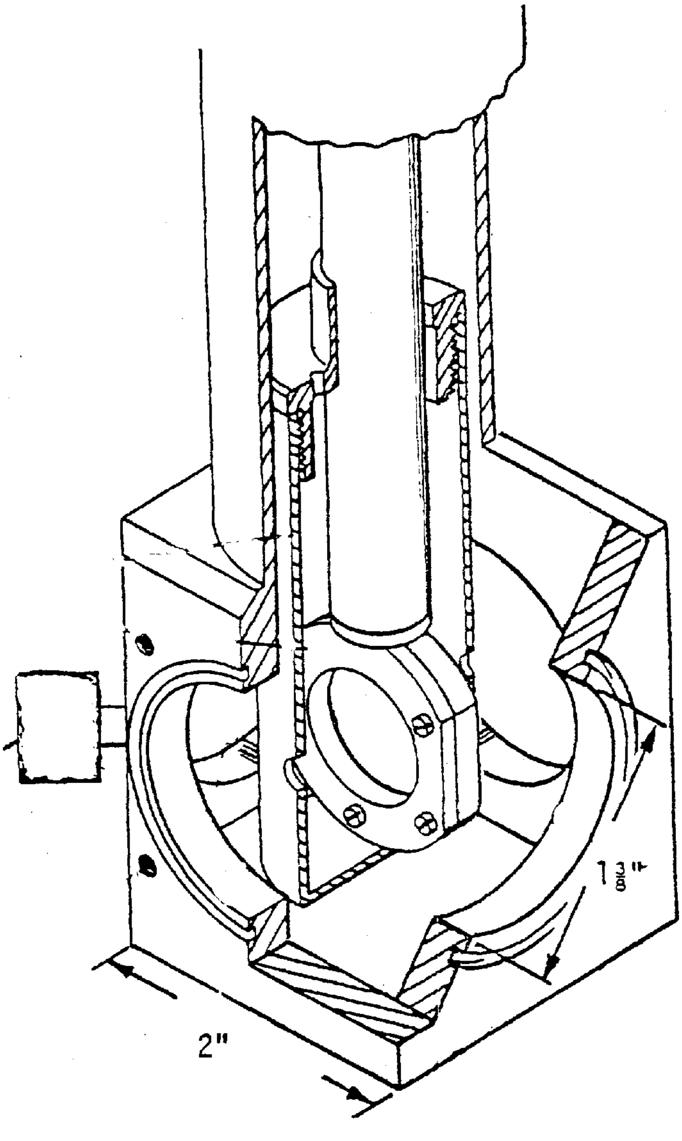


Figure III.5 Cold End of Cryotip Assembly fo CS-202 System region of the spectrum is scanned repeatedly during spray-on to monitor build-up of the matrix on the windows. In order to achieve a steady flow rate the needle valve is opened a little more as the pressure in the gas line decreases. For a 1000 : 1 matrix, spray-on time typically is about 40 minutes, after which spectra are recorded at required values of resolution.

Samples can then be annealed by slowly raising the temperature of the matrix until it becomes mobile and when this has been achieved the spectra can be rerun after recooling.

4. Synthesis and Separation of dl- and meso-2,4-dichloropentanes and isomers of 2,4,6-trichloroheptane

The starting material for the synthesis of these chlorohydrocarbons was the relevant pentane or heptane diol or triol. Chlorination of these diols or triols was effected by the synthesis in situ of a Vilsmeier reagent (112) which was generated by the reaction of phosphorous pentachloride with dimethylformamide. The actual chlorinating agent produced in this case is dimethylchloromethylene ammonium chloride $|Me_2 N = CH Cl|^+ Cl^-$ Chlorination of each diol or triol was carried out by adding it to a suspension of the Vilsmeier reagent in dimethylformamide as described below.

In the first instance 140 g (148 ml) of dry dimethyl formamide was cooled to 0^{o}C. 50 g of phosphorous pentachloride was slowly added to this with constant mechanical stirring of the solution. During this time the solution became yellow-orange in colour and after a short while a deposit of white crystals appeared in the orange solution. The solution had been allowed to become warm and was next cooled down to 0^{o}C again, by this time all of the phosphorous pentachloride had been added.

9.2 g of the diol was next placed in a dropping funnel together with a small quantity of dimethylformamide ($\sim$1 ml) and then slowly added to the solution of the chlorinating agent while stirring constantly.

During the addition of the diol or triol it was noted that the temperature of the solution rose to around 50°C and the colour of the solution changed to a pale red.

The mixture was next heated to 100°C by using an electric heating mantle and was maintained at this temperature for approximately thirty minutes, during which time the solution became dark red in colour.

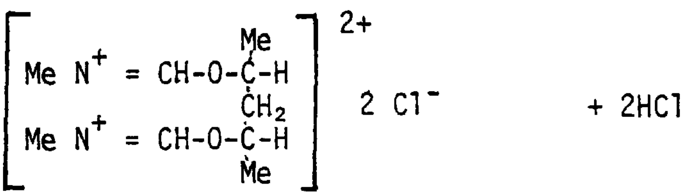
After the thirty minutes had elapsed the mixture was allowed to cool and was then poured into 250 ml of water. The solution was then extracted with two 25 ml portions of ether and the resulting solution was distilled in order to remove the solvents. The relevant chlorohydrocarbon was distilled over at the appropriate temperature and weighed.

The following equations are used to describe the reactions taking place in the above synthesis.

$$[(CH_3)_2N = CHCl]^+\ Cl^- + ROH \longrightarrow [(CH_3)_2N = CHOR]^+\ Cl^- + HCl$$

$$(CH_3)_2N^+ = CH\text{-}O\text{-}R\ Cl^- \xrightarrow{S_{N2}} (CH_3)_2N\text{-}CHO + RCl$$

$$2\ [(CH_3)_2N = CHCl]^+\ Cl^- + Me\text{-}CHOH\text{-}CH_2\text{-}CHOH\text{-}Me \longrightarrow$$



$$\left[\begin{array}{l} Me\ N^+ = CH\text{-}O\text{-}\overset{Me}{C}\text{-}H \\ \qquad\qquad\qquad\ \ CH_2 \\ Me\ N^+ = CH\text{-}O\text{-}\underset{Me}{C}\text{-}H \end{array}\right]^{2+} 2\ Cl^- \qquad + 2HCl$$

$$\longrightarrow 2\ (CH_3)_2N\text{-}CHO + Me\text{-}CHCl\text{-}CH_2\text{-}CHCl\text{-}Me$$

The yield of 2,4-dichloropentane obtained was 4 g.

The yield of 2,4,6-trichloroheptane obtained was 3.2 g.

The separation of the isomers of the dimer and trimer model compounds was achieved by the use of preparative gas chromatography. A Pye Unicam model 105 chromatograph was employed in order to achieve separation and was fitted with the following column.

The column was of 2 m length and 8 mm i.d. packed with 20 wt-%

Bentone 34 and Apiezon L on 30 - 50 mesh Celite. The column temperature was 150°C and 150 ml/min hydrogen carrier gas flow was used.

Identification and examination of fractions by i.r. indicated that the separations of the isomers achieved 99% purity.

All the compounds studied other than those described above were supplied by British Petroleum Trading Ltd.

CHAPTER IV

Vibrational Spectra of Saturated Chloro-Hydrocarbons

A. Variable Temperature and Matrix Isolation Studies of 2-Chlorobutane

1. Introduction
2. Experimental
3. Variable Temperature Infrared and Raman Studies
4. Matrix Isolation Studies

B. 2,4-Dichloropentane (± and meso) and 2,4,6-Trichloroheptanes (Syndiotactic, Heterotactic, Isotactic)

1. Introduction
2. Matrix Isolation Studies
3. Variable Temperature Studies
4. Variable Temperature Raman Studies

CHAPTER IV

A. Variable Temperature and Matrix Isolation Studies of 2-Chlorobutane

1. Introduction

Previous studies (5) have determined the presence of three rotational isomers in the liquid phase for 2-chlorobutane corresponding to three different positions given the notations S_{HH}, S_{CH} and S_{HH}', a notation which specifies the particular orientations about the carbon-carbon bonds on each side of the C-Cl bonds. The S_{HH} notation indicates that the four carbon atoms lie all in one plane while in the S_{CH} and S_{HH}' conformations they are non-planar (Figure IV.1). It has been suggested (113) that the planar S_{HH} conformation is predominant and this is confirmed in this study.

In this study 2-chlorobutane has been examined in the gas phase and by various matrix isolation infrared studies. Complete assignments for 2-chlorobutane in matrix isolation have been listed. Particular attention has been paid in the matrix isolation studies to the regions of the spectra at 600 cm^{-1} - 700 cm^{-1}, 1000 cm^{-1} - 1150 cm^{-1} and 1400 cm^{-1} - 1500 cm^{-1}, where notable changes in intensity of certain bands have been observed.

A variable temperature infrared study has been carried out in CS_2 solution at low temperatures enabling values of ΔH^{Θ} to be calculated for the thermodynamic equilibria between conformers. A variable temperature Raman study has also been carried out on 2-chlorobutane in the liquid phase as an independent measure of validity. These measurements enable ΔH^{Θ} values to be obtained for two equilibria and are compared with previous studies (49) for equilibria in the liquid state by i.r.

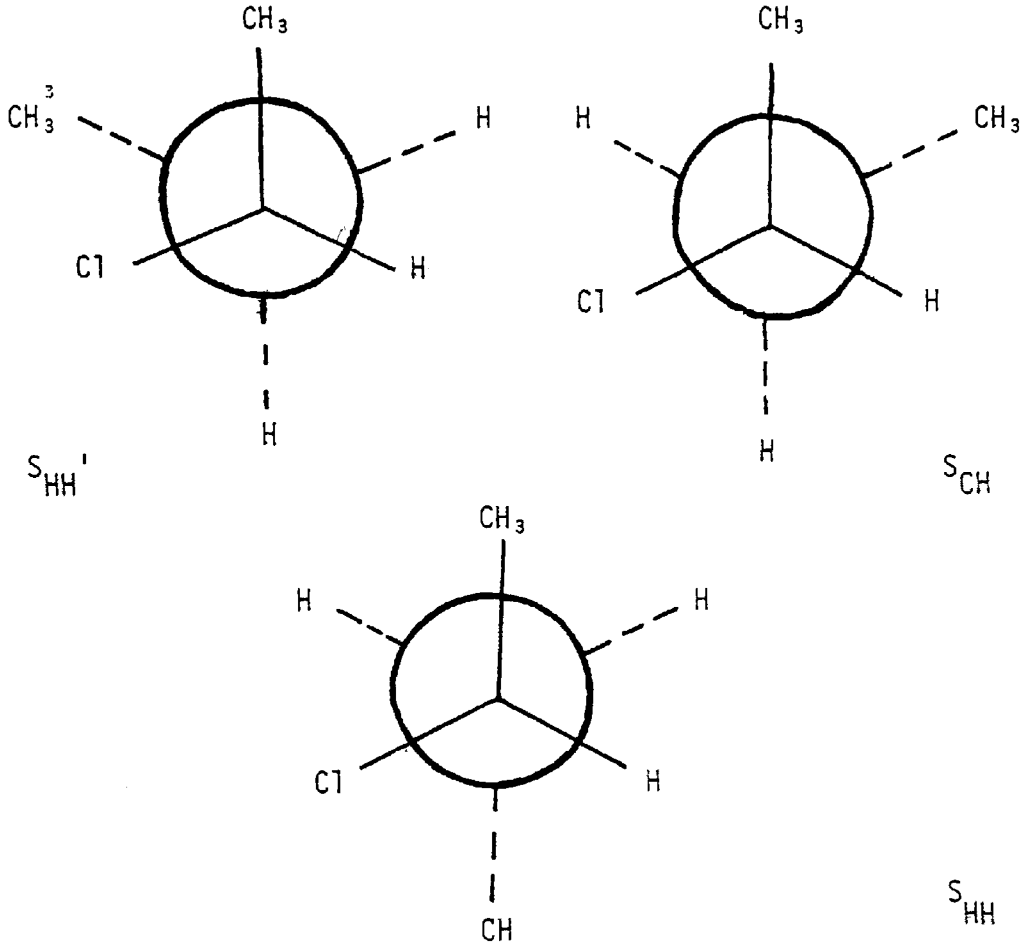


Figure IV.1 Conformational Isomers of 2-Chlorobutane S_{HH}', S_{CH}, S_{HH}

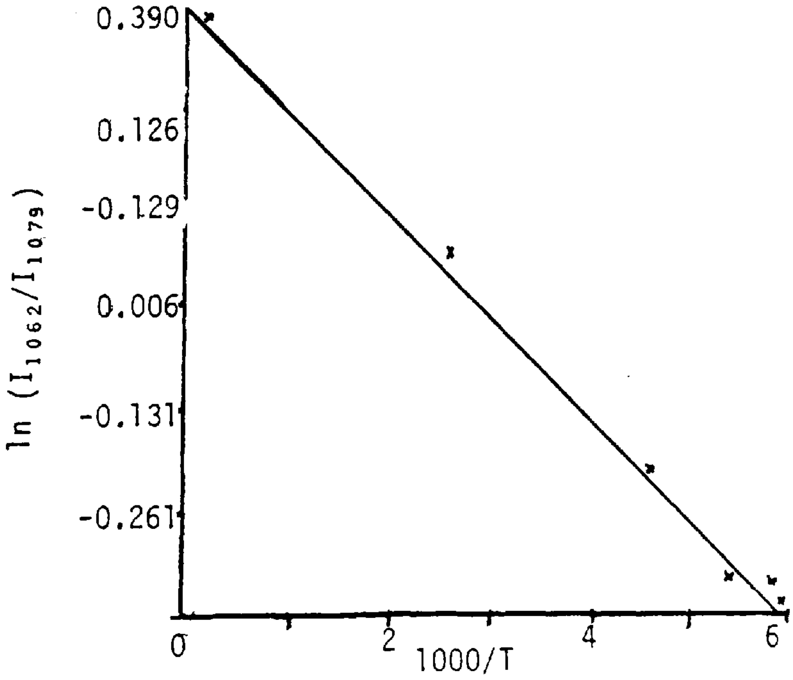


Figure IV.2 Plot of ln (I_{1062}/I_{1079}) versus $\frac{1000}{T}$ for 2-chlorobutane

2. Experimental

Infrared spectra of 2-chlorobutane were recorded on the P.E. model 580. Samples were examined either as liquid, gas or in solution in CS_2. Gaseous samples were examined using a 10 cm KBr cell. Matrix isolated samples were recorded as described in Chapter III using matrix : sample ratios from 1000 : 1 to 4000 : 1.

Raman spectra were recorded on an Anaspec model 33 laser Raman spectrometer using an argon ion laser, samples were held in capillary tubes. Low temperature Raman work was carried out using an Oxford Instruments Model DN704 Cryostat. The temperature was displayed on a digital temperature controller and was measured by using a temperature sensor attached to the heat exchanger.

3. Variable Temperature Infrared and Raman Studies

The infrared variable temperature study was performed by using a 10% solution of 2-chlorobutane in CS_2. All spectra were recorded using 0.5 mm KBr cells. The spectra were recorded over a range of liquid temperatures down to the freezing point of the solution. However, crystal samples have not been obtained because of practical difficulties involved in the technique. Benedetti and Cecchi (113) have observed in this study that these bands decrease markedly as the temperature is lowered and it has been assumed, from their work, that these bands would disappear on annealing.

All band frequencies agree with those of previous workers, the bands which have been noted to change in intensity in this study have been marked in the table of assignments having been worked out from previous force field calculations (114).

For both i.r. and Raman studies two sets of bands have been used in order to obtain values of $\Delta H^{\ominus}$ for different conformational equilibria. A pair of bands at 1062 cm^{-1} and 1078 cm^{-1} are observed to decrease and increase respectively in relative intensity on cooling within the range +30°C to -112°C. These are assigned (113) to the high (S_{CH}) and low (S_{HH}) energy conformers respectively. A graphical determination of $\Delta H^{\ominus}$ is shown (Figure IV.2) and the results may be summarized as follows:

I.r.	S_{HH}	S_{CH}	$\Delta H^{\ominus}$ kJ mol^{-1}
	1078↑	1062↓	2.24 ± 0.53

The three remaining sets of measurements may be summarized in a similar manner;

Raman	S_{HH}	S_{CH}	$\Delta H^{\ominus}$ kJ mol^{-1}
	1075↑	1064↓	2.27 ± 0.6
	S_{HH}	S_{HH}'	
I.r.	1023↑	1013↓	3.23 ± 0.7
Raman	1110↑	1118↓	3.67 ± 0.21

A variable temperature study of 2-chlorobutane was also carried out at low temperatures using the Digilab F.T.-15C Fourier transform spectrophotometer. Conditions used were similar to those where a variable temperature study was carried out on the P.E. model 580 so that a direct comparison of results could be effected. It was found that the Fourier transform instrument had no significant advantage over the P.E. 580 spectrometer for this type of study under the operating conditions used. However, since the instrument was available only for a limited period on loan, it was possible that it was not fully operational. Some test measurements on a solid polystyrene film indicated that this was probably the case.

4. Matrix Isolation Studies

Matrix isolation of 2-chlorobutane was carried out using a number of different techniques in order to achieve satisfactory annealing of the samples.

The following variations of the matrix isolation technique were used;

(i) Matrix gas : sample ratios of 1000 : 1, 2000 : 1 and 4000 : 1 were used, i.e. alteration of the sample concentration in the matrix.

(ii) The temperature of the input gas was altered and this was achieved by use of a bath surrounding a coil of the copper tubing through which the gas was sprayed. The bath was filled either with ice or with solid CO_2. The purpose of using this technique was to alter the temperature at which the gas was sprayed onto the cold window to form the matrix. The temperature of the window was held at 8K in each case and the i.r. spectra were recorded at 2 cm^{-1} resolution. The matrix temperature was then slowly raised and an attempt made to anneal the matrix as described earlier.

(iii) The matrix gas to be mixed with the sample was altered, e.g. by using krypton in place of argon.

After each complete spectrum of the matrix was recorded at 8K, the cryostat temperature was raised slowly to around 40K, held there for approximately 10 minutes and recooled to 8K in an attempt to anneal the matrix.

Taking each of three regions of the spectra of interest separately, the following changes were observed.

A. 600 cm^{-1} - 700 cm^{-1}

In all cases examined, the band at 609 cm^{-1} which corresponds to the S_{HH} C-Cl stretch increases in intensity after annealing and the two high energy conformer bands at 630 cm^{-1} and 670 cm^{-1} decrease in intensity after annealing. This is expected and is found to be in agreement with what happens to 2-chlorobutane in variable temperature studies.

The greatest change in intensity of these three bands is observed in matrix isolation spectra using argon as the matrix material, a ratio of 2000 : 1, M : S and a spray-on temperature of 0°C. Some asymmetry on the band at 670 cm^{-1} is observed on annealing the matrix (Figure IV.3).

B. 1000 cm^{-1} to 1150 cm^{-1}

Three pairs of bands in this region show temperature dependence by change in intensity on cooling. After annealing and running spectra it is found that the bands at 1018 cm^{-1}, 1065 cm^{-1} and 1112 cm^{-1} have all increased considerably in intensity. It is assumed from these results and from previous work (113) that bands at 1025 cm^{-1}, 1080 cm^{-1} and 1112 cm^{-1} are assigned to the predominant S_{HH} conformer.

C. 1400 cm^{-1} - 1500 cm^{-1}

The bands at 1447 cm^{-1} and 1460 cm^{-1} show a marked change in intensity on annealing to a greater degree than is evident from variable temperature work. The band at 1447 cm^{-1} shows a tendency to decrease in intensity while the band at 1460 cm^{-1} is found to increase in intensity. This would seem to indicate that the 1460 cm^{-1} band has a greater, if not total proportion of S_{HH} conformer (Figure IV.4).

In addition to the above we notice from all spectra that after annealing the two bands at 1287 cm^{-1} and 1297 cm^{-1} both increase in intensity but that this increase is more marked in the 1287 cm^{-1} band.

Overall, annealing of the sample was best achieved by use of Argon as Matrix gas, a M : A ratio of 1000 : 1 and a spray-on temperature of 0°C. (Figure IV.7).

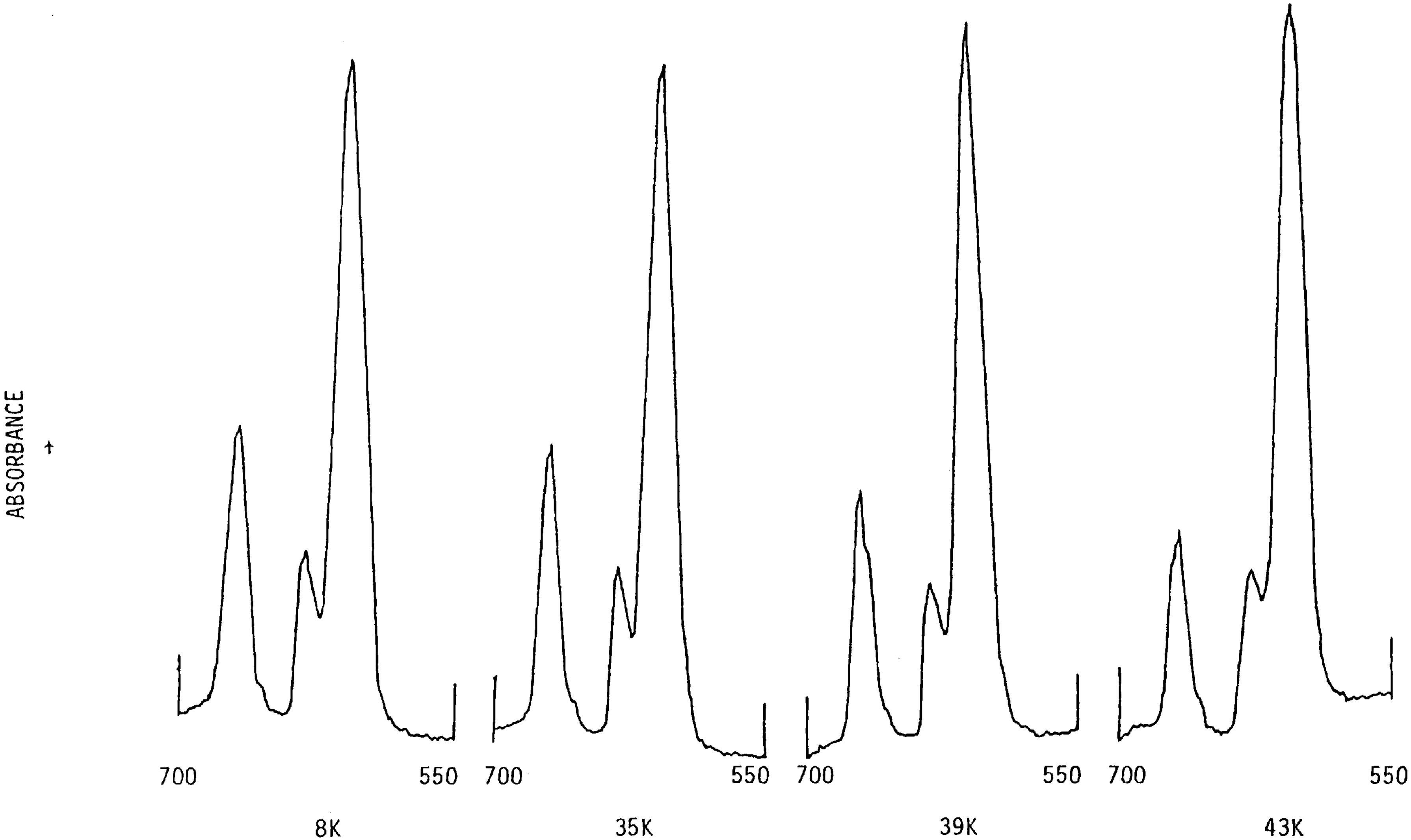


Figure. IV.3

2-CHLOROBUTANE

M.I. 4000 : 1 Argon

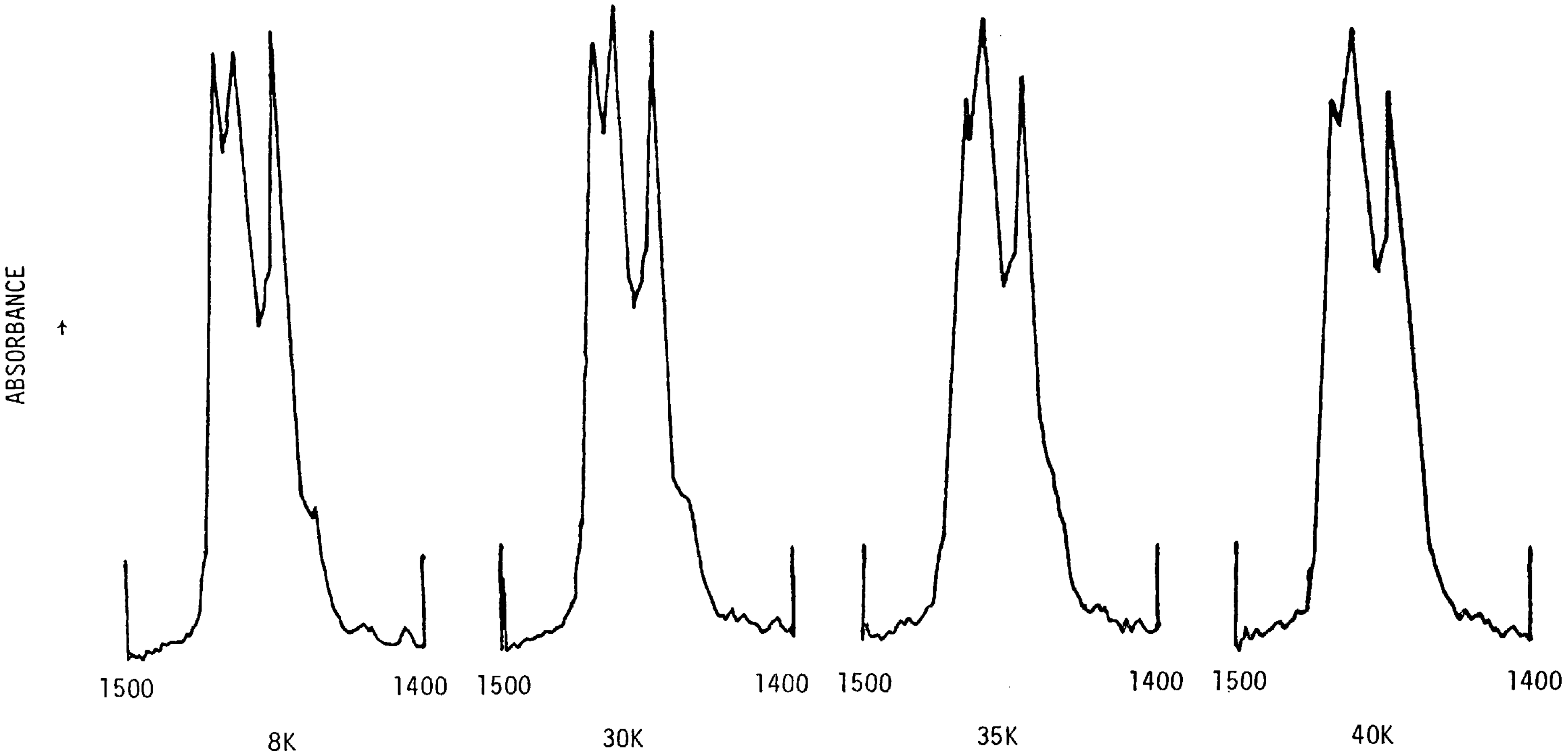


Figure IV.4

2-CHLOROBUTANE
M.I. 1000 : 1 Argon

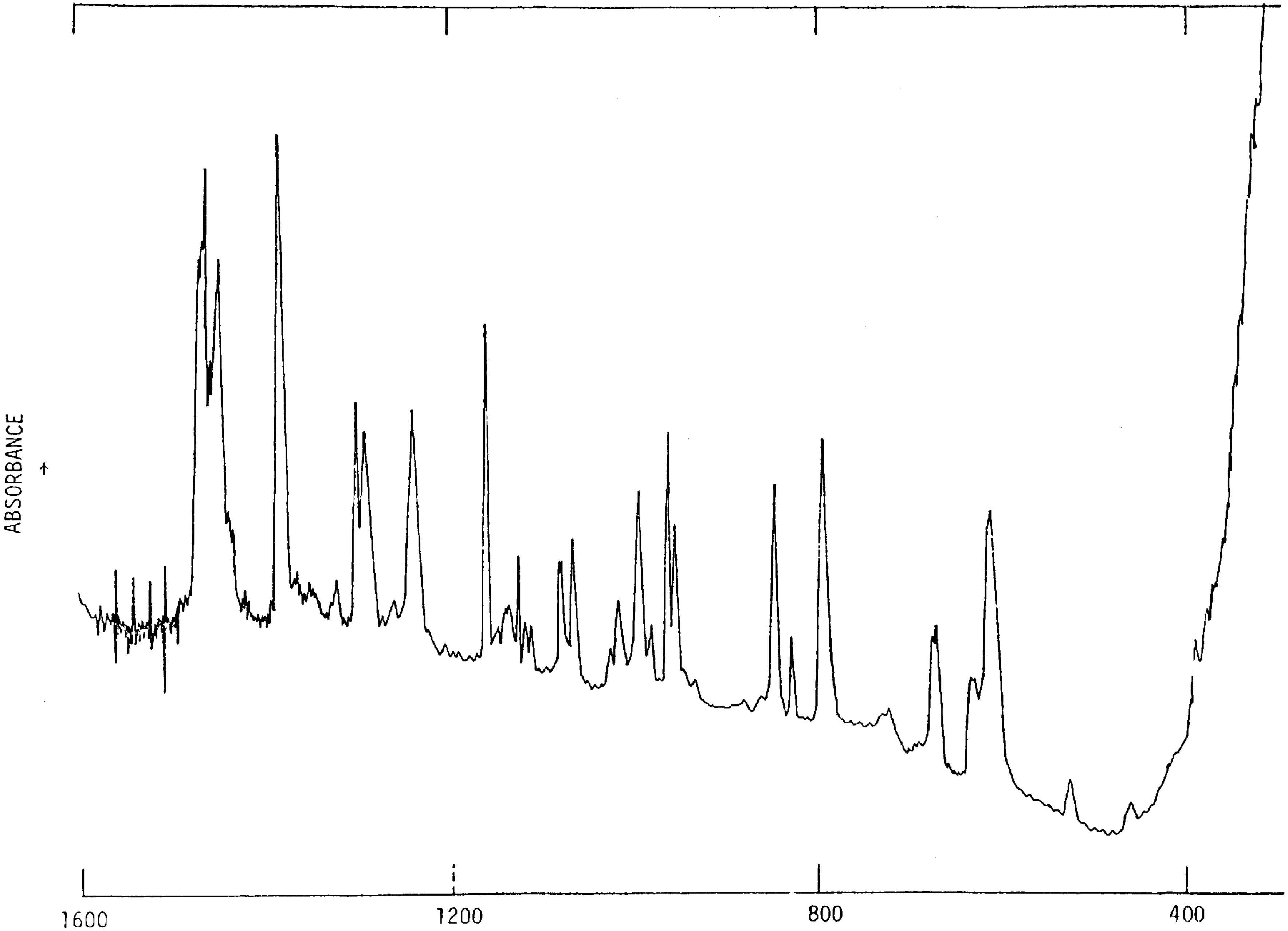


Figure IV.5 2-CHLOROBUTANE

M.I. **1000 : 1** **Argon** 23K Unannealed

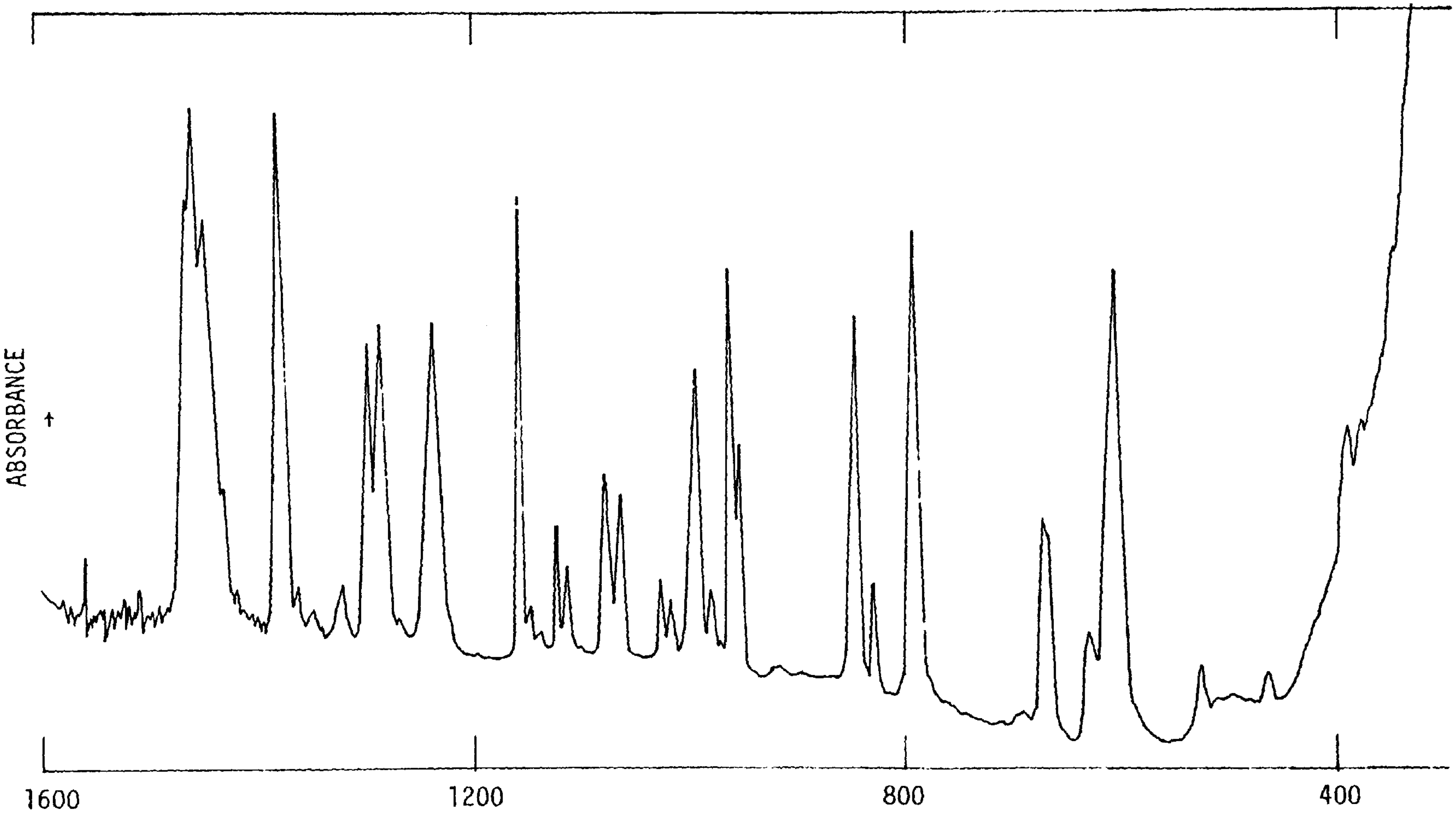


Figure IV.6

2-CHLOROBUTANE

M.I. 4000 : 1 Argon 8K Unannealed

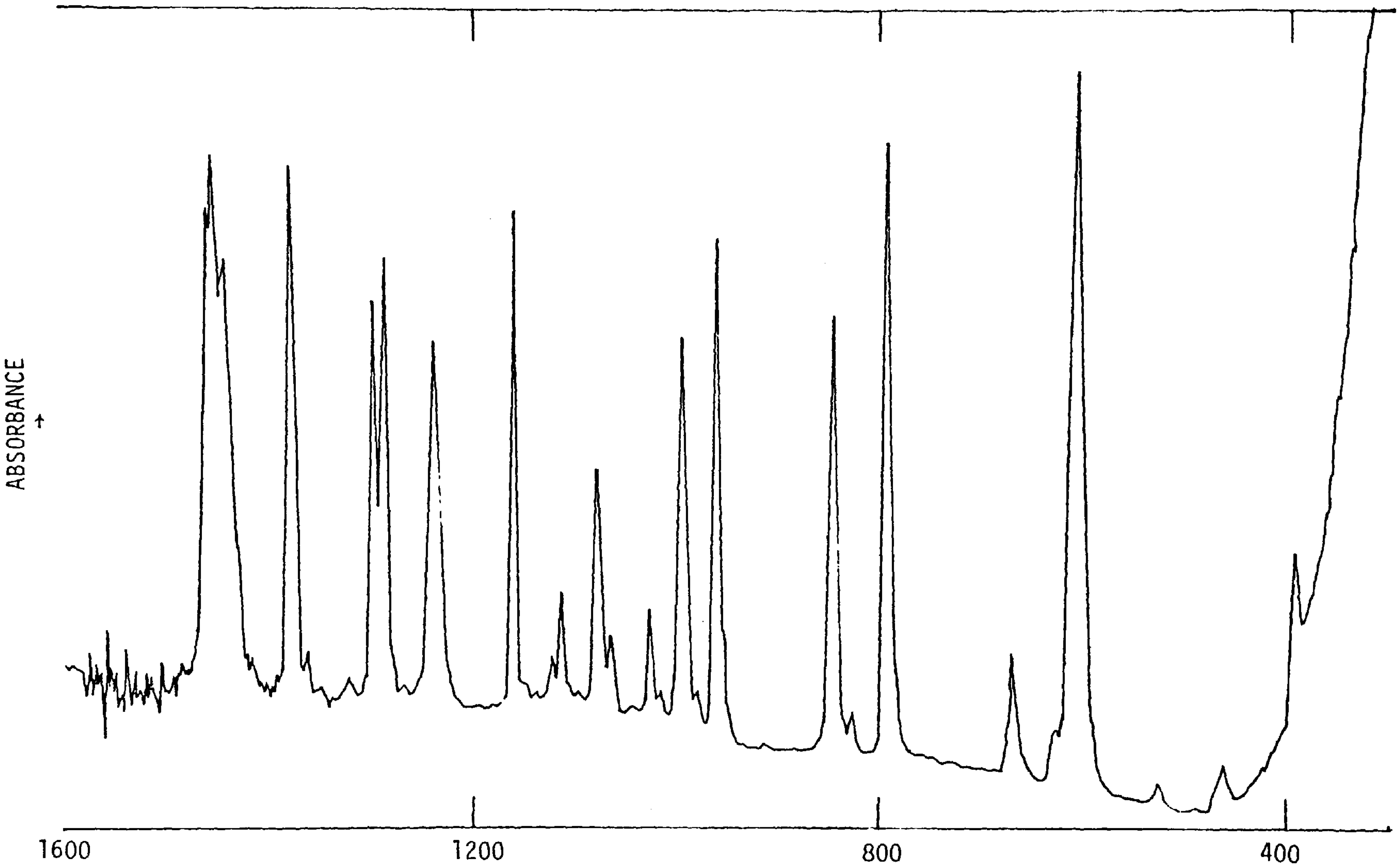


Figure IV.7

2-CHLOROBUTANE
M.I. 4000 : 1 Argon 8K Annealed

Comparing Figure IV.5 and IV.6, it can be seen that the spectra obtained by using the closed cycle system are a considerable improvement upon those observed from the AC2L system. The closed cycle system achieves a much lower temperature at which the matrix is sprayed onto the window, and the matrix seems to give much sharper, better resolved peaks.

5. High Resolution Gas Phase Spectra

High resolution gas phase spectra were carried out on many bands in the region 1400 cm^{-1} to 500 cm^{-1}. No rotational fine structure was observed on any of the bands in this region. Particular attention was paid to the C-Cl stretching region in order to observe any asymmetry on bands in this region which may have been due to isotopic splitting since some liquid spectra had originally shown asymmetry on the low frequency side of the band at 670 cm^{-1}.

However, no asymmetry or band broadening was observed in this region which would seem to indicate that any asymmetry found on this band in other phases is probably due to the presence of CO_2 and is not attributed to the 2-chlorobutane spectrum.

Table IV.1 2-Chlorobutane - Vibrational Assignments

(I.r. and Raman)

Assignments	Matrix Isolation Ratio in Argon $^1/_{4000}$ Temp. = 8K	Rel. Int.	Infrared 10% Soln. CS_2	Rel. Int.	Raman Liquid	Rel. Int.
					320	m
S_{CH}					374	m
S_{HH}					388	m
S_{CH}					420	w
S_{HH}	462	w	461	w	465	m
S_{HH}'	527	w	525	w	527	m
S_{HH} C-Cl stretch	609 ↑	vs	609 ↑	s	609 ↑	s
S_{HH}' C-Cl stretch	629 ↓	m	628 ↓	m	628 ↓	m
S_{CH} C-Cl stretch	670 ↓	m	670 ↓	m	670 ↓	m
	793	s	793	s	795	s
S_{HH}'	828	m	828	m	828	m
S_{HH}, S_{CH}'	848	s	848	s	848	s
CH_2 rock S_{CH}	862	vw				
S_{CH}, S_{HH}'	952	s	952	s		
CH_3 rock S_{HH}	961	s	961	s	961	s
S_{CH}	979	w	979	w		
S_{HH}, S_{HH}'	994	s	992	m	994	s
S_{HH}'	1018 ↓	w	1013 ↓	m		
S_{HH}	1026 ↑	m	1023 ↑	m	1025	m
S_{CH}	1065 ↓	m	1062 ↓	m	1064 ↓	m
S_{HH}	1080 ↑	m	1078 ↑	m	1075 ↑	s

Table IV.1 continued

Assignments	Matrix Isolation Ratio in Argon $^1/_{4000}$ Temp. = 8K	Rel. Int.	Infrared 10% Soln. in CS_2	Rel. Int.	Raman	Rel. Int.
S_{HH}	1112 ↑	m	1110 ↑	w	1110 ↑	
S_{HH}'	1125 ↓	m	1121 ↓	m	1118 ↓	m
S_{CH}	1140	m	1145	m	1118	m
S_{HH}' CH_3 rock						
CH_3 rock	1150	w				
	1160	s	1158	s	1159	s
CH bend	1240	s	1238	s	1238	s
CH_2 wag	1270	vw	1265	w	1270	m
CH_2 wag	1290 ↑	s	1288	s	1288	s
CH_2 twist	1300 ↑	s	1298	s		
	1321	m	1321	m		
CH def.	1350	w	1350	w		
	1363	w	1362	w		
CH_3 def. (symm)	1380	vs	1380	vs		
CH_2 def. (symm)	1431 ↓	sh	1380	vs		
	1447 ↓	s	1448	s		
CH_2 bend	1460 ↑	vs	1460	vs		
CH_2 def. (asymm)	1464 ↓	sh				

Abbreviations

m = medium, s = strong, w = weak, sh = shoulder, vs = very strong.

def. = deformation

↑ = relative intensity of band increases with decreasing temperature

↓ = relative intensity of band decreases with decreasing temperature

B. 2,4-dichloropentanes ((±)and meso) and 2,4,6-trichloroheptanes (Syndiotactic, Heterotactic, Isotactic).

1. Introduction

In this section studies are carried out by low temperature infrared analysis on dichloro and trichloro models of poly (vinylchloride), i.e. the 2,4-dichloropentanes and the 2,4,6,-trichloroheptanes. It is hoped that the studies undertaken of these compounds will provide additional information on conformational structure in the P.V.C. polymer chain, by analysing assignments in the C-Cl stretching frequency region.

When discussing conformations we have assumed a staggered molecular model in which angles of -60^0, $+60^0$ and $+180^0$ have been adhered to for the dihedral angle of a given C-C-C-C unit.

For each of the isomers of the above model compounds, certain configurations are known and the most important influence on the frequency of any particular C-Cl pair is the nature of the two atoms trans to the chlorine atom across both neighbouring C-C bonds. The assignments in this region of the spectra of the model compounds can be used in order to understand many of the features of solid P.V.C. samples, but it is necessary to note that the model compounds are liquids and that conformations not present in the liquid may however be present in the solid polymer.

When there is interaction between the C-Cl stretching vibrations and skeletal C-C-C bending modes, the C-Cl stretching frequency will exhibit extreme sensitivity to the conformational structure of the molecule.

In the case of S_{HH} conformations where the Cl atom is trans to two hydrogens across the C-C bonds the interaction is weak and in the case of S_{CH} conformations where the Cl atom is trans to one hydrogen across one bond and trans to a carbon across the other bond the interaction is strong leading to an increase in the C-Cl stretching frequency. S_{HH} stretching vibrations for compounds with several Cl atoms which are separated by CH_2 groups exhibit different frequencies determined by the extent to which the corresponding C-C-C angle is affected by vibrations of the neighbouring Cl atom.

From previous studies (5) it is possible to determine frequency ranges for the different types of conformations, i.e. S_{HH} 608 - 637 cm^{-1} and S_{HC} 655 - 675 cm^{-1}.

The symbols T, G and G' describe the conformation of the chain as trans or gauche, where G' represents the gauche conformation which is staggered through 120^0 from trans in the opposite direction from the standard G conformation. (Figure IV.8).

(±) and meso 2,4-dichloropentanes

Previous work (4,115) has indicated that the (±) isomer has six possible conformations: i.e.

i.e.	TT	$(S_{HH}\ S_{HH})$
	GG	$(S_{CH}\ S_{CH})$
	TG	$(S_{HH}\ S_{CH})$
	TG'	$(S_{HH}\ S_{HH}')$
	GG'	$(S_{HH}'\ S_{CH})$
	G'G'	$(S_{HH}'\ S_{HH}')$

In the case of this isomer the TT conformation has been found to be most stable, using the aforementioned staggered approximation. It has been stated previously (4) that only two of the above six conformations are present at room temperature, i.e. the TT and GG (Figure IV.9) conformations. However, weak bands were later observed in the diagnostic C-Cl stretching region indicating that other conformations were present.

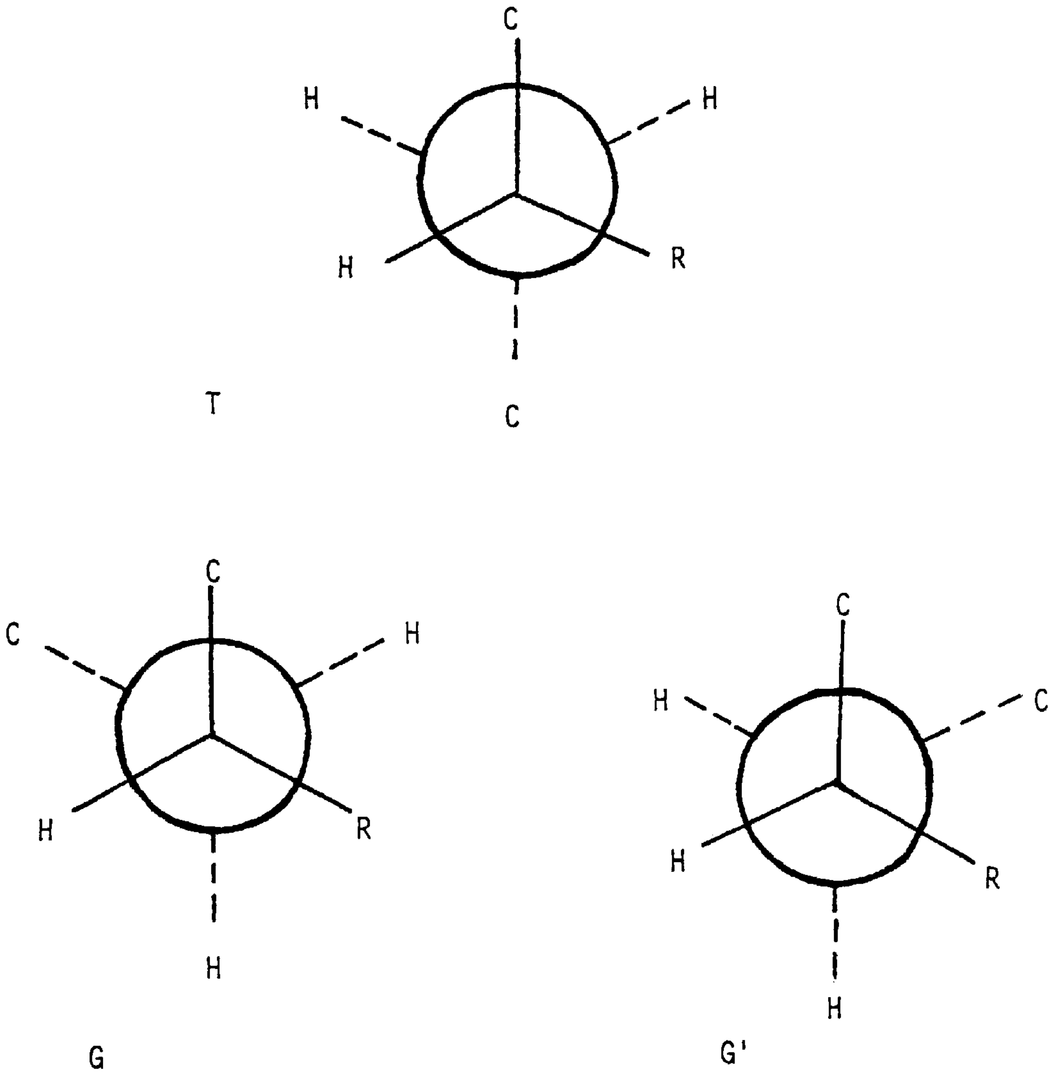


Figure IV.8 Diagrammatic representation of the terms T, G and G'.

Moore and Krimm (116) have found evidence by force field calculations that as well as the TT and GG conformations measurable quantities of the TG', TG and GG' conformations are present at room temperature in the case of the isomer.

In matrix isolation studies at low temperature certain weak bands can be observed in the spectra of the (±) isomer and have been assigned in this study to GG and GG' conformations.

In the case of the meso isomer of 2,4-dichloropentane previous studies have again shown that there are six possible conformations:

i.e.	TT	$(S_{HH}\ S_{HH})$
	TG'	$(S_{HH}\ S_{HH}')$
	TG	$(S_{HH}\ S_{CH})$
	G'G	$(S_{HH}'\ S_{CH}')$
	GG	$(S_{CH}\ S_{CH})$
	G'G'	$(S_{HH}'\ S_{HH}')$

Previous workers (4) have indicated in this case that only the TG conformation is present at room temperature. (Figure. IV.9). However, weak bands were later observed in the diagnostic C-Cl region indicating that there are other conformations present. In the case of this isomer, Moore and Krimm have shown that the TG' and TT conformations exist as well as the preferred TG conformation.

Matrix isolation studies show that the TG' conformation is present as well as the preferred TG conformation.

The (±)-2,4-dichloropentane has a configuration which corresponds to syndiotactic P.V.C. while the meso isomer has a configuration corresponding to isotactic P.V.C.

Syndiotactic, Heterotactic and Isotactic 2,4,6-trichloroheptanes

The trimer model compound for P.V.C., 2,4,6-trichloroheptane consists of three separate sterochemical isomers characterised as syndiotactic, heterotactic and isotactic according to the configurations of the fraction concerned.

It is hoped that low temperature infrared and Raman studies carried out on these three isomers will add more information on the assignments of the structure of the P.V.C. chain.

The following conformations for the three isomeric forms have been taken into consideration in this present work:

Syndiotactic TCH	T T T T	T T G G	G G T T	
	S_{HH} S_{HH} S_{HH}	S_{HH} S_{HC} S_{CH}	S_{HC} S_{CH} S_{HH}	
Isotactic TCH	T G T G	G' T T G	T T T G'	T T T T
	S_{HH} S_{CH} S_{CH}	S_{HC} S_{HH} S_{CH}	S_{HH} S_{HH} $S_{H'}^{H}$	S_{HH} S_{HH} S_{HH}
Heterotactic TCH	T T T G	T T G' T	G G T G	
	S_{HH} S_{HH} S_{CH}	S_{HH} S_{HC} S_{HH}	S_{HC} S_{CH} S_{CH}	

The T, G, G' notation has the same significance as already described for the 2,4-dichloropentanes. The most stable conformation of the 2,4,6-trichloroheptanes have been well studied and are deduced as:

Syndiotactic TCH	T T T T	(S_{HH} S_{HH} S_{HH})
Heterotactic TCH	T T T G	(S_{HH} S_{HH} S_{CH})
Isotactic TCH	T G T G	(S_{HH} S_{CH} S_{CH})

Normal coordinate calculations carried out by Moore and Krimm (116) examine bands in the diagnostic C-Cl stretching frequency region of the spectra of the three stereoisomers and have assigned both predicted and observed room temperature bands in this region. In the present study comparison is made with these assignments at low temperatures.

2. Matrix Isolation Studies

Matrix isolation studies have been carried out on all isomers of both dimer and trimer model compounds.

Taking the dimer model first, observations are described below. The matrix isolated spectra of both and meso isomers were recorded at 2.0 cm^{-1} resolution and in certain regions of the spectra, particularly the C-Cl stretching regions around 600 cm^{-1} -700 cm^{-1} and the CH_2 deformation region around 1400 cm^{-1} spectra were recorded at 0.5 cm^{-1}. (Figure IV.10).

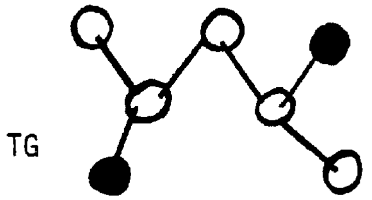
In the case of the C-Cl stretching region bands were observed at the following frequencies:

(±)-2,4-DCP	Meso-2,4-DCP
520 cm^{-1} w	552 cm ^{1} w
612 cm^{-1} s	626 cm ^{1} s
635 cm ^{1} s	650 cm^{-1} w
718 cm ^{1} w	688 cm^{-1} s

Considering the (±)isomer the bands at 612 cm^{-1} and 634 cm^{-1} are assumed from previous calculations and observations (4, 116) to be attributed to the preferred TT $(S_{HH}\ S_{HH})$ conformer. From previous predictions by calculations of force fields for the conformations the band at 718 cm^{-1} is assigned to the GG conformer and the band at 520 cm^{-1} is assigned to the GG' conformation.

Previous workers (115) observed a band at around 680 cm^{-1} in the liquid state which was found to be temperature dependent, decreasing with decrease in temperature. No band was observed near this frequency region in the matrix isolation spectra and it is assumed that this band

TT and GG conformers for(±)-2,4,dichloropentane



○ c

● Cl

TG conformation of meso-2,4-dichloropentane

Figure IV.9 Conformational structure of some rotational isomers of (±)- and meso-2,4-dichloropentanes.

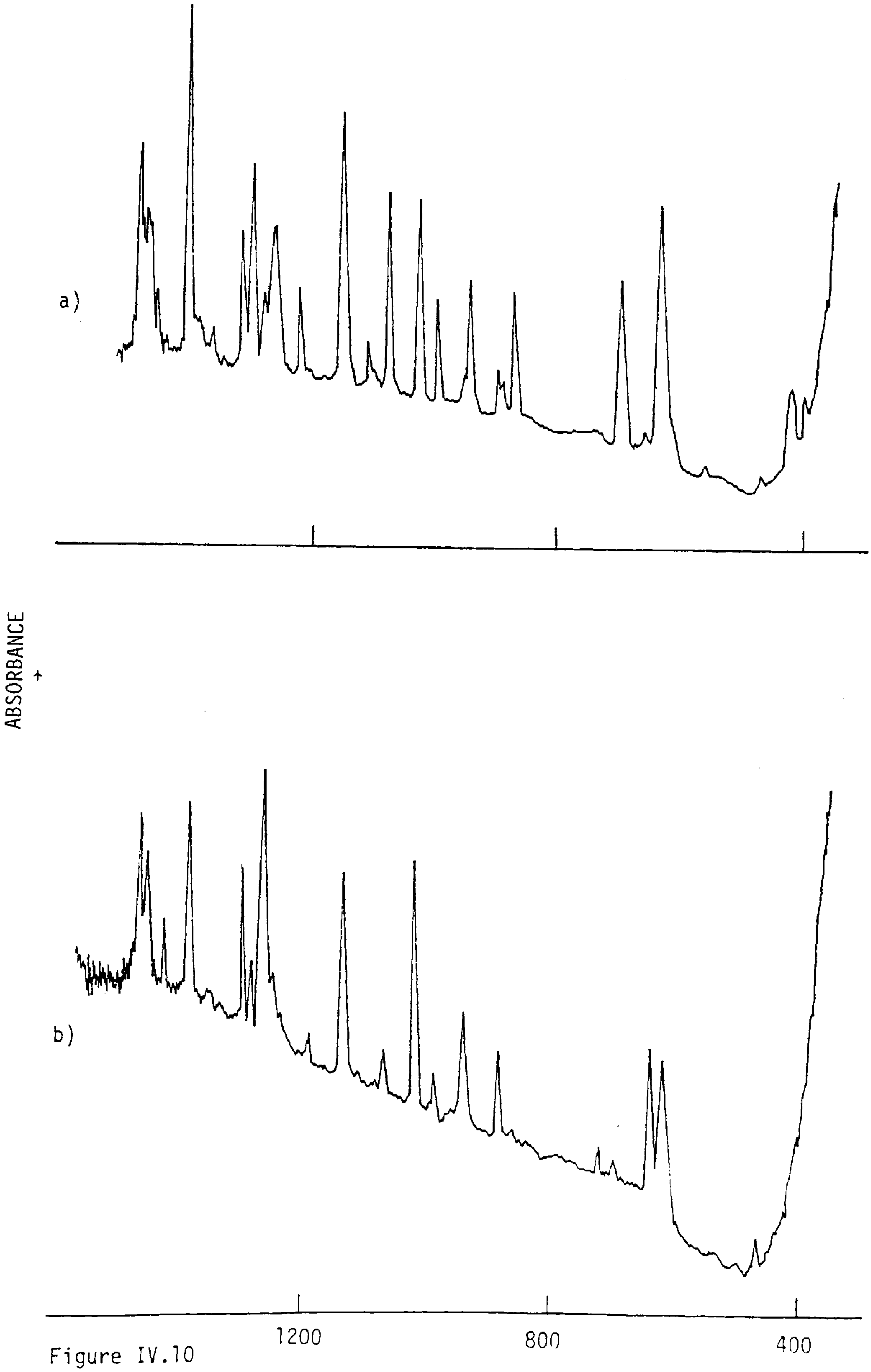


Figure IV.10

a) Meso-2,4-dichloropentane M.I. 1000 : 1 Argon 23K

b) (±)-2,4-dichloropentane M.I. 1000 : 1 Argon 23K has disappeared at these very low temperatures since a weak band is observed at 687 cm^{-1} in the liquid phase at room temperature for this isomer.

These results seem to indicate that as well as the preferred TT conformation at low temperatures significant amounts of GG and GG' conformations are present and assuming the 687 cm^{-1} band to be due to the G'G' conformation (116) we assume that there is no G'G' conformation present at very low temperature although there is some present at room temperature. These conclusions must be taken into account when discussing the chain conformation of P.V.C.

In the case of the meso isomer strong bands are observed at 626 cm^{-1} and 688 cm^{-1} and are assigned to the preferred TG conformation (S_{HH} S_{CH}). Weak bands are observed at 552 cm^{-1} and 650 cm^{-1} and from the predicted bands of Moore and Krimm have been assigned to the TG' (S_{HH} $S_{HH'}$) conformation.

This result again leads to the conclusion that when considering the chain conformation of P.V.C. at low temperature deviations from the expected favourable staggered arrangements have to be taken into account.

Matrix isolation studies have also been carried out on the three isomeric forms of the trimer model in various matrix gas materials and at various concentrations and all three samples have been annealed in the matrix. The following observations have been made again concentrating on the diagnostic C-Cl stretching region at high resolution.

Syndiotactic T.C.H.

Two bands are observed in the spectra of this isomer at matrix isolation conditions, i.e. bands at 608 cm^{-1} and 648 cm^{-1} corresponding to room temperature bands at 608 cm^{-1} and 640 cm^{-1}. The higher frequency band increases in intensity on annealing the matrix. These bands have been assigned to the T T T T conformer as they are characteristic of S_{HH} type C-Cl stretching vibrations. No other bands are observed in the C-Cl stretching region. No shoulder is seen to appear at 604 cm^{-1} which was observed by previous workers (117) on solidification in the liquid phase.

Heterotactic T.C.H.

Three bands are observed in the C-Cl stretching frequency region in the case of this isomer, i.e. bands at 610 cm^{-1}, 628 cm^{-1} and 688 cm^{-1} and no intensity change is observed in the bands on annealing the various matrices studied. These bands are attributed to contributions from both T T T G and T T G T conformations as these bands are characteristic of S_{HH} and S_{CH} type vibrations. (Figure IV.11).

Isotactic T.C.H.

In the C-Cl stretching region of the matrix isolated spectra studied in this case two bands are observed at 619 cm^{-1} and 688 cm^{-1} and no intensity change occurs in these bands on annealing the matrix. Contributions from T G T G and G' T T G conformations are attributed to these bands in the isotactic isomer.

3. Variable Temperature Studies

A low temperature variable temperature study of the dichloro compounds has been carried out by Schneider et al (115) who were mainly concerned with changes in the C-Cl stretching region of the spectra. The study yielded estimated values of $\Delta H^{\ominus}$ for different conformations of the dl isomer from the bands in this area of the spectra.

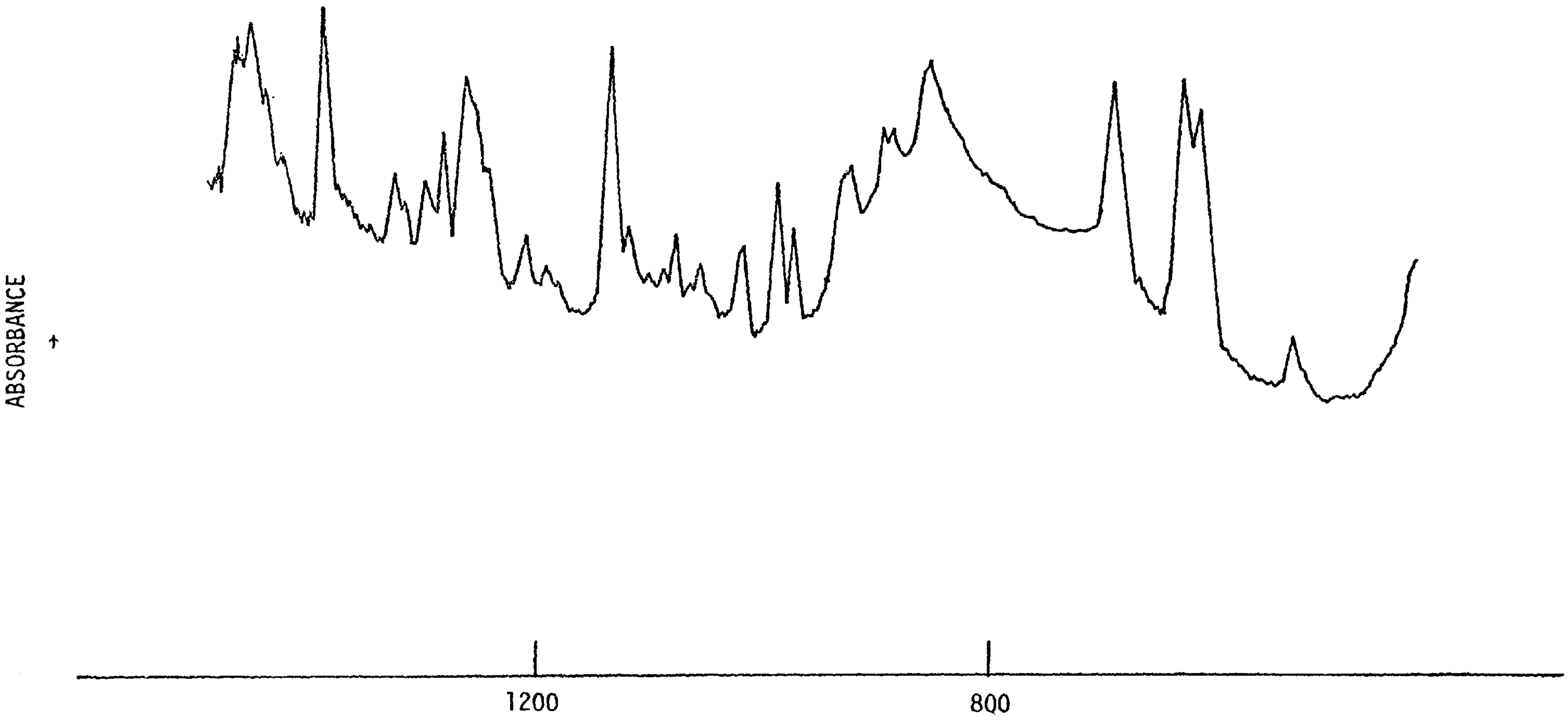


Figure IV.11 Heterotactic 2,4,6-trichloroheptane

M.I. 4000 : 1 Argon 8K

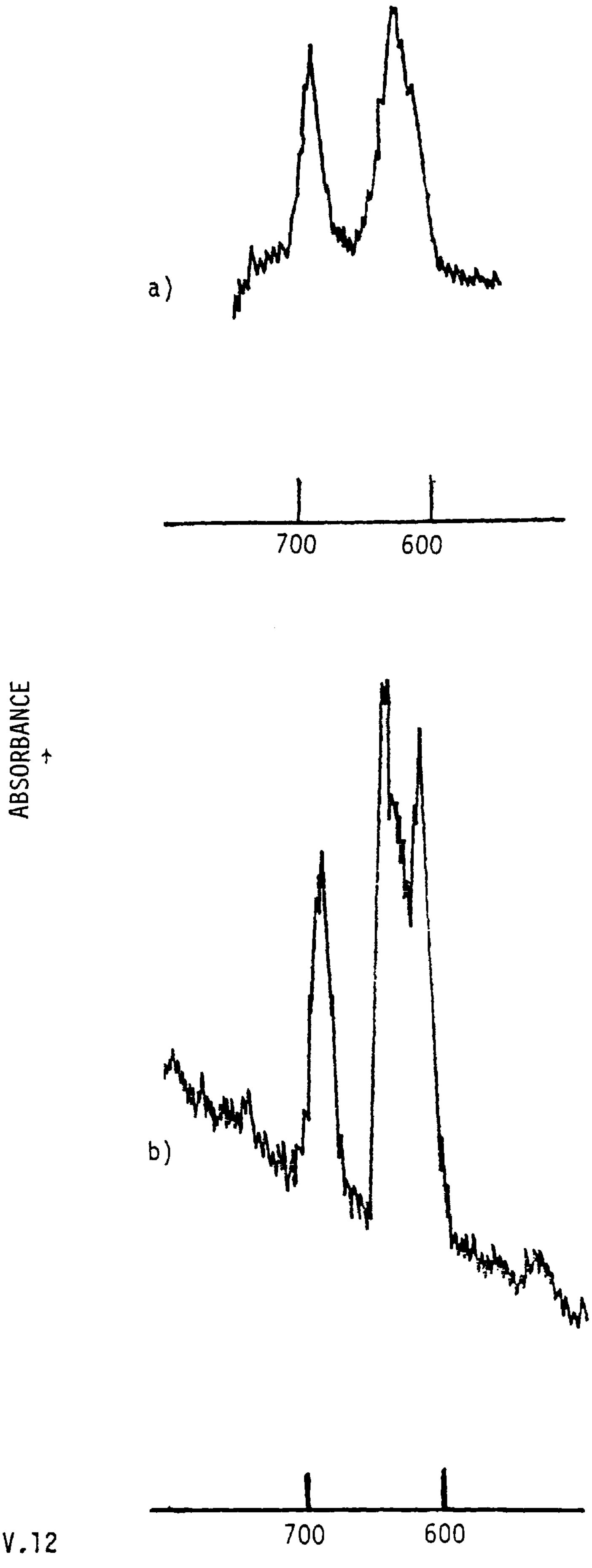


Figure IV.12

a) Isotactic 2,4,6-trichloroheptane Raman Spectrum 100K

b) Heterotactic 2,4,6-trichloroheptane Raman Spectrum 100K

In the present study, low temperature measurements have been made in 10% solution in CS_2 and the spectra have been examined over a range of temperatures from $30^{o}C$ to $-110^{o}C$ for conformational changes in band intensities.

In the case of (±)-2,4-dichloropentane the bands at 1065 cm^{-1} and 983 cm^{-1} appear to be temperature dependent and a $\Delta H^{\ominus}$ calculation has been carried out using these bands. The band at 1065 cm^{-1} is assigned to the high energy TG conformer and the 983 cm^{-1} to a low energy conformer (TT).

1065 cm^{-1}	TG	S_{HH} S_{CH}
983 cm^{-1}	TT	S_{HH} S_{HH}

The band at 1065 cm^{-1} was seen to decrease in intensity relative to the band at 983 cm^{-1} as the temperature was decreased. A value for $\Delta H^{\ominus}$ for the equilibrium between these two conformers was calculated as 8.9 ± 0.28 kJ mol^{-1}.

In the case of meso-2,4-dichloropentane bands at 1009 cm^{-1} and 1091 cm^{-1} were used for the variable temperature study and these bands were assigned to the preferred TG conformation (S_{HH} S_{CH}) and TG' conformation (S_{HH} $S_{HH'}$) respectively.

It was observed that on cooling the band at 1091 cm^{-1} decreased in intensity [redacted] relative to the band at 1009 cm^{-1}. On this basis a value of $\Delta H^{\ominus}$ has been calculated for the equilibrium between these conformers, i.e. S_{HH} S_{CH} $\rightleftharpoons$ S_{HH} $S_{HH'}$ as 1.26 ± 0.32 kJ mol^{-1}.

These values of $\Delta H^{\ominus}$ have been used in order to obtain the relative concentrations of the three conformers in the solution and these concentration values have been used in the Beer - Lambert equation to obtain values of extinction coefficients, all other parameters being shown.

Extinction coefficients for conformer bands at 1065 cm^{-1} and 983 cm^{-1} have been calculated to be as follows:

ε 983 = 27.3 m^2 mol^{-1} (TT conformation)

ε 1065 = 19.6 m^2 mol^{-1} (TG conformation)

4. Variable Temperature Raman Studies

Raman studies of the trimer model compound 2,4,6-trichloroheptane are of help in verifying the assignments for P.V.C. which have been observed previously in Raman spectra (118).

Previous studies of Raman spectra of the C-Cl stretching regions of P.V.C. samples prepared by various techniques have led to assignments for nine Lorenztian peaks in the spectrum. Two of these peaks were attributed to Ag and B_3g vibrational species of crystalline material while the other seven peaks were attributed with reasonable confidence to specific structures in the amorphous region.

The C-Cl stretching vibrations of the heterotactic and isotactic portions of the trimer model occur at slightly different frequencies for the various conformations than those previously observed in the I.r. spectra of the same compound.

Room temperature Raman spectra of the isotactic portion reveal two bands in the C-Cl stretching region at 623 cm^{-1} and 680 cm^{-1}. The latter band most likely corresponds to the band at 692 cm^{-1} which was observed by Robinson et al (118) in the Raman spectra of P.V.C. samples. Previous assignments (119) also seem to support this reasoning.

Raman spectra of the heterotactic portion reveal a band at 688 cm^{-1} which should also be taken into account when studying structures of the P.V.C. polymer by Raman spectroscopy (Figure IV.12). This observation seems to agree well with the suggestion made by Robinson et al (118) that the band at 692 cm^{-1} for P.V.C. is due to isotactic material as opposed to syndiotactic.

As deduced in the previous i.r. work the band at 686 cm^{-1} is assigned to the T G T G conformation of the isotactic portion which is in agreement with the assignments made by Pohl and Hummel in this region of the spectrum of P.V.C.

The band observed at 623 cm^{-1} in the Raman spectra of the isotactic portion of 2,4,6-trichloroheptane corresponds to the band at 623 cm^{-1} in the Raman spectra of P.V.C. assigned by Robinson et al to isotactic material.

In the case of the heterotactic portion of the trimer compound two other bands are observed in the C-Cl stretching region of the Raman spectra at 610 cm^{-1} and 638 cm^{-1}.

The latter band most likely corresponds to the band observed at 634 cm^{-1} in the Raman spectra of P.V.C. which corresponds to a bent $S_{HH'}$ structure.

In the present Raman study it is observed that in the case of the heterotactic portion the band at 638 cm^{-1} decreases in intensity suggesting a tendency towards less ordered conformations corresponding to thermal degradation in P.V.C. samples.

Unfortunately, in this study it has not been possible to obtain spectra of the syndiotactic crystalline type isomer of 2,4,6-trichloropentane but studies made of the other portions seem to confirm well the deductions of the structure of the amorphous region of the spectra of P.V.C. made by Robinson et al (118).

Table IV.2 (±)-2,4-dichloropentane,

Vibrational Assignments (I.r.)

Assignments	Infrared Soln. in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{1000}$ Temp. = 23K	Rel. Int.
	460	w	461	w
			520	w
C-Cl stretch	607	s	612	s
C-Cl stretch	628	s	635	s
C-Cl stretch	690	w		
C-Cl stretch	715	w	718	w
CH_2 rock	875	m	878	m
	938	s	940	s
	976	m	980	m
CH_3 rock	1014	vs	1016	vs
CH_3 rock	1067	m	1070	m
	1105	vw	1106	vw
	1127	s	1130	vs
	1191	m	1191	m
	1258	vs	1260	vs
			1279	m
	1288	s	1290	s
	1325	w	1327	w
	1379	s	1379	s
			1419	w
			1441	m
			1447	s

Table IV.3 Meso-2,4-dichloropentane, Vibrational Assignments (I.r.)

Assignments	Infrared Soln. in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{1000}$ Temp. = 23K	Rel. Int.
			394	w
			412	m
			465	w
C-Cl stretch	550	w	552	w
C-Cl stretch	619	vs	626	s
C-Cl stretch	650	sh	650	w
C-Cl stretch	683	s	688	s
	855	s	860	s
CH_2 rock	883	m	880	m
			889	m
	926	m	930	s
	980	m	985	m
	1005	m	1012	s
CH_3 rock	1060	s	1062	s
CH_3 rock	1090	m	1092	w
	1130	vs	1138	s
	1196	m	1203	m
	1238	s	1245	s
	1275	s	1260	m
	1287	m	1282	s
			1295	m
	1335	w	1340	w
	1357	m	1365	vw

Table IV.3 continued

Assignments	Infrared Soln. in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{1000}$ Temp. = 23K	Rel. Int.
CH_2 def.			1382	s
CH_2 def.			1420	m
CH_2 def.			1431	w
			1448	s

Table IV.4 Syndiotactic 2,4,6-trichloroheptane (I.r.)

Assignments	Infrared Soln. in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{1000}$ Temp. = 8K	Rel. Int.
C-Cl stretch	608	s	608	s
C-Cl stretch	632	s	632	s
CH_2 rock	858	m	858	m
	880	vw	880	vw
	890	vw	888	w
	930	m	932	m
	974	s	974	s
	1018	w	1020	w
CH_3 rock	1054	m	1054	m
	1105	w	1105	m
	1119	w	1119	w
	1140	s	1140	s
	1225	m	1125	m
	1240	s	1240	s
	1265	s	1265	vs
	1274	w	1274	w
	1318	m	1317	m
	1355	w	1355	w
	1380	s	1380	s
			1422	m
			1488	s

Table IV.5 Isotactic 2,4,6-trichloroheptane (I.r.)

Assignments	Infrared Soln in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{1000}$ Temp. = 8K	Rel. Int.	Raman Liquid	Rel. Int.
	495	w	495	w		
C-Cl stretch	563	vw	560	vw	550	m
C-Cl stretch	619	s	629	s	623	s
C-Cl stretch	688	s	688	s	686	s
	852	m	852	m	852	m
CH_2 rock	882	m	882	m	880	m
	895	m	890	m		
	918	m	918	m	918	m
	972	m	972	m		
	1005	m	1006	m	1009	m
	1015	m	1015	m		
	1028	m	1028	m		
CH_3 rock	1044	m	1044	m		
CH_3 rock	1071	sh	1072	sh		
	1080	m	1080	m		
	1102	w	1102	w		
	1123	s	1123	s	1123	s
	1178	m	1178	m	1178	m
	1190	w	1190	w	1193	w
	1205	m	1205	m		
	1235	s	1235	s	1238	m
C-H bend	1252	s	1252	s	1257	m
CH_2 wag	1277	m	1277	m	1277	m
CH_2 wag	1288	m	1288	m		

Table IV.5 continued

Assignments	Infrared Soln. in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{1000}$ Temp. = 8K	Rel. Int.	Raman Liquid	Rel. Int.
	1312	m	1321	m	1321	m
	1334	w	1334	w	1336	m
	1353	w	1353	w		
	1385	s	1385	s		
CH_2 def.			1417	vw	1418	w
CH_2 def.			1430	m	1430	m
CH_2 def.			1447	s	1446	s
					1460	s

Table IV.6 Heterotactic 2,4,6-trichloroheptane (I.r.)

Assignments	Infrared Soln. in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{2000}$ Temp. = 8K	Rel. Int.	Raman Liquid	Rel. Int.
	525	w	525	w	530	w
C-Cl stretch	610	s	610	s	610	s
			628	s		
C-Cl stretch	628	s			638	s
C-Cl stretch	688	s	688	s	688	s
	850	m	850	m	850	w
CH_2 rock	880	m	880	m	880	w
	892	m	892	m	892	w
	918	m	920	m	918	m
	967	m	967	m	985	m
	984	s	984	m		
	1011	m	1012	m		
CH_3 rock	1052	m	1052	m	1056	m
CH_2 rock	1072	m	1072	m		
	1083	sh	1083	w		
			1110	w	1110	w
	1125	s	1125	m	1127	s
	1172	vw	1172	sh	1172	w
	1185	w	1185	w		
	1204	m	1204	m	1204	m
	1232	sh	1232	sh		
	1245	m	1245	m		
C-H bend	1255	s	1255	s	1255	m

Table IV.6 continued

Assignments	Infrared Soln. in CS_2 (10%)	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{2000}$ Temp. = 8K	Rel. Int.	Raman Liquid	Rel. Int.
CH wag	1273	m	1273	m		
CH wag	1288	m	1288	m		
	1311	w	1311	w		
	1321	m	1321	m	1321	m
	1343	vw	1343	vw	1343	m
	1360	w				
	1383	s	1383	s	1383	m
CH_2 def.			1421	w	1425	w
CH_2 def.			1438	m	1438	m
CH_2 def.			1448	s	1448	s
			1458	s	1458	s

CHAPTER V

Vibrational Spectra of Unsaturated Chloro-Hydrocarbons

A. The Vibrational Spectra and Conformational Properties of Allyl Chloride

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2. Experimental
3. Variable Temperature I.r. Studies
4. Matrix Isolation Studies
5. High Resolution Gas Phase Studies

B. The Vibrational Spectra, Conformational and Thermodynamic Properties of 2-Chlorobuta-1,3-Diene (chloroprene) and Propenoyl Chloride

1. Introduction
2. Experimental
3. 2-Chlorobuta-1,3-Diene
4. Propenoyl Chloride
5. Vibrational Assignments
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CHAPTER V

A. The Vibrational Spectra and Conformational Properties of Allyl Chloride

1. Introduction

Allyl chloride has been shown (9) to exist as two conformational isomers, viz. cis and gauche (Fig. V.1). Various studies have previously been carried out on allyl chloride in order to determine vibrational assignments (9) and the major conformation of the molecule; electron diffraction studies of allyl chloride (120) have shown the gauche conformer to be the predominant species.

In this chapter allyl chloride has been studied by infrared and Raman techniques at low temperatures, at room temperature in the gas phase and at very low temperatures by matrix isolation techniques.

Gas phase spectra of allyl chloride have been recorded at high resolution and rotational fine structure was observed on certain bands. Calculations of rotational spacings have been made from these observations.

A variable temperature study was carried out on allyl chloride in CS_2 solution at low temperatures which enabled a $\Delta H^{\ominus}$ calculation to be carried out for the conformational equilibrium involved.

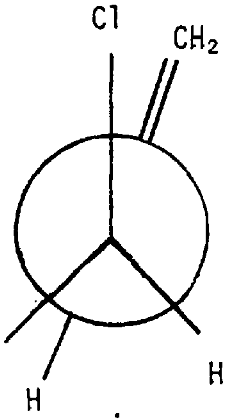
Various matrix isolation techniques have been employed in order to facilitate annealing of the sample. The techniques employed were

(i) alteration of the sample concentration in the matrix,

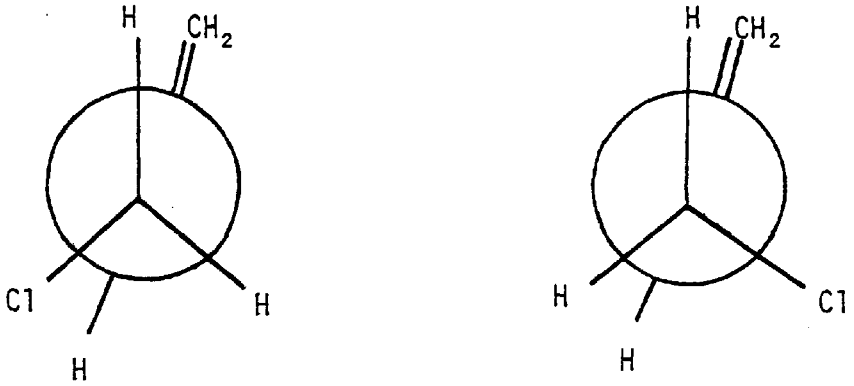
(ii) alteration of the temperature of the input gas,

(iii) changing the matrix material.

The best annealing conditions for this molecule appeared to be by spraying onto the window at room temperature with Argon as the carrier gas and



cis



gauche

Figure V.1 Conformational Structures of the cis and gauche rotational isomers.of Allyl Chloride an M : A ratio of 4000 : 1; in other words in the case of allyl chloride the only factor which appears to make a significant difference to annealing is dilution.

2. Experimental

All i.r. spectra were recorded on the Perkin-Elmer 580 spectrophotometer. Raman spectra were recorded on the Anaspec Model 33 Research Grade Laser Raman Spectrometer using an argon ion laser. For the variable temperature i.r. study samples were studied using a 0.5 mm KBr cell with the allyl chloride samples diluted with CS_2 to give a 10% solution. Spectra were recorded over a range of temperatures from +30°C to the freezing point of the solution. A range of six temperatures from +30°C to -90°C was used in order to calculate $\Delta H^{\ominus}$ for the conformational equilibrium.

Gas phase i.r. spectra were recorded using a 10 cm KBr cell at a pressure of 12 mm and the spectra were recorded on scan mode 9B which gave a value of 0.6 cm^{-1} resolution.

In order to anneal the matrix after recording the complete spectrum of the matrix isolated sample, the cryotip temperature was slowly raised to 0 K, held there for 12 - 15 minutes and then the matrix was recooled to 8 K.

Altering the temperature of the input gas was achieved by use of a bath containing either ice or solid CO_2 which was placed around the coil of copper tubing through which the gas was sprayed and kept there until sufficient material had been sprayed onto the window. Spectra were then recorded in the usual manner.

3. Variable Temperature I.r. Studies

A low temperature infrared study was performed on allyl chloride in

10% solution with CS_2. A pair of conformer bands was then used in order to obtain a value for $\Delta H^\ominus$ for the equilibrium, <u>gauche</u> allyl chloride $\rightleftharpoons$ <u>cis</u> allyl chloride where the <u>gauche</u> conformer is the low energy form. A range of temperatures between +30°C and -90°C was used for the calculations. The value of $\Delta H^\ominus$ quoted was obtained from intensity measurements at these temperatures.

The bands used occur at frequencies of 1175 cm^{-1} and 1098 cm^{-1}, the band at 1175 cm^{-1} disappearing on cooling and corresponding to the high energy band.

Previous workers (88) obtained a value for $\Delta H^\ominus$ from i.r. studies on the liquid using bands at 590 cm^{-1} and 550 cm^{-1}. They obtained a value for $\Delta H^\ominus$ of 1·85 kJ mol^{-1}. However, a different value is quoted in Chapter II, Table II.11, and this is because the latter value is determined by averaging the results obtained for $\Delta H^\ominus$ from a number of methods. The value obtained in this study of $\Delta H^\ominus$ for allyl chloride in 10% CS_2 solution was 1.1 ± 0.7 kJ mol^{-1}.

4. <u>Matrix Isolation Studies</u>

Matrix isolation of samples was achieved at temperatures of 8K at the matrix site, sample ratios of 1000 : 1, 2000 : 1 and 4000 : 1 were used with argon and krypton as the matrix gases. Mixtures were sprayed onto the caesium iodide windows at temperatures of either 23K or 8K and i.r. spectra were recorded at various values of resolution.

On annealing the matrix under these conditions, dramatic changes were observed in the spectra.

Bands appeared in the annealed spectra at the following frequencies:

1406 cm^{-1}

1261 cm^{-1}

982 cm^{-1}

940 cm^{-1}

892 cm^{-1}

The above bands have all been assigned to the predominant gauche conformation from comparison with previous work, particularly in the gas phase (9) (Figs. V.2 and V.3).

Bands at 1246 cm^{-1}, 1102 cm^{-1}, 938 cm^{-1} and 594 cm^{-1} increase in intensity on annealing, these bands also being assigned to the gauche conformation.

Bands at 513 cm^{-1}, 560 cm^{-1}, 1055 cm^{-1} and 1177 cm^{-1} which are all assigned to the high energy cis conformer are seen to disappear after annealing under these conditions.

The above observations seem to add weight to the conclusion that the gauche conformation is the predominant form of the allyl chloride molecule, and serve to confirm the assignments of particular bands to the respective conformers.

5. High Resolution Gas Phase Studies

High resolution spectra in the gas phase were recorded for the $=CH_2$ band at 1417 cm^{-1} and the $=CH_2$ rock at 988 cm^{-1}. These bands have C contours with characteristic central Q bands and rotational fine structure was observed on both bands, (Figs. V.4 and V.5).

Rotational constants A, B and C were calculated in units of cm^{-1} for both cis and gauche conformations using the CART computer programme.

For the cis conformer the values of these rotational constants are:

$A = 0.79007\ cm^{-1}$

$B = 0.09412\ cm^{-1}$

$C = 0.09163\ cm^{-1}$

Using these values of A, B and C gives a value for the rotational spacing $1.40\ cm^{-1}$.

However, the same calculation performed on the <u>gauche</u> conformer yields the value of the rotational constants:

$A = 0.71025\ cm^{-1}$

$B = 0.09403\ cm^{-1}$

$C = 0.09092\ cm^{-1}$

From which we obtain a value of $2\ (A-B) = 1.23\ cm^{-1}$.

A plot of 12 peaks found on each side of the Q bands at 988 cm^{-1} gave two straight line plots with slopes of 1.26 and 1.22 respectively, (Fig. V.6) These values hence confirm that the structure of the conformer giving rise to the band at 988 cm^{-1} is <u>gauche</u>.

The band at 988 cm^{-1} is a very strong fundamental corresponding to the $=CH_2$ rock, the other conformation being observed at 1053 cm^{-1}. This band at 1053 cm^{-1} is very much weaker in intensity and hence it is predicted that the predominant room temperature isomer is <u>gauche</u> having already deduced this from rotation - vibration studies performed on the 988 cm^{-1} band at high resolution in the gas phase.

Table V.1 Comparison of Infrared Liquid, Infrared Matrix, Infrared Gas and Raman Liquid Vibrational Spectra of Allyl Chloride (cm^{-1})

Assignments	Infrared Liquid	Rel. Int.	Infrared Matrix	Rel. Int.	Infrared Gas	Rel. Int.	Raman Liquid	Rel. Int.
ν_1 CCC def.							412	s
ν_1 CCC def. (c)			513 ↓	w			511	w
ν_2 CH = bend (c)			560 ↓	w	548	w		
ν_2 CH = bend (g)			594 ↑	s	593	m	590	s
ν_{1+3} CCC + CCl def.	690	w					690	sh
					743	s		
					751	s		
ν_4 C-Cl str	738	vs	742	s	759	s	738	vs
ν_5 CH_2 rock	898	s	898	w			894	vw
(g)			892	w				
ν_6 CH_2 = wag (c)			920	w	922	s		
ν_6 CH_2 = wag	941		932	vs	930	s		
ν_7 C-C str (g)	941	vs	938	m	938	s	939	m
(g)			940	m				
(g)			982	m	985	m		
			988	w	988	m		
ν_8 CH_2 twist (g)	987	vs	991	s	995	m		
ν_8 CH_2 twist (c)	1048	w	1055 ↓	vw				

Table V.1 continued

Assignments	Infrared Liquid	Rel. Int.	Infrared Matrix	Rel. Int.	Infrared Gas	Rel. Int.	Raman Liquid	Rel. Int.
ν_9 CH_2 = rock (g)	1098	w	1102 ↑	w	1101	w	1100	w
					1127	w		
					1139	w		
					1148	w		
					1171	w		
ν_{10} CH_2 twist (c)	1175	w	1177 ↓	w	1177	w	1175	w
ν_{10} CH_2 twist	1201	w	1204	w			1200	s
			1231	w				
(g)			1246 ↑	w				
					1253	s		
ν_{11} CH_2 wag (g)	1259	vs	1261	vs	1261	s	1262	s
			1269	w	1269	s		
ν_{12} CH = bend	1291	m	1297	m	1290	m	1290	vs
(g)			1406	m				
ν_{13} CH_2 = bend	1412	vs	1414	vs	1412	m	1414	vs
					1417	m		
ν_{13} CH_2 = bend (c)			1431	w	1422	m		
					1447	m		
					1442	m		
ν_{14} CH_2 bend	1445	s	1446	s	1457	m	1445	s
					1648	m		
ν_{15} C = C str	1645	m	1648	m	1657	m	1648	m

Table V.1 continued

Assingments	Infrared Liquid	Rel. Int.	Infrared Matrix	Rel. Int.	Infrared Gas	Rel. Int.	Raman Liquid	Rel. Int.
ν_{16} sym CH_2 str	2960	m	2962	m	2962	m	2960	m
ν_{17} asym CH_2 str	2990	m	2998	m	2979	m	2985	m
					3000	m		
ν_{18} CH = str	3021	m	3020	m	3010	m		
					3095	m		
					3099	m		
ν_{19} asym CH_2 = str	3090	m	3100	m	3105	m	3090	m

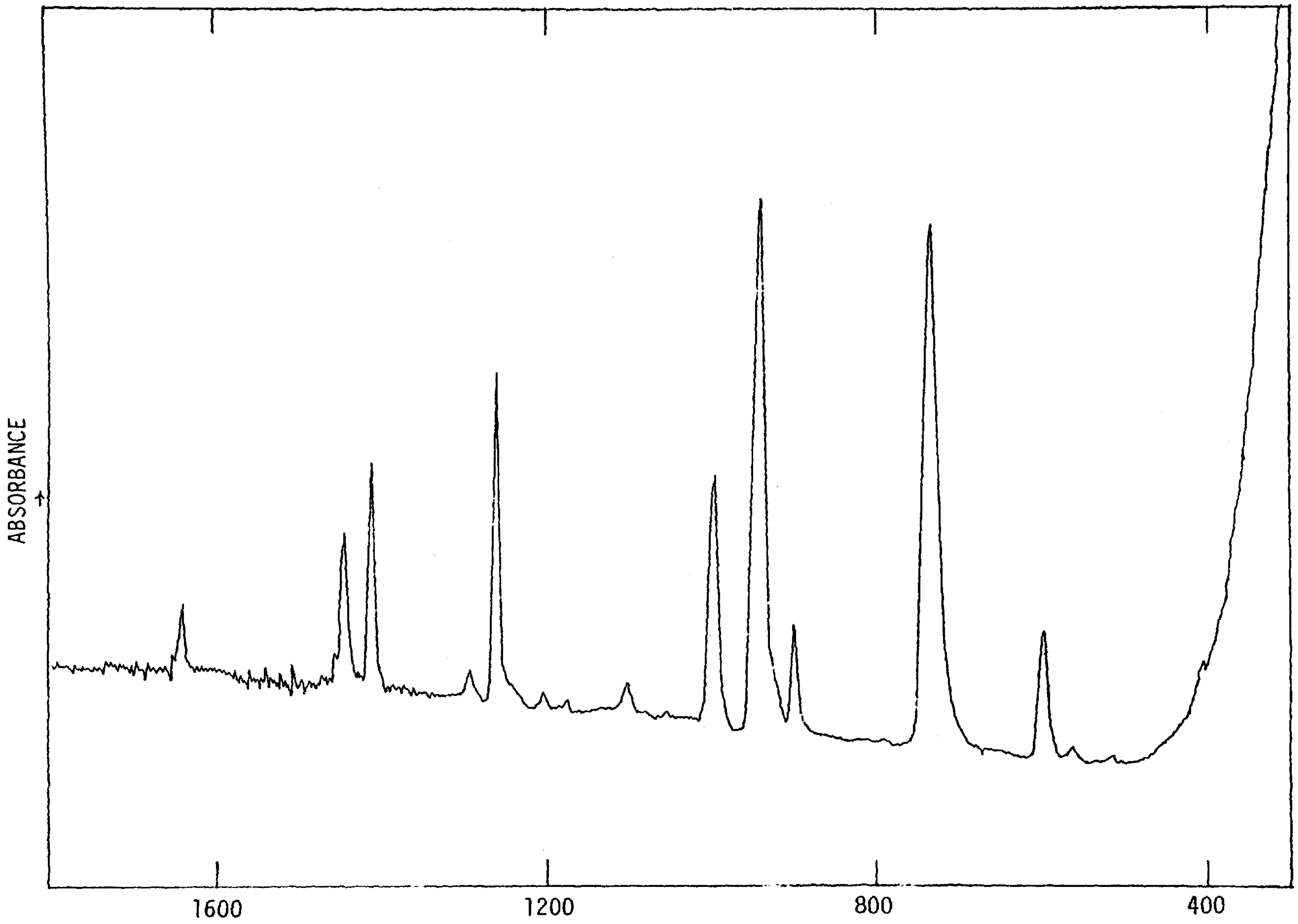


Figure V.2 ALLYL CHLORIDE

M.I. 4000 : 1 Argon 8K Unannealed

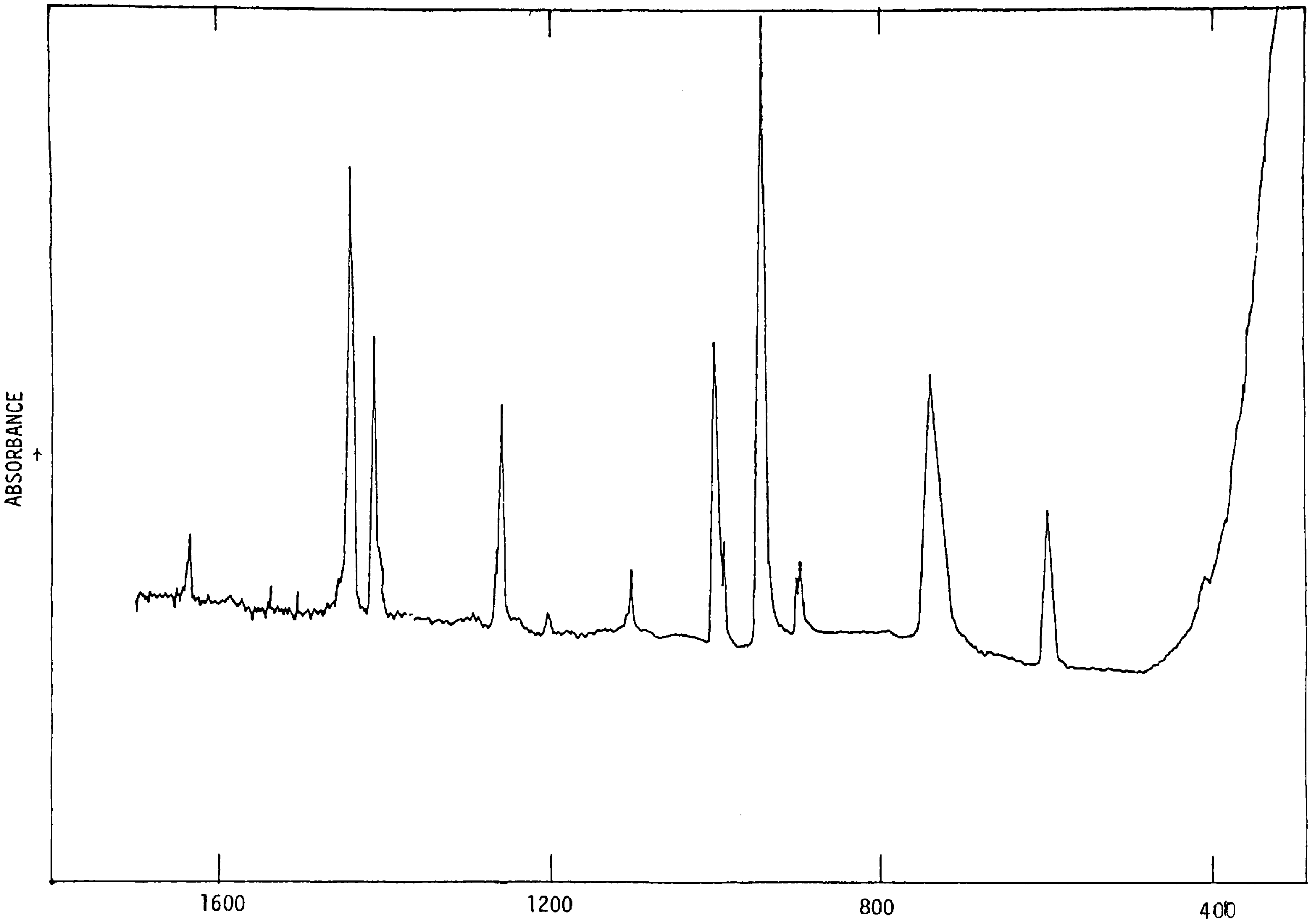


Figure V.3 ALLYL CHLORIDE M.I. 4000 : 1 Argon 8K Annealed

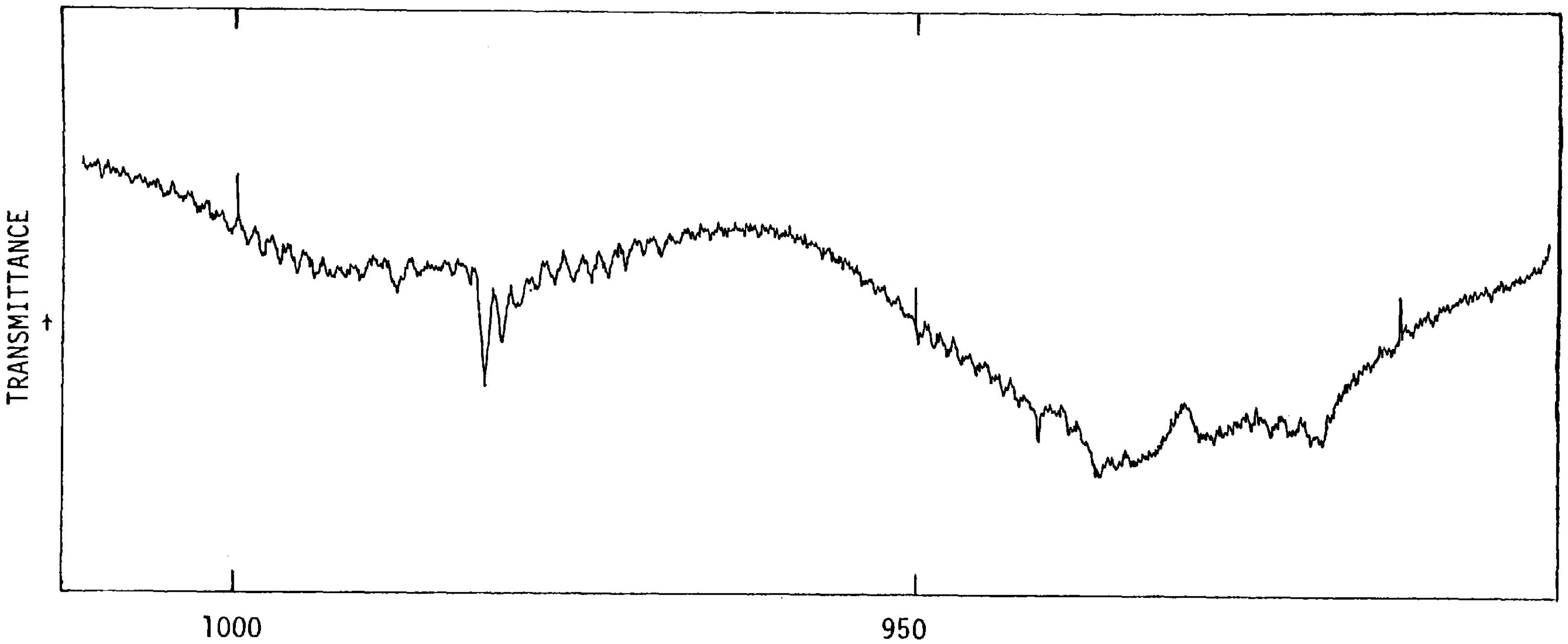


Figure V.4 ALLYL CHLORIDE

Gas at 12mm Hg pressure and a 100mm pathlength

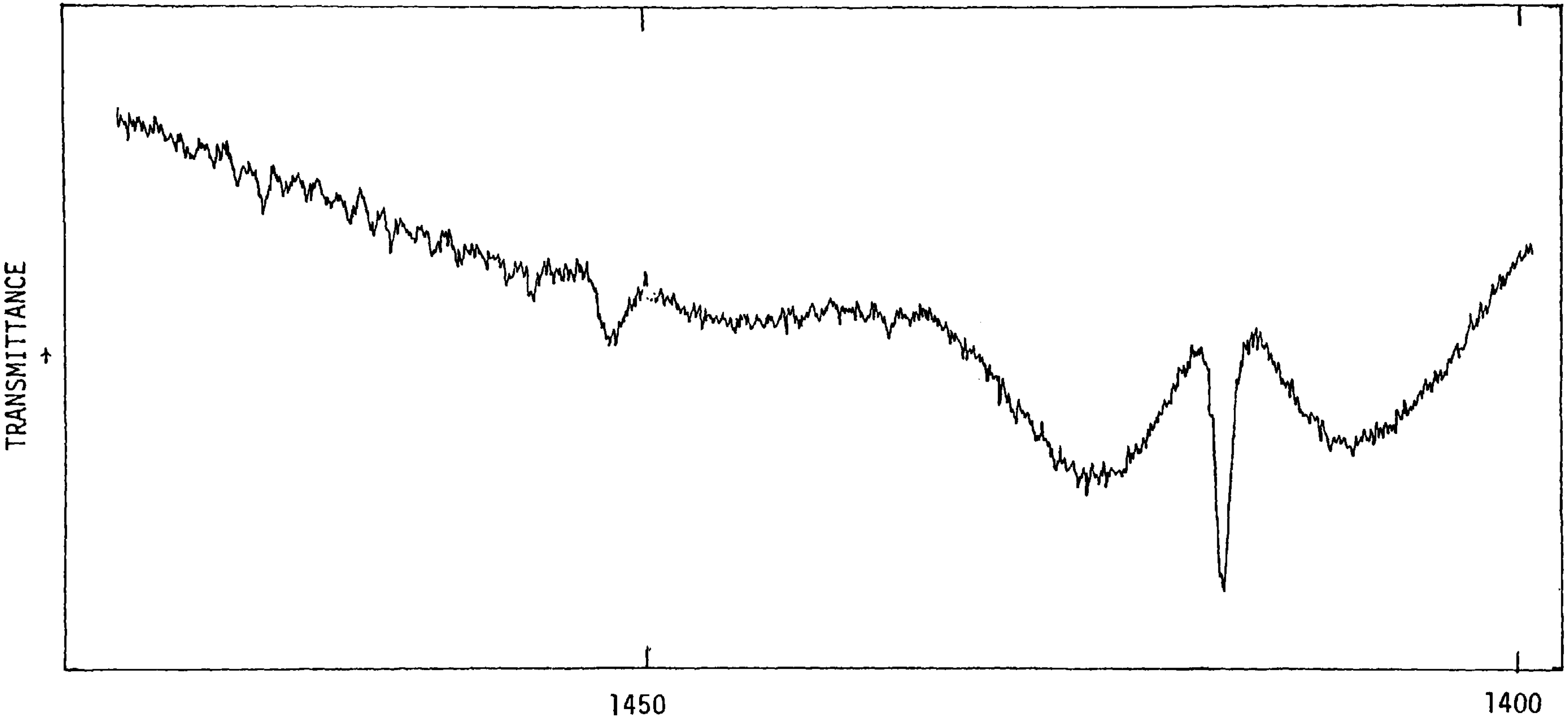


Figure V.5

ALLYL CHLORIDE

Gas at 12mm Hg Pressure and 100mm Pathlength

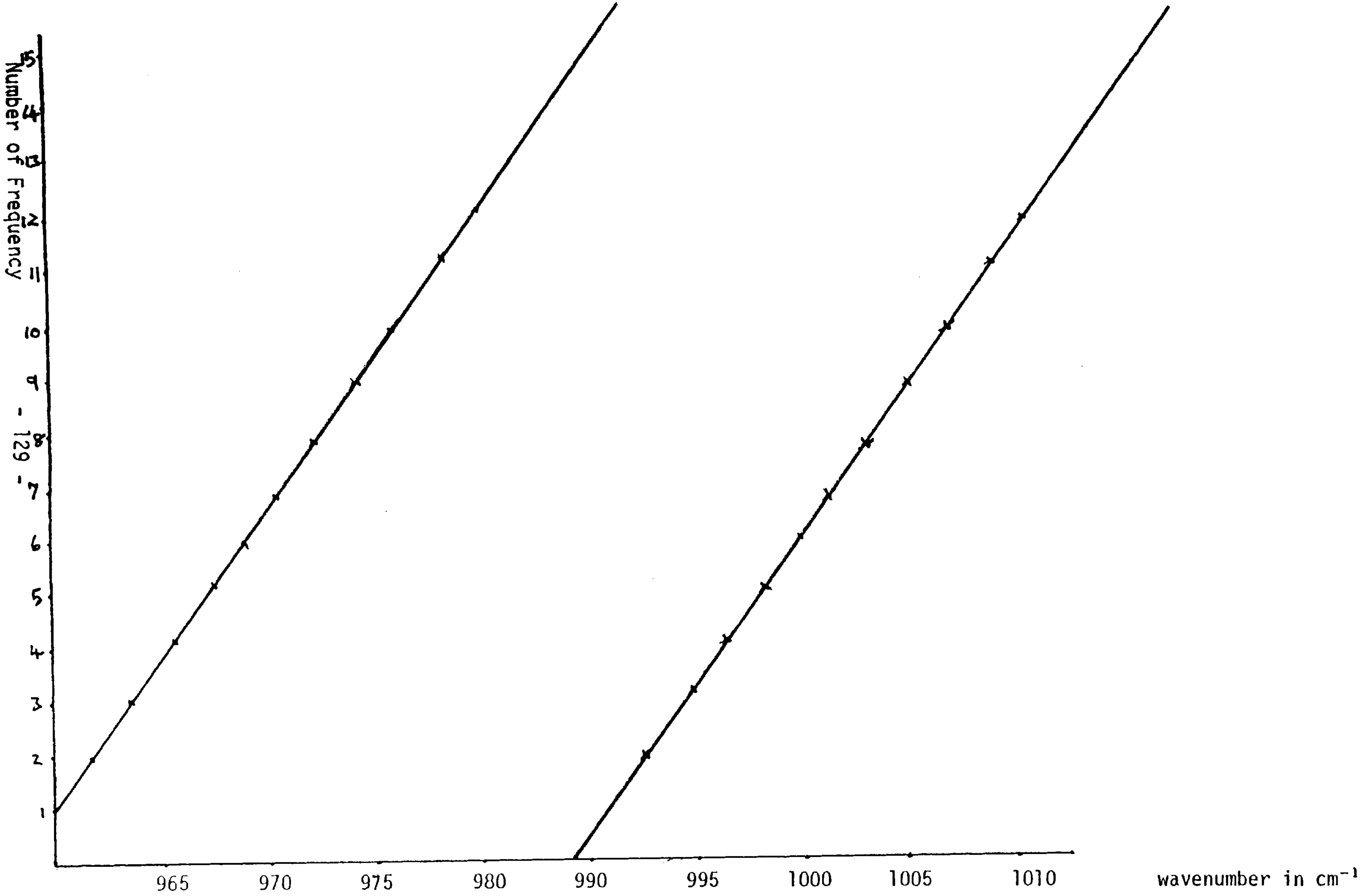
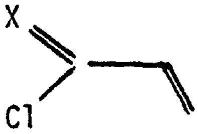


Figure V.6 Plot of wavenumber versus number of frequency to find rotational spacing for allyl chloride

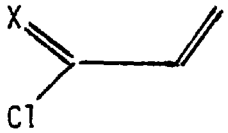
B. The Vibrational Spectra, Conformational and Thermodynamic Properties of 2-chlorobuta-1,3-diene (chloroprene) and Propenoyl Chloride

1. Introduction

The most stable conformer of 2-chlorobuta-1,3-diene was first proposed to be planar s-*trans* I to explain the nature of the vibrational spectrum (121,122). Bands which were strong in either the infrared or Raman spectrum were generally found to be weak in the other spectrum, thus indicating that the molecule is close to being planar.



I



II

X = CH_2 ... 2-chlorobuta-1,3-diene

X = O ... propenoyl chloride

The results of an electron diffraction study (123) confirmed that the predominant conformer was s-*trans*, although a slightly non-planar structure could not be ruled out. Recently, the microwave spectrum of s-*trans* 2-chlorobuta-1,3-diene was assigned (124) and the small value obtained for the initial defect is good evidence for the planarity of the molecule.

The only evidence (122) which has been obtained for the presence of a high energy conformer of 2-chlorobuta-1,3-diene is meagre, and gave no indication as to whether this conformer was planar s-*cis*, II, or skewed out-of-plane to a *gauche* structure. The comparison of the infrared spectra of liquid and solid 2-chlorobuta-1,3-diene revealed only small differences; one very weak band in the spectrum of the liquid phase at 1127 cm^{-1} was absent in that of the solid phase, also the 1632 cm^{-1} band apparently diminished in intensity on freezing. It was stated that if a high energy conformer was present then the enthalpy difference between the conformers, $\Delta H^{\ominus}$, was probably greater than 2 kcal mol^{-1} (8 kJ mol^{-1}). More recent studies of the vibrational spectrum (125,128) have concentrated predominantly on the spectrum of the gaseous phase and no further evidence for the presence of the high energy conformer has been obtained.

The conformational situation in propenoyl chloride is somewhat of a contrast to that of 2-chlorobuta-1,3-diene. Here a substantial amount of high energy conformer is present at room temperature, and a number of vibrational bands have been assigned to this conformer (128,130). The reason for this higher concentration is that $\Delta H^{\ominus}$ is relatively low, 2.75 ± 0.24 kJ mol^{-1} for the gaseous phase (128). The more stable conformer is known to be s-trans from the results of a microwave study (131); most of the observed lines could be assigned to this conformer. The structure of the high energy conformer is not known with certainty, but evidence was put forward recently that it is planar s-cis (128). The asymmetric torsional modes of both conformers were observed to give rise to similar depolarised Raman bands with only P and R branches, thus it was concluded that both conformers belonged to the same point group. This conclusion seems reasonable as strong experimental evidence has been put forward that the high energy conformer of propenoyl fluoride is s-cis (132).

It is desirable that accurate thermodynamic data is available for such compounds as they are of commercial interest. The available data on 2-chlorobuta-1,3-diene has been collected together (133), this is incomplete and may not be reliable. For propenoyl chloride values for the ideal gas thermodynamic functions have been calculated by statistical methods (134). For these calculations the mathematical model used was based on the known conformational situation in this molecule, but the values used for some of the fundamental frequencies (134) have since been altered significantly (128,135). This indicates that the published values for the thermodynamic functions may be of poor accuracy, and so these will be reexamined.

2. Experimental

2-chlorobuta-1,3-diene and propenoyl chloride were obtained from British Petroleum Trading Ltd. and Aldrich Chemical Corporation, respectively as 98% purity liquid samples. The i.r. spectrum of propenoyl chloride showed peaks due to hydrogen chloride gas, but no other impurities.

The i.r. spectrum of 2-chlorobuta-1,3-diene was recorded between 4000 and 400 cm^{-1}, using a Perkin-Elmer 580 ratio-recording spectrophotometer, for the gaseous, liquid, frozen solid and solution (in CCl_4) phases and also in a low temperature argon matrix using an Air Products Closed Cycle Helium Cryostat. The resolution used varied with phase, but gaseous samples were examined at up to 0.5 cm^{-1} resolution. Propenoyl chloride was examined as a gas and in matrix isolation under similar conditions.

The observed vibrational spectra of 2-chlorobuta-1,3-diene and propenoyl chloride are listed in Tables V.2 and V.3, respectively. The infrared frequencies listed in Table V.2 - V.4 are expected to be accurate to ±1 cm^{-1} (±0.3 cm^{-1} for those values listed to one decimal place in Table V.4, which refer to sharp Q branches). The Raman frequencies are expected to be accurate to ±3 cm^{-1}. Figures V. 7 and V. 8 show i.r. spectra of bands of particular interest.

3. 2-Chlorobuta-1,3-Diene

(i) Variable Temperature Studies

A careful study of the Raman spectra of both liquid and frozen solid 2-chlorobuta-1,3-diene was made, but no significant differences in the two spectra were observed which could be attributed to the presence of a high energy conformer.

A low temperature i.r. study on 2-chlorobuta-1,3-diene by Szasz and Sheppard (122) reported that a very weak band in the spectrum of the liquid phase at 1127 cm^{-1} was absent in the spectrum of the solid phase. This observation was confirmed in the present work, also another weak band in the liquid phase at about 690 cm^{-1} disappeared on going to the solid state. This was taken as evidence of the existence of a high energy conformer, but it is not possible to assign either peak unamibiguously to a specific vibration and so it was not possible to measure a meaningful $\Delta H^{\ominus}$.

In the spectrum of the liquid phase the C-Cl stretch at 630 cm^{-1} is intense and broad but on freezing this band sharpens to reveal a weak band at 660 cm^{-1} which is probably the $=CH_2$ twist expected in this region (127, 136).

Spectra of 2-chlorobuta-1,3-diene in CCl_4 solution show a weak band at 895 cm^{-1} which is hidden under a strong band at about 870 cm^{-1} in the spectrum of the liquid phase. Buta-1,3-diene also has a weak infrared band at 892 cm^{-1} which has been assigned to the $=CH_2$ rocking mode, and so the 2-chlorobuta-1,3-diene band at 895 cm^{-1} is likely to be due to the same mode.

(ii) Matrix Isolation Studies

A study of theinfrared spectrum of propenoyl chloride in a low temperature inert matrix has been reported by Redington and Kennedy (130) and bands due to both conformers were plainly visible. A similar study was therefore undertaken for 2-chlorobuta-1,3-diene in order to try and obtain further evidence for a conformational equilibrium. Mixtures of argon and 2-chlorobuta-1,3-diene at ratios of between 400 : 1 and 2000 : 1 were slowly sprayed onto the window of a cryotip held at 8K and the infrared spectrum recorded. It was observed that the bands are broad at 500 : 1, resolve into doublets at 1000 : 1 and are completely resolved at 2000 : 1. An expanded portion of the spectrum of the 2000 : 1 mixture is shown in Fig. V.7 together with the corresponding spectra obtained after one and two annealings. Annealing was performed by slowly warming the argon mixture to 50K at which temperature the spectrum showed changes and the pressure in the cryotip increased. The spectrum was recorded after recooling to 8K. The wavenumber values of the bands in the matrix, solid, liquid, carbon tetrachloride solution and gas are given in Table V.2.

A notable feature in Fig. V.7 is the presence of additional bands corresponding to the CH=CH twist and the CH_2 wag. These modes appear at 975 and 922 cm^{-1} respectively in the vapour state and at 974 and 922 cm^{-1} respectively in the solution state. (Fig. V.8).

In the argon matrix the lower wavenumber mode gives rise to a strong band at 919 cm^{-1} and a weak satellite at 924 cm^{-1}, the relative intensities did not change on annealing. The higher wavenumber mode gave rise to a pair of bands at 974 and 976 cm^{-1} together with a sharp band at 982 cm^{-1}. The intense band at 974 cm^{-1} diminishes considerably and the medium intensity band at 976 cm^{-1} diminishes by a lesser amount on annealing. By contrast the strong band at 982 cm^{-1} increases considerably in intensity. On further annealing the pair of bands near 975 cm^{-1} becomes very weak whilst that at 982 cm^{-1} intensifies further. No comparable changes are observed

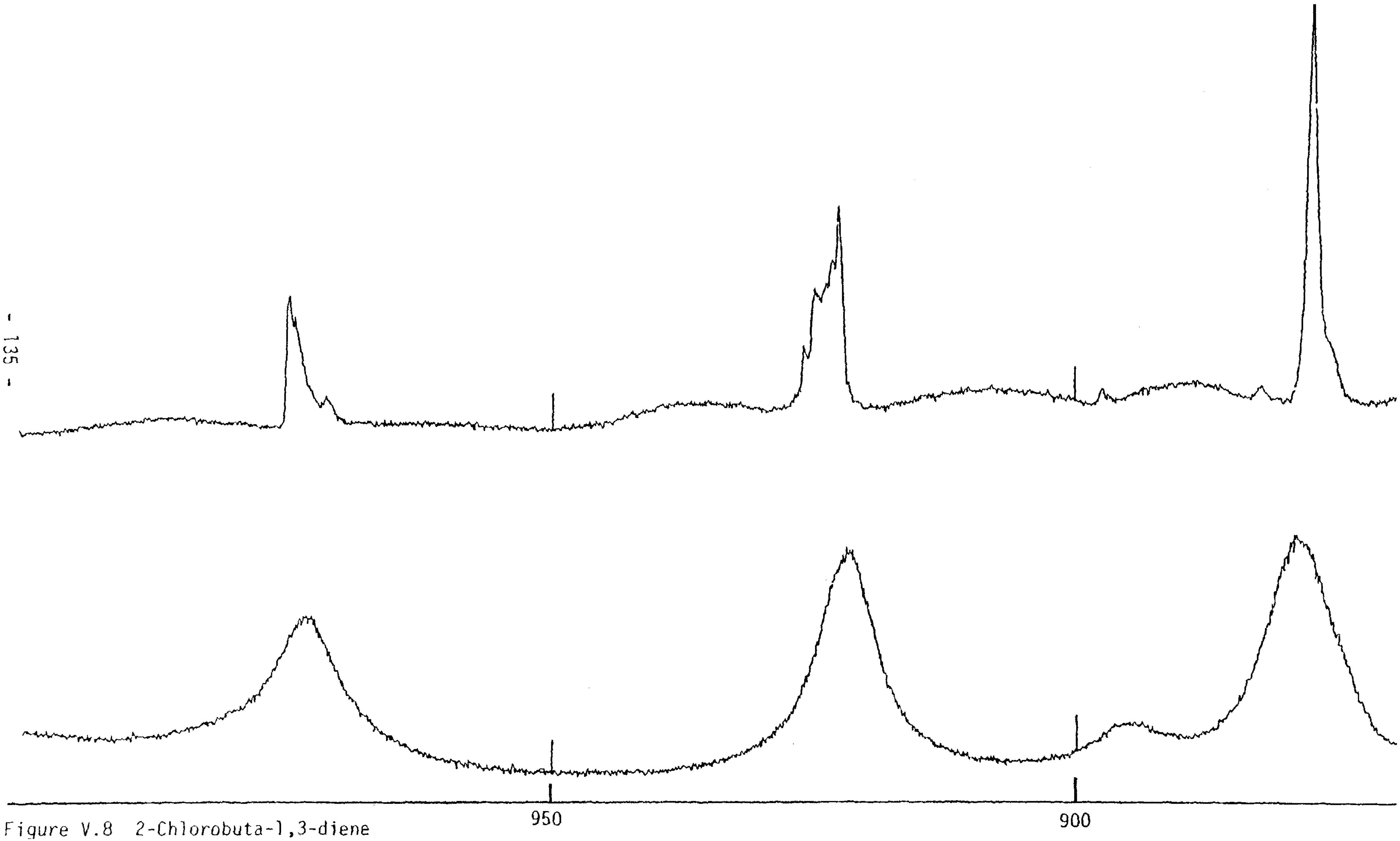


Figure V.8 2-Chlorobuta-1,3-diene
a) Gas Phase 10mm Hg at 100mm pathlength (b) Solution CCl_4 10% at 0.5mm pathlength

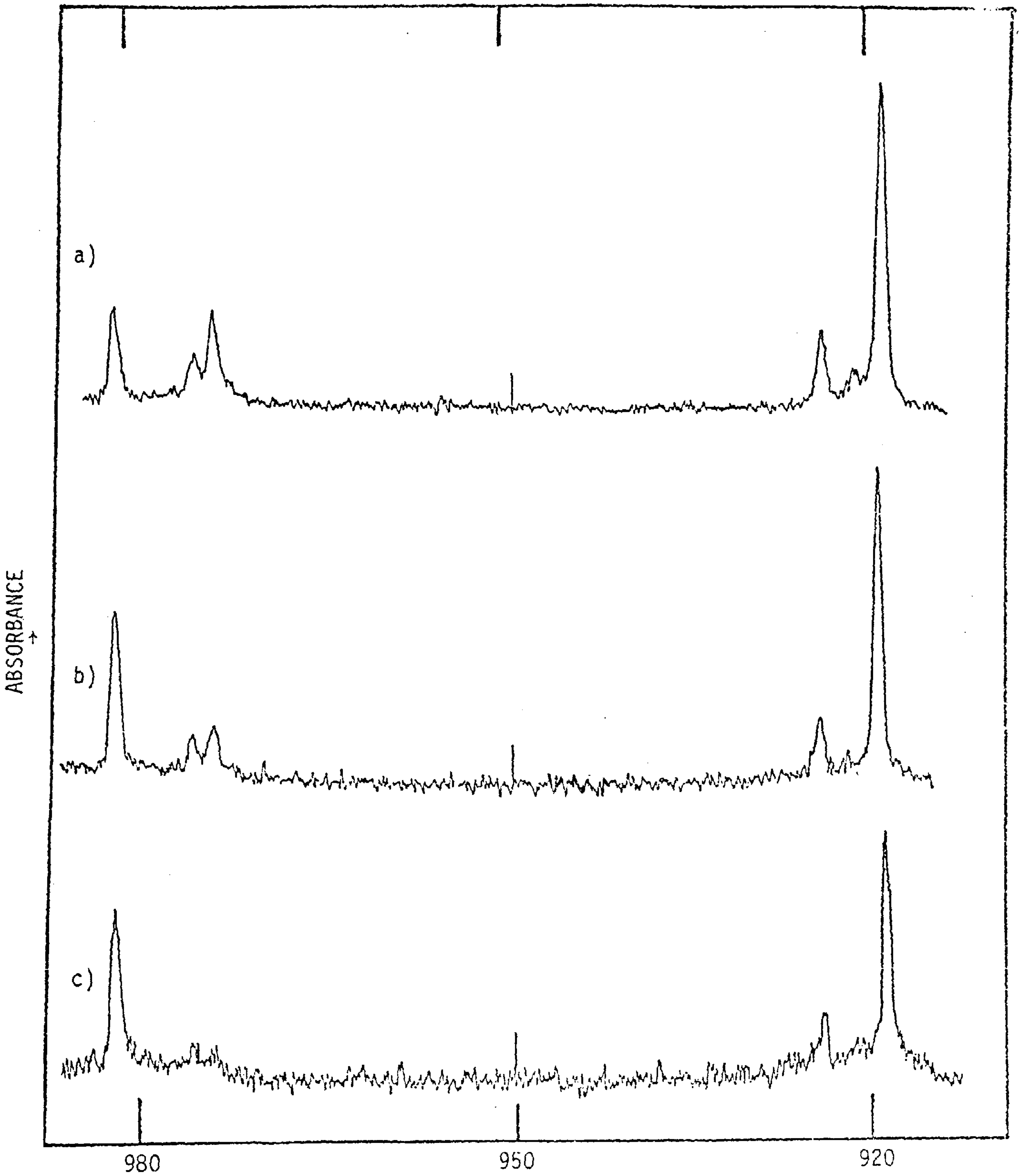


Figure V.7 2-CHLOROBUTA-1,3-DIENE

(a) M.I. 2000 : 1 Argon Unannealed

(b) M.I. 2000 : 1 Argon One Annealing

(c) M.I. 2000 : 1 Argon Two Annealings

elsewhere in the matrix isolation spectrum of 2-chlorobuta-1,3-diene

It is probable that a high energy conformer is responsible for satellite bands. If the equilibrium is too slow to be changed under annealing conditions the satellite at 924 cm^{-1} may be due to a high energy conformer. Alternatively if the equilibrium is sufficiently fast then the feature near 975 cm^{-1} may be due to a high energy conformer. It is considered that the annealing changes support the latter possibility and that the features near 975 cm^{-1} are those of the high energy form, whereas the feature at 924 cm^{-1} may be a multiple site effect. These conclusions are tentative and further experiments may provide more definitive results.

(iii) The Spectrum of the Gaseous Phase

The spectrum of gaseous 2-chlorobuta-1,3-diene was recorded at high resolution above 400 cm^{-1}, the low frequency spectrum has already been reported (128). A numberof prominent Q branches were observed in the spectrum of which those at 877, 922.5 and 975 cm^{-1}, associated with the out-of-plane CH deformation modes, are shown in Fig. V.8. Several of the Q branches had prominent side bands or fine structure. Similar side bands have already been reported for the cis CH wagging modes of s-trans and s-cis propenoyl chloride (137), and these bands have been explained as being caused by a mixing of the vibrational potential functions of the out-of-plane deformations with those of the asymmetric torsional modes, which are also out-of-plane for both conformers. This interaction leads to a series of hot bands of the deformation mode which arise from successively higher energy levels of the asymmetric torsion. In the spectrum of 2-chlorobuta-1,3-diene the corresponding deformation mode at 735.7 cm^{-1} also shows a series of such hot bands at 743.3, 732.8, 731.5 and 730.0 cm^{-1}

Measurements (127) on the relative intensities of these bands led to an average value for the torsional frequency of 120 cm^{-1}, and similar bands near the weak fundamental at 522 cm^{-1} (at 520 and 518 cm^{-1}) led to a value of 138 cm^{-1}. These values may be compared with the observed value (128) of 146.8 cm^{-1}; the rather poor agreement is probably due to perturbation of intensities and the difficulty of measuring these weak bands, but the similarity in magnitude between the calculated and observed torsional frequencies is taken in supporting the interpretation provided.

4. Propenoyl Chloride

The infrared spectrum of gaseous propenoyl chloride was recorded at higher resolution than before for two reasons. Firstly, Cowles et al (132) predicted that the spectral region near 975 cm^{-1} should contain bands due to both the trans CH=CH wagging and $=CH_2$ wagging modes (out-of plane deformations) as the spectra of a range of α, β unsaturated carbonyl compounds all showed two bands in this region. Only one band at 974 cm^{-1} was observed with the available resolution (130,135) and previously the $=CH_2$ wagging mode had been assigned to a band at lower frequency (130). Secondly, because propenoyl chloride is isoelectronic to 2-chlorobuta-1,3-diene many of the fundamental modes of these two compounds have similar descriptions, therefore simultaneous consideration of the spectra of both molecules should result in the most accurate assignments being made and enable a better understanding of unusual spectral features.

Redington and Kennedy (130) studied the spectra of the gaseous phase and of the molecule isolated in argon and nitrogen matrices at 400 : 1. Bands in both gas and matrix phases were assigned to the s-cis high energy conformer, and several bands in the matrix showed shoulders stronger in the nitrogen matrix than in the argon matrix (130). The presence of these shoulders and behaviour on annealing was not discussed, but an estimate of 25% s-cis at room temperature was given, and complete assignments were given for both conformers.

In the present work, high resolution gas spectra showed weaker peaks near a number of the s-trans fundamentals, but most of these can be assigned as s-cis fundamentals with reasonable confidence, due to the relatively low enthalpy difference between the conformers. Three such bands were previously unreported and only observed with the improved resolution available, at 1397.2, 938 and 977 cm^{-1}, as listed in Table V.4.

Peaks at 495, 607, 701, 743, 756 and 980 cm^{-1} show additional weak peaks. The additional peaks on the s-trans and s-cis C-Cl stretch bands at 607 and 701 cm^{-1} are not properly resolved. These may be due to isotope splitting or another effect, but it is not possible to decide.

The high resolution spectrum of propenoyl chloride between 760 and 730 cm^{-1} has recently been reported (137). By analogy, the additional weak side bands listed above are all concluded to arise from a similar interaction between the torsion and higher frequency fundamental vibration.

A complex absorption occurs between 990 and 970 cm^{-1}. Fig. V.9 shows this region at high resolution and shows at least eight sharp bands. Peaks at 980.6 and 975 cm^{-1} have been considered s-trans fundamentals, with peaks at 983 and 977 cm^{-1} as the respective s-cis, although these assignments are ambiguous.

In the present work, the matrix isolation values for propenoyl chloride reported in Table V.3 showed only minor changes from previous values.

Figure V.9

PROPENOYL CHLORIDE

Gas phase 6mm Hg at 100mm pathlength

5. Vibrational Assignments

The assignments for both compounds have been considered together because of the similarity of their structures. Table V.4 shows the selected assignments. Both compounds are members of the C_s point group in the more stable s-trans conformers and hence their vibrations are both infrared and Raman active. For both of these compounds the in-plane A' vibrations should show A/B hybrid gaseous phase band contours in the infrared spectrum and polarised Raman lines, the out-of-plane A" vibrations should show C type band contours and depolarised Raman lines. Propenoyl chloride has 13A' and 5A" vibrations, 2-chlorobuta-1,3-diene has 17A' and 7A" vibrations.

(i) Propenoyl Chloride

The assignments given for propenoyl chloride in Table V.4 agree with previous assignments (130) above 1200 cm^{-1}. The strong band at 1149 cm^{-1} and weak band at 938 cm^{-1} were assigned (130) to the $=CH_2$ rock and C-C stretch respectively. These assignments have been modified by comparison with propenal (128,129), which shows a strong band at 1158 cm^{-1} due to the C-C stretch and another strong band at 914 cm^{-1} which was assigned to the $=CH_2$ rock. Assignment of the C-C stretch to a strong mode at 1149 cm^{-1} supports the assignment of the corresponding vibration in 2-chlorobuta-1,3-diene to a strong band at 1225 cm^{-1}.

The assignments of the out-of-plane vinyl modes are altered from those of Redington and Kennedy (130), who assigned the bands at 649 and 756 cm^{-1} to the cis wag and $=CH_2$ wag of the s-trans conformer. The $=CH_2$ wag has been assigned to bands at 975 and 977 cm^{-1} shown in Fig. V.4.

for the s-*trans* and s-*cis* conformers in agreement with Cowles et al (135). The *cis* wag is assigned to the complex bands near 750 cm^{-1} for the s-*trans* and s-*cis* conformers.

The other fundamentals are assigned to the same vibrations as previous (130). The s-*cis* frequencies detected using matrix isolation techniques are used in Table V.4, unless gas phase values are available. Frequencies below 300 cm^{-1} have been taken from the low frequency Raman and infrared study by Durig et al (128).

The above reassignment of the *cis* wag to the bands near 750 cm^{-1} leaves the bands previously assigned (130) to this mode for both conformers unassigned. Weak bands were observed in the gaseous phase at 649 and 542 cm^{-1}, and assigned to the s-*trans* and s-*cis* conformers, respectively (130). This assignment appears questionable as neither band was observed in the spectrum of the low temperature matrix, and we consider that these bands are difference bands which therefore have no intensity at low temperatures. The 649 cm^{-1} band may be assigned to $755.7 - 106.8 = 648.9$ cm^{-1}, the 542 cm^{-1} band to the combination $1149 - 607 = 542$ cm^{-1}. One of the corresponding expected sum combinations, at 1756 cm^{-1} was not observed, presumably as it was swamped by the strong C=0 bands observed at 1720 and 1785 cm^{-1}.

Observations of sum and difference bands of the 756 and 107 cm^{-1} fundamental modes is not surprising, as these modes have been shown to interact by observation of the complex vibration-torsion bands discussed elsewhere (137). Furthermore, it is not surprising that the 1149 and 607 cm^{-1} fundamentals also show combination bands as these are both assigned to skeletal stretching modes.

(ii) 2-Chlorobuta-1,3-Diene

The previous assignments made for this molecule (127,140) were similar to each other, and a normal coordinate study upholds these assignments (136); however it should be pointed out that neither the force constants nor the potential energy distributions calculated were reported. The assignments listed in Table V.4 above 1000 cm^{-1} are the same as before, although slightly different in frequencies; therefore no further comments are necessary. The C-C stretch at 1225 cm^{-1} in the infrared spectrum is strong for a vibration that is normally weak in the infrared, but the only other assignment for this band is to the C-H bend, assigned at 1279 cm^{-1}. The present assignments agree with those of equivalent vibrations in a range of similar molecules such as buta-1,3-diene and 2-methylbuta-1,3-diene (141).

Spectra of 2-chlorobuta-1,3-diene as a solution, isolated in a matrix and as a solid showed two bands at about 897 and 660 cm^{-1} normally hidden by the strong bands at 877 and 638 cm^{-1}. The band at 897 cm^{-1} is assigned to the symmetric =CH_2 rock which is found at 892 cm^{-1} in buta-1,3-diene; this mode has been assigned to a weak Raman band (127) at 931 cm^{-1} although a previous study assigned it at 890 cm^{-1}. The band at 660 cm^{-1} is assigned as a =CH_2 twist as this mode has been predicted (127,140) in this frequency region, variously at 697 and 630 cm^{-1}.

Examination of Fig. V.7 shows a weak band at 924 cm^{-1} in the spectrum of the matrix, close to the strong =CH_2 wagging fundamental at 919 cm^{-1}. As mentioned already, the weak band corresponding to this in the Raman spectrum of the liquid has been assigned (128) to the =CH_2 rock, but it is considered that a more likely assignment for this band is to a combination of the C-Cl wag, A", with the in-plane bending mode, A', 410 + 517 = 927 cm^{-1}. The combination has A" symmetry and thus is allowed to be in Fermi resonance with the A" $=CH_2$ wag at 919 cm^{-1}. This may also explain why the matrix and gaseous phase frequencies for the $=CH_2$ wag differ more than for the other CH wagging modes.

The frequencies listed in Table V.4 below 400 cm^{-1} have been selected from studies of the low frequency region (125,128).

6. Molecular Structure of 2-Chlorobuta-1,3-Diene

In order to calculate the most accurate barriers to internal rotation of 2-chlorobuta-1,3-diene it was considered necessary to calculate the most probable molecular structure, as the internal rotation constant, F, depends on the structure. The structure proposed from the early electron diffraction results (123) was used to calculate the principal moments of inertia of the molecule, and it was found that these did not agree satisfactorily with those calculated from the microwave rotational constants (124).

The principal moments of inertia have been calculated for 2-chlorobuta-1,3-diene and three isotopically substituted molecules from the reported rotational constants (124). From these data, the substitution coordinates of the three substituted atoms have been calculated using Kraitchman's equations (142), and these coordinates are listed in Table V. along with the principal moments of each isotope. The difference between the observed and calculated moments and substitution coordinates are listed in this table for the structure based on the electron diffraction results (123).

The structure of the molecule was altered using a least square iterative programme which allowed any number of bond angles or lengths to be varied simultaneously. As expected, the calculated moments were very sensitive to the C-Cl bond length and C=C-Cl bond angle, and interaction of these two parameters alone reduced the standard deviation of the fit to 1 Amu. Å². The two other skeletal angles C=C-C were found to be significant in the fit of the data and so these were iterated simultaneously with the C-Cl bond lengths and the C=C-Cl angle to give the best fit. It was found that changes in the C=C and C-C bond lengths gave results which had dispersions much larger than the observed changes, and so these were held constant at the original values.

The final structure obtained for 2-chlorobuta-1,3-diene is listed in Table V.6 , and the fit of the spectral data is shown in Table V.5 . The structural values have been rounded to 0.01 Å for the bond lengths and 0.1° for bond angles, thus incurring a higher degree of error in the tabulated differences than was actually obtained in the final fit, which had a standard deviation of 0.056 Amu. Å², and values of (Observed-Calculated) scattered well between -0.1 and +0.1.

7. Asymmetric Potential Function of 2-Chlorobuta-1,3-Diene

The far infrared spectrum of gaseous 2-chlorobuta-1,3-diene has been previously reported (128), a total of six Q branches were observed between 150 and 130 cm⁻¹. These bands were assigned to the torsional mode of the s-trans conformer, but no torsional data was observed for the high energy conformer. It was decided to calculate the asymmetric potential function using the previous s-trans torsional data (128) and the value of ∿ 8.2 kJ mol⁻¹ (685 cm⁻¹) calculated from the statistical data presented below. The data were fitted to a potential function of the type

$$V_\alpha = \tfrac{1}{2} \Sigma_i V_i (1 - \cos i \alpha)$$

using coefficients V_1 up to V_4. The internal rotation constant, F, was calculated as a function of the dihedral angle, α, using the s-trans structure listed in Table V. 6 with normal abundance masses, and by simply varying the dihedral angle from 0 to 180°. The values of F_α calculated at intervals of 6° were then fitted to a Fourier series

$$F_\alpha = F_0 + \Sigma_i F_i \cos i \alpha$$

Values of F_1 up to F_4 were considered significant and so higher terms were dropped from the calculations, resulting in values of $F_0 = 1.6117$, $F_1 = 0.0896$, $F_2 = 0.1936$, $F_3 = 0.0151$ and $F_4 = 0.0160$.

Initial calculations on the potential function were made using values for V_1 and V_2 of 685 and 2000 cm^{-1}, as it was realised that V_1 and $\Delta H^\ominus$ would be similar. It was immediately apparent that the V_2 value was about 1000 cm^{-1} too small, because this function calculated the torsional transitions to become 30 cm^{-1} low. Increasing V_2 by this amount calculated the transitions in the correct frequency region, but accurate fitting was only achieved if V_4 was included in the fit. V_3 was then found to be insignificant, and so was held to zero while V_1, V_2 and V_4 were simultaneously iterated for the final fit.

The final potential function is shown in Fig. V.10, resulting from values of the potential coefficients in cm^{-1} (with dispersions):-

$$V_1 = 693\ (0.06),\ V_2 = 3214\ (5.8),\ V_4 = -134\ (1.9).$$

The six pieces of observed torsional data were all fitted to better than 0.1 cm^{-1} so this is a very satisfactory fit, considering that the experimental error on the torsional frequencies was probably ±0.2 cm^{-1}.

It was found possible to fit the data to a threefold potential function with a lesser degree of accuracy using the coefficients

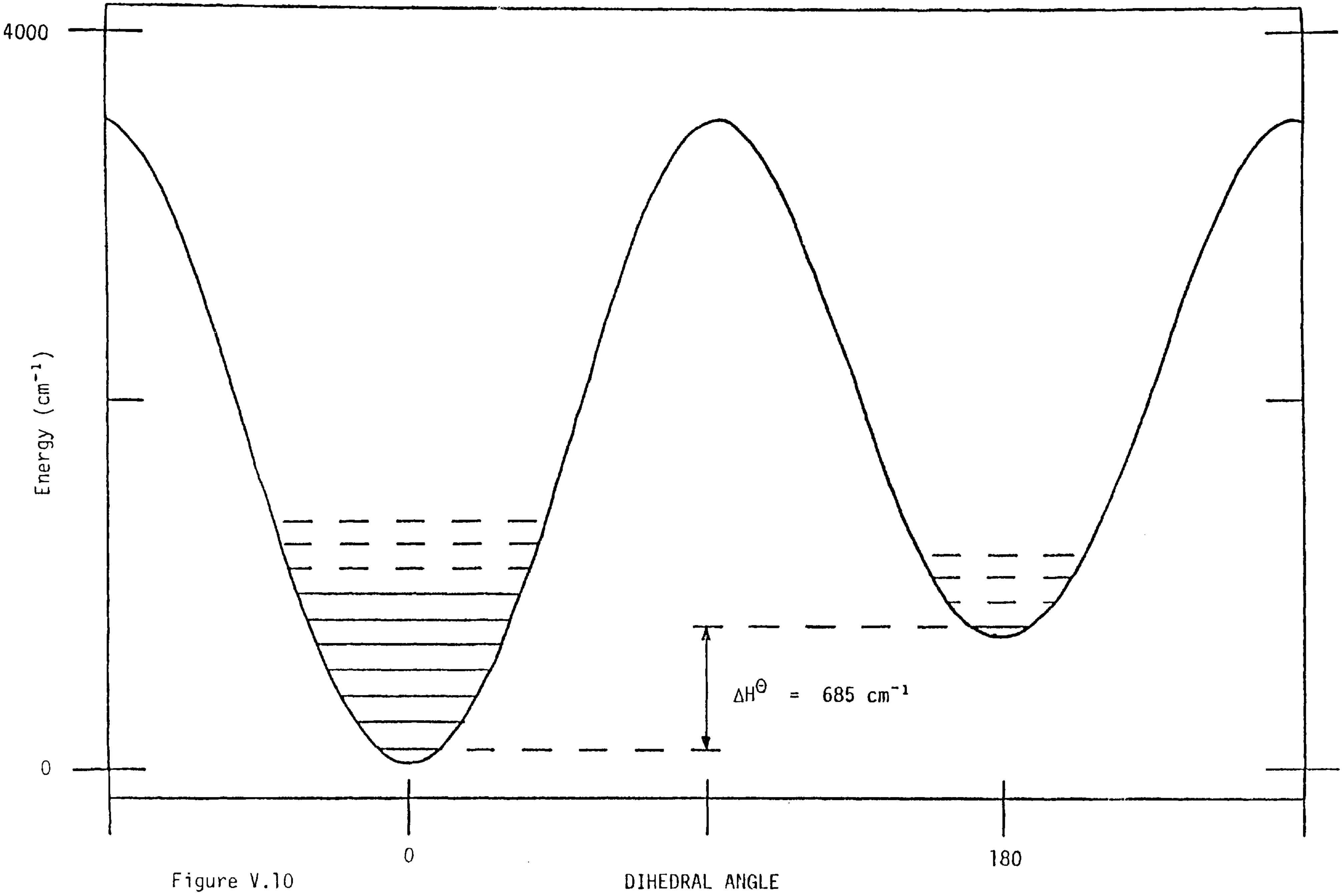


Figure V.10

Asymmetric potential function of 2-chlorobuta-1,3-diene

$V_2 = 2547\ (27)$, $V_3 = 703\ (2)$, $V_4 = -318\ (9)$.

However, the value calculated for V seems to be much larger than has been obtained for similar molecules (143), which may indicate that the s-*trans*$\rightleftharpoons$gauche model is incorrect. The difference in V between the two-fold and threefold model arises from the fact that the s-*trans* barrier is at a smaller angle than 90° in the threefold case, thus effectively altering the s-*trans* potential well.

8. Thermodynamic Functions

(i) 2-Chlorobuta-1,3-Diene

The available data for the thermodynamic functions of 2-chlorobuta-1,3-diene is very limited (133), being restricted only to estimated values of the heat capacity. These values were estimated by summing group contributions by the method of Rihani and Doraiswamy (144). The various methods of calculating heat capacities of gases have been compared (145), wherein it has been shown that a more reliable system (in most cases) has been devised by Benson, which was found to have an average error of 1.1% instead of 3.2% for the method of Rihani and Doraiswamy.

The two estimation methods give values for $C_p^{\ominus}$ at 300K of 96.1 $JK^{-1}\ mol^{-1}$ (Benson) and 90.2 $JK^{-1}\ mol^{-1}$ (Rihani and Doraiswamy). Clearly theses values are incompatible in this case and so it was decided to calculate new values for the thermodynamic functions of 2-chlorobuta-1,3-diene by summation of the functions of similar compounds. It is reasonably accurate (146) to calculate the functions of a chloro compound R - X from those of the methyl analogue R - Me, and so the thermodynamic functions for 2-chlorobuta-1,3-diene were calculated from the relationship

F (2-chlorobuta-1,3-diene) = F (2-methylbuta-1,3-diene) - F (propene) + F (chloroethane).

The calculated values are given in Table V.7 . The data used was from Stull et al. (146) for propene and chloroethane, that for 2-methylbuta-1,3-diene has been calculated by previous workers (141). The value calculated at 300K by this method is 93.0 JK^{-1} mol^{-1}, which appears to be reasonable when compared with the values given on the previous page.

The calculated values for $S^{\ominus}$ and $C_p^{\ominus}$ were found to be higher than the values calculated by statistical methods for the pure s-*trans* conformer, which is good evidence for the presence of a second conformer. An equilibrium mixture of conformers has higher entropy and heat capacity than for each conformer because of the resulting heat and entropy of mixing.

The statistical values calculated for the two conformers used the following data. The fundamental frequencies were taken from Table V.4 , the s-*cis* torsional frequency was estimated to be 130 cm^{-1} from the asymmetric potential function presented above. The principal moments were taken from Table V.5 , and a mean value for ^{35}Cl and ^{37}Cl isotopes were calculated using the normal isotopic ratio of 0.755 : 0.245. The s-*cis* moments were calculated in a similar manner using the proposed molecular structure listed in Table V. 5 , and a dihedral angle of 180^{0}. The molecular weight was taken as 88.052, which again includes the isotopic mixture.

The resulting values were then combined, in the manner described previously (134,141), to fit the values calculated for the thermodynamic functions from those of other compounds, listed in Table V.7 as A. Firstly, the $S^{\ominus}$ values were fitted using the expression

$$S^{\ominus} = X_T S_T^{\ominus} + X_C S_T^{\ominus} - R\,(X_T \ln X_T + X_C \ln X_C)$$

where the subscripts T and C refer to s-*trans* and s-*cis* respectively.

X_C is related to X_T by the expression $X_C = 1 - X_T$, and the calculated values of X_C and $S^\ominus$ (column B) are listed in the Table. As expected the values of X_C increase gradually with temperature from 0.035 at 300K to 0.201 at 1000K. Using these values of X_C, the $C_p^\ominus$ values were fit by varying $\Delta H_o^\ominus$ in the expression

$$C_p^\ominus = X_T\, C_{p,T}^\ominus + X_C\, C_{p,c}^\ominus + \left(\frac{X_T\, X_C}{R}\right) \frac{\Delta H_o^\ominus}{T} + \left[\frac{H_c^\ominus - H_{o,c}^\ominus}{T} - \left(\frac{H_T^\ominus - H_{o,T}^\ominus}{T}\right)\right]^2$$

The resulting fit $C_p^\ominus$ values (column B) and calculated $\Delta H_o^\ominus$ values at each temperature are shown in Table V.7. Ideally, all $\Delta H_o^\ominus$ values would be equal but the small scatter on the calculated values shows that the model used for the system is reasonable, leading to a value of $\Delta H_o^\ominus$ of 8.3 ± 0.6 kJ mol^{-1}. From these results values for the free energy, $-(G^\ominus - H_o^\ominus)/T$ were calculated, varying no parameters, using the expression

$$-\left(\frac{G^\ominus - H_o^\ominus}{T}\right) = S^\ominus - X_T \left(\frac{H_T^\ominus - H_{o,T}^\ominus}{T}\right) + X_C \left(\frac{H_C^\ominus - H_{o,c}^\ominus + \Delta H_o^\ominus}{T}\right)$$

The resulting values are in excellent agreement with those in column A, even though no fitting was performed.

In order to use the resulting value of $\Delta H_o^\ominus$ to calculate the asymmetric potential function, it was necessary to calculate $\Delta H^\ominus$ using the expression

$$\Delta H^\ominus = \Delta H_o^\ominus + T\Delta C_p^\ominus = 8.2 \text{ kJ mol}^{-1} \ (686 \text{ cm}^{-1})$$

(ii) Propenoyl Chloride

The thermodynamic functions of propenoyl chloride have previously been reported by Compton (134); these values were calculated by statistical methods allowing for the known presence of a conformational equilibrium. Since a number of changes have been made in the vibrational frequencies, it was considered necessary to recalculate the values.

The values for the moments of inertia used are the same as before (134). A slightly more accurate value of $\Delta H^{\ominus}$ has been reported (128), 2.57 kJ mol^{-1}, which leads to a value for ΔH_0 of 2.49 kJ mol^{-1}. The vibrational frequencies listed in Table V.4 were used for the two conformers.

9. Discussion

The analysis of the spectra of 2-chlorobuta-1,3-diene recorded in gaseous, liquid, solid, solution and inert matrix phases has revealed a number of weak bands present in the spectra of the fluid phases and unannealed matrix which are absent in those of the solid and annealed matrix. This result is good evidence that a small but significant concentration of a high energy conformer is present at room temperature in the fluid phases of this compound. Further evidence has been gained from analysis of the thermodynamic data, the values calculated for the thermodynamic functions of 2-chlorobuta-1,3-diene using data from other compounds could only be fitted statistically if a small concentration of s-cis conformer was allowed for.

The results of this fitting procedure indicate that some 4% of the molecules are s-cis at room temperature, and that $\Delta H^{\ominus}$ is approximately 8.2 kJ mol^{-1}. It is not possible to put error limits on these values, but as a guide the standard deviation of the calculated $\Delta H^{\ominus}$ values is 0.4 kJ mol^{-1}.

Unfortunately no evidence has been obtained for the structure of the high energy conformer, which has been assumed to be planar s-cis. In a recent review of the calculated asymmetric potential functions of molecules with internal rotation (143) the conformational situation in substituted butadienes was discussed. Experimental evidence now exists that buta-1,3-diene, 2-methylbuta-1,3-diene, propenoyl fluoride and chloride, propenoic acid and ethanedial all exist as a mixture of planar conformers, and so there seems no reason why 2-chlorobuta-1,3-diene should not follow this pattern.

Examination of Table V.4 shows that the presented vibrational assignments for the two molecules are similar, most vibrational modes having frequencies which differ little between the two compounds. In general, the in-plane vibrations have similar frequencies, apart from the bending mode observed at 521 cm^{-1} and 450 cm^{-1} for 2-chlorobuta-1,3-diene and propenoyl chloride, respectively. The out-of-plane modes are less similar in frequency.

The molecular structure calculated for 2-chlorobuta-1,3-diene and presented in Table V.6 is similar to that of propenoyl chloride, apart from the obvious changes due to substitution of a $C=CH_2$ group for a $C=O$ group. The skeletal angles are similar and differ less than the sums of the experimental accuracies, the only notable difference being in the carbon-chlorine [redacted] bond lengths that of propenoyl chloride was calculated (111) to be 1.82 ± 0.02 Å.

The asymmetric potential function of 2-chlorobuta-1,3-diene, shown in Fig.V.10 has been calculated using the $\Delta H^{\ominus}$ value obtained by statistical methods, and so cannot be very accurate outside of the s-<u>trans</u> well, which has a barrier of 249.1 cm^{-1} (2.98 kJ mol^{-1}). However, it is instructive to compare the values of V_2 and V_4 obtained (3215 and -135 cm^{-1}, respectively) with those of similar compounds which have an sp^2 - sp^2 carbon-carbon linkage (143). The V_2 value is exceptionally high, and may be compared with the values obtained previously (143) for buta-1,3-diene, 2-methylbuta-1,3-diene and propenoyl choride, 2068 cm^{-1}, 2742 cm^{-1} and 1734 cm^{-1}, respectively. Because this barrier probably arises from the conjugation between the C=C double bonds present in all these molcules, it would appear that replacement of a hydrogen in buta-1,3-diene by first a methyl and then by a chlorine increases the level of conjugation successively. It is well known that a methyl group has a mild electron donating effect, but the electron withdrawing chlorine can only increase conjugation by back-donation of its electron pairs. This physical model can be substantiated comparing the V_2 values and C-Cl bond lengths of 2-chlorobuta-1,3-diene and propenoyl chloride, the latter has a much lower V_2 and longer C-Cl bond which indicates that in the carbonyl compound extended conjugation is less favourable. This is probably a result of propenoyl chloride having two electron rich (and electron withdrawing) atoms. Comparison of the V_4 value obtained with those of buta-1,3-diene, 2-methylbuta-1,3-diene and propenoyl chloride (-49, -150, -123 cm^{-1}, respectively) shows a good agreement, especially between those compounds which are monosubstituted at position 2 (including the chloride). The rather large V_4 value obtained using a pair of gauche high energy conformers may be an indication that this model is incorrect. It appears that in general (143), V_4 values outside the range ±200 cm^{-1} are rarely encountered.

Another comparison may be made between the calculated ΔH^{Θ} values of 2-chlorobuta-1,3-diene, 2-methylbuta-1,3-diene (141) and propenoyl chloride (128), which have been calculated to be 8.2, 4.59 and 2.57 kJ mol^{-1}, respectively. An increase in ΔH^{Θ} may arise from two factors, either a stabilisation of the s-trans conformer (which also increases the s-trans barrier), or a destabilisation of the s-cis comformer. A chlorine atom and a methyl group have similar volumes and so any steric effects arising should be similar, but the electronic effects of the chlorine atom are likely to be strong. Thus, the larger $\Delta H^{\ominus}$ in 2-chlorobuta-1,3-diene, relative to the methyl compound, may well arise from a non-bonded attraction between the chlorine on carbon 2 and the hydrogen on carbon 4 which are only about 2.7 Å apart, less than the sum of the Van der Waals radii, 3 Å. However, in propenoyl chloride this attraction is replaced by a non-bonded repulsion between the chlorine and oxygen lone pairs, and so the chloride has a much lower $\Delta H^{\ominus}$.

The tabulated values for the thermodynamic functions are significantly different from those previously published (133,134). The differences arise from the more accurate vibrational assignment used for propenoyl chloride, and the alternative method of calculating the 2-chlorobuta-1,3-diene values.

The fitting of the thermodynamic functions of 2-chlorobuta-1,3-diene by statistical methods involved some inherent assumptions. The observation that the derived values (A in Table V.7) were higher than calculated for the s-*trans* conformer alone was taken as evidence that a high energy conformer exists, but this does not allow definition of the structure of that conformer. The s-*trans* s-*cis* model was used for the system because it was felt unlikely that *gauche* conformers would be present. There are some checks on the results which, although they will not prove the model to be correct or not, will at least show whether the overall model is self-consistent. Firstly, the values obtained for X_C should increase with temperature, while those obtained for $\Delta H^{\ominus}_{0}$ should remain approximately constant. Secondly, the calculated concentration of the s-*cis* conformer is known to be low because of the general weakness of the s-*cis* vibrational bands. Thirdly, the calculated values of X_C and $\Delta H^{\ominus}_{0}$ should approximately fit the relationship

$$-RT \ln \frac{X_C}{X_T} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Using a value of 8.2 kJ mol⁻¹ for $\Delta H^{\ominus}$ and allowing for the statistical value of $\Delta S^{\ominus}$ leads to values of X_C at 298 and 1000K of 0.036 and 0.26, respectively. The latter value is somewhat higher than that given in Table V.7, but the 298K value agrees well with the calculated value of 0.035. A fourth check on the model is that the statistical values for $-(G^{\ominus} - H_0)/T$ agree well with the values in column A even though no fitting was performed. Thus it is considered that the model used to derive the thermodynamic functions is self-consistent.

The probable accuracy of the tabulated thermodynamic functions is hard to assess. Those for the propenoyl chloride should be accurate to ±0.5 JK^{-1} mol^{-1} at low temperatures, but it is expected that anharmonicities at higher temperatures in the gas will incur deviations from statistical values. The 2-chlorobuta-1,3-diene values are likely to have larger errors than this even at low temperatures due to the derivation method, but it is hoped that they are correct to within ± 2 JK^{-1} mol^{-1} at room temperature.

Table V.2 2-Chlorobuta-1,3-Diene - I.r. and Raman Spectra (cm^{-1})

Assignments	Infrared Gas Path-Length 100 mm Pressure 30 mm Hg	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{500}$ Temp. 23K	Rel. Int.	Liquid Path-Length 0.1 mm	Rel. Int.	Solid Path-Length 0.1 Temp. 100K	Rel. Int.	Soln. in CCl_4 Path-Length 0.1 mm Conc. 10% w/v	Rel. Int.	Raman Liq.	Rel. Int.	Raman Solid	Rel. Int.
													34	s
													60	m
													66	m
													91	s
													100	m
													110	m
											160	w	172	w
													180	w
													195	vw
skeletal bend											254	m	258	m
											300	vw		
C-Cl bend	386	w	388	w							390	m	391	m
C-Cl wag	409	w	410	w					410	vw	410	vw	412	vw
C-Cl wag			418	w									421	w
skeletal bend	521	w	517	w	521	m	521	m	520	w				
											532	s		
	525	w	525	w			580	vw					525	w

Table V.2 continued

	550	w					592	vw			592	vw		
C-Cl stretch	638	s	630	s	630	s	630	s	632	s	650	vs	630	vs
	641	s	634	s										
$=CH_2$ twist			660	w			660	w					664	vw
C-Cl stretch	700	w	692	w	690	m	685	vw			695	vw		
cis wag	735	m	737	w	739	m	741	m			741	w	742	w
					770	vw	771	w					750	vw
					780	vw	789	vw			800	vw		
					835	vw	830	w	840	vw				
	867	m												
$=CH_2$ wag	877	vs	876	vs	885	vs	885	vs	880	vs	886	m		
$=CH_2$ rock	890	m	883	w					895	m			882	vw
			896	s										
	908	m	902	w										
			910	vw										
			919	w										
$=CH_2$ wag	922	vs	924	s	922	vs	925	vs	922	vs	921	w	921	w
	937	m									928	m	928	vw
	965	m												
trans wag	975	s	974	s	974	s	980	s	974	s	980	w	982	vw
	1015	m	1000	w					1005	m				
$=CH_2$ rock	1025	w	1022	m	1020	s	1019	s	1020	m	1022	m	1020	w
	1030	vw					1046	vw					1025	w

Table V.2 continued

			1075	vw	1074	w	1075	m	1062	w	1075	vw		
							1100	w						
							1110	vw						
									1120	w				
$=CH_2$ rock	1132	m	1130	w	1127	w	1124	w	1126	w				
			1150	vw	1146	w	1154	m						
			1192	vw	1194	w								
C-C stretch	1224	s	1220	vs	1215	s	1212	s	1220	vs	1216	s	1215	w
	1230	s												
C-H bend	1279	m	1265	w	1260	m	1288	m			1276	w	1276	w
			1288	vw	1290	m					1286	vs	1292	vs
	1353	m	1306	vw			1303	m						
asym $=CH_2$ scissor	1361	m	1363	s	1360	s	1360	s	1360	s	1364	w	1366	vw
	1369	m												
	1390	m									1385	m	1391	m
sym $=CH_2$ scissor	1396	m	1398	m					1396	w				
	1400	m			1400	m	1409	m						
			1420	m	1420	w	1420	m	1418	w	1420	vs	1423	s
					1460	vw	1461	w			1465	vw	1445	vw
	1535	m			1530	w	1520	w			1540	w		
							1550	w						
			1562	vs			1563	m						

Table V.2 continued

											1567	w		
asym C=C stretch	1583	s	1589	vs	1580	s	1580	s	1583	vs	1585	s	1587	m
	1594	vs												
			1600	s	1602	m	1600	m	1605	m				
sym C=C stretch	1628	w	1634	s	1630	s	1629	s	1630	w	1635	vs	1630	vs
	1641	w					1640	w						
							1650	vw						
							1660	vw						
					1712	vw	1720	w						
	1752	m												
	1767	m	1778	m	1763	m	1778	m			1790	w		
			1855	m	1847	m	1855	m						
			1910	vw	1918	vw	1910	w						
			1950	vw	1940	w	1950	w						
							2022	w						
			2045	vw										
			2100	vw	2100	w	2100	w						
			2210	vw	2215	w	2210	w						
			2255	vw	2255	w	2255	w						
					2308	w	2305	w						
			2420	vw	2430	w	2420	w						
			2475	vw	2480	w	2475	w						

Table V.2 continued

			2510	vw	2510	w	2520	w				
			2580	vw	2580	w	2575	w				
			2640	w	2640	w	2640	w				
			2780	w	2780	wq	2780	w			2795	vw
			2850	w	2840	w	2840	w			2840	w
					2860	w	2860	w				
					2904	w	2900	w			2910	w
							2940	w			2940	w
			2980	w	2980	w					2985	vw
sym $=CH_2$ stretch	3020	m					3020	m	3020	w		
sym $=CH_2$ stretch	3030	m	3030	w			3040	w			3020	vs
											3035	vw
=CR-H stretch	3070	w	3060	w	3060	w						
asym $=CH_2$ stretch	3115	m	3104	m	3105	w	3100	m	3108	w	3107	w
asym $=CH_2$ stretch	3124	m	3120	w								
			3162	w								
			3208	w	3210	w	3208	w				

Table V.3 Propenoyl Chloride - I.r. and Raman Spectra (cm^{-1})

Assignments	Infrared Gas Pathlength 100 mm Pressure 50 mm Hg	Rel. Int.	Matrix Isolation Ratio in Argon $^1/_{1000}$ Temp. 8K	Rel. Int.	Infrared Liquid	Rel. Int.	Infrared Solid	Rel. Int.	Raman Liquid	Rel. Int.
					Ref. 130		Ref. 130		Ref. 130	
							145	vw		
					266	vw	267	w	269	m
C-Cl bend (t)					380	w	386	vw	390	w
C-Cl wag (c)			432	vw	437	m	434	s	445	s
skeletal bend (c)			441	vw			441	w		
skeletal bend (t)	450	m	447	vw						
	488	w								
C-Cl wag (t)	495	w	496	w	496	m	496	s	501	vw
	502	w								
	555	w			580	w	591	m		
C-Cl stretch (t)	607	w	605	m	607	s	615	m	615	s
	620	m								
	645	w								
	649	w			671	vw	665	vw		
	655	w								

Table V.3 continued

							682	w		
	701	w								
C-Cl stretch (c)	710	m	705	m	7703	s			711	w
	720	s								
cis wag (c)	743	w	743	w	737	w				
							752	s		
cis wag (t)	756	m	756	w	753	m	757	s		
	769	vw								
	795	w								
	810	vw								
	863	vw								
	872	vw					901	vw		
			936	m						
$=CH_2$ wag (t)	935	s	936	m	932	s	941	s	932	vw
$=CH_2$ wag (c)	938	vs	939	w						
trans wag (t)	976	vs	974	vs	955	s	970	s	980	w
trans wag (c)	980	vs	977	w	975	s	973	s		
			999	vw			1001	s		
	1050	w			1040	vw	1042	vw		
CH_2 rock	1070	w			1072	w			1080	vw

Table V.3 continued

	1086	w			1095	vw	1095	vw		
	1146	s								
C-C stretch	1149	s	1149	vs	1143	s	1152	s	1151	w
	1160	s								
	1186	vw			∼1190	vw	1175	vw		
	1200	vw								
	1249	w			1244	w				
C-H bend			1285	w	1277	2	1278	m		
									1290	s
	1300	w			1295	w	1295	vw		
	1342	vw			1347	vw	1345	w	1352	2
sym $=CH_2$ scissor	1399	m	1395	m	1393	s	1396	m	1399	s
	1404	m					1402	m		
combination band	1437	m	1430	vw	∼1430	w	1431	m	1435	w
	1611	w	1615	w	1608	m				
C=C stretch (t)	1620	m			1617	w	1618	m	1620	vs
C=C stretch (c)	1626	m	1626	w						
	1640	w			1639	vw				
C=0 stretch	1730	m	1755	m	1755	vs	1740	s		

Table V.3 continued

$C=O$ stretch			1766	vs	1775	w			1767	vs
$C=O$ stretch (c)	1772	vs	1773	m						
$C=O$ stretch (t)	1784	vs	1780	m						
	1800	s								
	1872	w			1866	vw	1872	w		
	1950	w			1950	w				
=CR-H stretch									2989	w
	3040	w							3041	m
asym $=CH_2$ stretch	3120	w							3124	w
	3540	w								
	3545	w								

Table V.4 Fundamental Vibrations of 2-chlorobuta-1,3-diene and Propenoyl Chloride

2-chlorobuta-1,3-diene		Vibration	Propenoyl Chloride	
s-trans	s-cis		s-trans	s-cis
		A" out-of-plane Vibrations		
146.8[b]	130[c]	=C-C= torsion	106.8[b]	83[b]
408.5		C-Cl wag	495	432
660[d]		=CH_2 twist	-	-
735.7		cis wag	755.7	742.7
877.1		=CH_2 wag	-	-
922.5		=CH_2 wag	936	939
975.2	975[d]	trans wag	974	977
		A' in-plane Vibrations		
247[b]		skeletal bend	266.5[b]	254.6[b]
386[c]		C-Cl bend	380	361
521.5		skeletal bend	450	441
638	690	C-Cl stretch	607	710
890		=CH_2 rock	1070	-
1024.8	1132	=CH_2 rock	-	-
1224.8		C-C stretch	1149	-
1279		C-H bend	1285[d]	-
1361.9		asym =CH scissor	-	-
1396		sym =CH scissor	1396.1	1397.2
1583		asym C=C stretch	1620	1626
1628		sym C=C stretch	-	-
-		C=O stretch	1784	1772
3020		sym =CH stretch	-	-
3030		sym =CH stretch	3043	3043
3070		=CR-H stretch	2989	2989
3115		asym =CH stretch	-	-
3124		asym =CH stretch	3120	3120

a) Most frequencies were taken from Ref. 130

b) From Ref. 128

c) Estimated from the asymmetric potential function

d) Matrix Frequency

Table V.5 Experimental and Calculated Values for the Principal Moments of Inertia of Isotopic Species of 2-chlorobuta-1,3-diene, in units of amu. Å², and Substitution Coordinates, in Å.

Experimental[a]		Observed - Calculated	
		Initial Structure[b]	Final Structure[c]
$\underline{CH_2{=}^{35}CCl{-}CH{=}CH_2}$			
I_A	92.922	-1.78	-0.191
I_B	135.020	7.95	0.133
I_C	228.031	6.26	0.413
$\underline{CH_2{=}^{37}CCl{-}CH{=}CH_2}$			
I_A	94.300	-2.02	0.176
I_B	137.127	8.33	0.117
I_C	231.519	6.41	0.385
$\underline{CHD{=}^{35}CCl{-}CH{=}CH_2}$[d]			
I_A	96.031	-0.76	0.153
I_B	138.562	7.83	0.062
I_C	234.681	7.16	0.303
$\underline{CHD{=}^{35}CCl{-}CH{=}CH_2}$[e]			
I_A	100.164	2.85	0.065
I_B	135.055	3.83	0.151
I_C	235.313	6.78	0.310
Standard Deviation		6.05	0.245[c]

Table V.5 continued

Experimental[a]		Observed -	Calculated
		Initial Structure[b]	Final Structure[c]
Substitution Coordinates of Cl[f]			
a	1.013	0.080	-0.004
b	0.854	-0.006	-0.004
Substitution Coordinates of H cis to Cl[f]			
a	1.819	-0.029	-0.014
b	1.843	0.004	-0.010
Substitution Coordinates of H trans to Cl[f]			
a	0.171	-0.022	0.053
b	2.703	-0.045	-0.019

a) Taken from Ref. 124 conversion factor: 505391 MHz. Amu Å^2.

b) Taken from Ref. 123 with both CCC angles 122°, all C=C-H angles 120°, and C-H bond length 1.11 Å.

c) The final structure taken is presented in Table V.6. The actual iterative procedure used gave better results than indicated, using more decimal places in the variable bond angles and length, to give a standard deviation of 0.056.

d) Deuterium cis to chlorine.

e) Deuterium trans to chlorine.

f) In each case c = zero due to the planarity of the molecule.

Table V.6 Calculated Structural Parameters for 2-chlorobuta-1,3-diene[a]

Bond Lengths, Å		Bond Angles, Degrees	
C = C	1.36[b]	C = C (Cl)- C	120.4 (6)
C - C	1.46[b]	C = C (H) - C	125.0 (11)
C - Cl	1.70 (1)	C = C - Cl	120.9 (10)
C - H	1.11[b]	C = C - H	120.0[b]

a) Values in parentheses are the dispersions on the values given.

b) Not altered from the initial value.

Table V.7 Thermodynamic Functions[a] of Gaseous 2-Chlorobuta-1,3-Diene, in $JK^{-1}\ mol^{-1}$

T	S^θ		C_p^θ		$-(G^\theta - H_0^\theta)/T$		X_{cis}	ΔH_0^θ [b]
	A	B	A	B	A	B		
298.15	312.98	312.98	92.59	92.55	255.58	255.56	0.035	8.5
300.0	313.50	313.53	92.97	92.94	255.86	255.86	0.035	8.5
400.0	343.30	343.28	113.97	113.99	274.21	274.21	0.075	7.8
500.0	370.62	370.62	130.98	131.01	290.77	290.77	0.109	7.8
600.0	395.75	395.76	144.61	144.62	306.20	306.33	0.137	7.9
700.0	418.88	418.89	155.72	155.70	320.54	320.79	0.158	8.0
800.0	440.29	440.29	165.05	165.04	334.27	334.41	0.175	8.3
900.0	460.12	460.12	172.99	172.97	347.10	347.23	0.184	8.7
1000.0	478.75	478.75	179.77	179.76	359.45	359.47	0.201	8.9

a) A:- Values calculated by equation B:- Fitted Values

b) Units are $kJ\ mol^{-1}$. Average value is 8.3 $kJ\ mol^{-1}$.

Table V.8 Thermodynamic Functions of Gaseous Propenoyl Chloride in JK^{-1} mol^{-1}

T	$S^\ominus$	$C_p^\ominus$	$\left(\frac{H^\ominus - H_o^\ominus}{T}\right)$	$-\left(\frac{G^\ominus - H_o^\ominus}{T}\right)$	X_C
273.15	310.0	79.3	55.4	254.6	0.304
298.15	317.1	83.2	57.6	259.5	0.326
300.0	317.6	83.5	57.7	259.9	0.327
400.0	343.7	98.1	66.1	277.6	0.391
500.0	367.0	110.4	73.7	293.2	0.432
600.0	388.0	120.4	80.7	307.3	0.459
700.0	407.2	128.6	87.0	320.2	0.479
800.0	424.8	135.5	92.6	332.2	0.494
900.0	441.1	141.3	97.7	343.4	0.506
1000.0	456.3	146.2	102.3	354.0	0.515

CHAPTER VI

Conclusions

Chlorinated Hydrocarbons as Model Compounds for Poly (Vinyl Chloride)

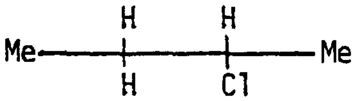
CHAPTER VI

Conclusions

Chlorinated Hydrocarbons as Model Compounds for Poly (vinyl chloride)

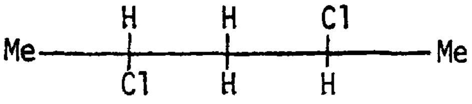
The vibrational spectroscopy of the following chlorinated hydrocarbons will now be discussed in relation to the structure of P.V.C.

2-chlorobutane

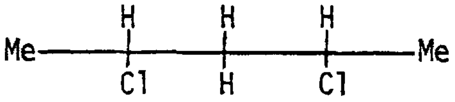


$$\mathrm{Me}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{+}}-\mathrm{Me}$$

(±)- and meso- 2,4-dichloropentane

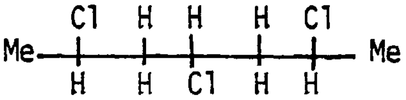


$$\mathrm{Me}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{+}}-\mathrm{Me}$$

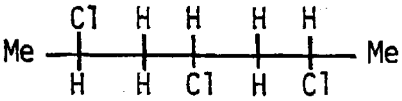


$$\mathrm{Me}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{+}}-\mathrm{Me}$$

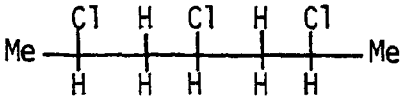
2,4,6-trichloroheptane (syndiotactic, heterotactic and isotactic)



$$\mathrm{Me}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{+}}-\mathrm{Me}$$



$$\mathrm{Me}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{+}}-\mathrm{Me}$$



$$\mathrm{Me}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{+}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{+}}-\mathrm{Me}$$

Some useful qualitative information is obtained from the matrix isolation spectroscopy described in the previous chapters relating to the structure of the model compounds themselves and hence in relation also to the P.V.C. polymer. All assignments for these compounds in the matrix phase have been tabulated in the relevant chapters; these spectra have been found useful in clarifying some previous assignments which were obtained in the liquid phase and were not so well-resolved.

Comparison was made of the matrix isolation spectra of the saturated hydrocarbons listed above and the unsaturated chlorosubstituted compounds (allyl chloride, 2-chlorobuta-1,3-diene). This shows that the annealing conditions used in the present work resulted in some reduction in the intensity of high energy conformer bands in the saturated compounds but failure to achieve isolation of low energy conformers in the final matrix. By contrast in the unsaturated compounds the spectra after annealing showed that only the low energy form was present in significant amounts.

Considering first of all the simplest of the above chlorinated hydrocarbons, i.e. 2-chlorobutane; all frequencies have been tabulated previously (113) in the liquid phase and the present assignments in the matrix isolation phase are in close agreement with these. Conformer bands are observed to increase or decrease in intensity as expected on annealing the matrix.

In the matrix isolation phase weak bands are observed which were not observed in the liquid or solid phase, at frequencies of 862 cm^{-1} and 1150 cm^{-1}. These bands can be assigned to certain conformers and are observed in the matrix isolation spectra due to the fact that all bands are better resolved in this phase. The band at 862 cm^{-1} is assigned to the CH_2 rocking mode of the S_{CH} conformation and the band at 1150 cm^{-1} is assigned to the CH_2 rocking mode of the S_{HH}' conformation. Another difference in the matrix isolation phase spectra is that the two bands at 1290 cm^{-1} and 1300 cm^{-1} both increase in intensity on annealing the matrix which was not observed in previous liquid phase low temperature studies (113).

Bands assigned to the CH_2 deformation region of the matrix isolation phase spectra show conformational dependence upon temperature on annealing of the matrix. Assignments of bands in this region of the spectra shows that previous assignments (113) were oversimplified. In the C-Cl stretching region of the spectra there is no evidence for isotopic splitting.

Studies of the (±)- and meso-2,4-dichloropentanes yieled some useful information in relation to conformational analysis of these two isomers.

Examination of the C-Cl stretching region of each isomer gives similar values for the frequencies of the major conformations as for those of the liquid phase; however in the case of the matrix isolation spectra these bands occur at slightly higher frequencies to those of the liquid phase spectra. The rest of this C-Cl stretching frequency region differs from previous spectra as follows.

Bands at frequencies of 612 cm^{-1} and 635 cm^{-1} in the matrix isolation phase which are of strong intensity are assigned to the preferred TT (S_{HH} S_{HH}) conformation and bands at 718 cm^{-1} and 520 cm^{-1} have been assigned to GG and GG' conformations respectively. There is no evidence for the TG conformation being present in this phase. It is thus concluded that at low temperatures as well as the preferred TT conformation there are present significant amounts of the GG and GG' conformations. Relating these results to P.V.C. indicates that at low temperatures the chain conformation may be altered to some less favourable skeletal structures in the case of the syndiotactic configuration. This means in fact that there may be more of the energetically unfavourable bent structures present in the chain configuration of the polymer. These are conformations which have previously been thought of as sterically disfavoured at low temperatures.

It is quite feasible that the above conformations are present at low temperatures since they both possess quite low conformer energy values as determined by Schneider (115).

In the case of the meso-2,4-dichloropentane strong intensity bands are observed at frequencies of 626 cm^{-1} and 688 cm^{-1} which are assigned to thepreferred TG (S_{HH} S_{CH}') conformation. This latter conformation is again an energetically disfavoured conformer species and could be indicative in this case that less favourable conformational structures may be present at low temperatures in the P.V.C. polymer chain. The presence of this TG' conformation at these low temperatures is reasonable when previous conformer energy calculations (115) are considered. Previous workers have calculated that the TG conformer is only slightly more stable than the TG' conformer whereas the other possible conformations are less stable than the TG species by a greater amount. Hence we can see that P.V.C. polymerised at low temperature may consist in the isotactic portion of some energetically unfavourable bent structures.

Another region of the spectra which has previously been thought of as being useful in conformational analysis of model compounds of P.V.C. is the CH_2 deformation region at ∿ 1430 cm^{-1}. Krimm et al (147) saw two overlapping peaks in this region of the spectrum which were dependent upon polymerization temperature. Later workers (148) then related these two bands to two different portions of the polymer chain, i.e. syndiotactic and disordered. From the intensity measurements of these bands at two different temperatures they then used the following equations (i) and (ii) in order to obtain a value for the degree of syndiotacticity α.

(i) $$\frac{\lambda_1 + 1}{\lambda_2 + 2} = \frac{1 + \exp(-\Delta E/RT)}{1 + \exp(-\Delta E/RT)}$$ in order to evaluate ΔE and

(ii) $$\alpha = \frac{1 + \exp(-\Delta E/RT)}{1 + \lambda}$$ in order to obtain α.

However Pohl and Hummel (119) have questioned whether these bands are as simple as the previous workers assumed or whether they are composed of contributory peaks. Maddams and Tooke (150) have used fourth derivative spectroscopy in order to sharpen up these bands and aid resolution of overlapping multiplets. They have found that the CH_2 deformation mode is composed of three components of which one is broader than the other two and probably consists of two overlapping components. They also found that syndiotacticity values obtained by Germar et al (148) and Nakajuma et al (151) are erroneous for low temperature polymers.

Matrix isolation studies of the model compounds of P.V.C. seem to confirm the above suspicions, since under these conditions the bands in this region of the spectrum are sharp and well-resolved and in all cases it can be seen that there are at least three bands present in this region of the spectrum.

2-chlorobutane reveals three bands in this region of the spectrum at frequencies of 1447 cm^{-1}, 1437 cm^{-1} and 1452 cm^{-1}. The 1447 cm^{-1} band is a strong intensity band, the other two being much weaker. The two weak bands exhibit temperature dependence under these conditions and could probably be assigned to high energy conformers of the CH_2 deformation mode.

In the case of the two dichloropentane isomers a similar occurrence is found in this region of the matrix isolation spectra. Bands are assigned to this mode for the (±) isomer at frequencies of 1419 cm^{-1}, 1441 cm^{-1} and 1447 cm^{-1}; the latter being of strongest intensity. The CH_2 deformation region of the spectra of meso-2,4-dichloropentane under matrix isolation conditions reveals bands at 1420 cm^{-1}, 1431 cm^{-1} and 1448 cm^{-1}. The band at 1448 cm^{-1} is the strongest in this case. From examination of this region of the spectra of the model compounds of P.V.C. it can be seen that previous assignments in this region of the spectrum in relation to the P.V.C. polymer at low temperatures was oversimplified and hence presents erroneous results for values of syndiotacticity.

The only other significant difference in the matrix isolation spectra of the dl isomer is the appearance of a band of medium intensity at 1279 cm^{-1} which is assigned to the CH_2 wag of the TT conformer from the calculations of Moore and Krimm (114).

In the case of the meso isomer two extra bands are observed in the matrix isolation spectra, both of which are of medium intensity, occuring at frequencies of 889 cm^{-1} and 1295 cm^{-1}. These bands are most likely to belong to the TG' conformation and are assigned to CH_3 rocking and CH_2 wagging modes respectively.

Matrix isolation spectra of the three isomeric forms of 2,4,6-trichloroheptane have been studied and frequencies tabulated in Chapter IV.

In the case of the syndiotactic isomer, in the C-Cl stretching region of the spectrum two strong intensity bands are observed at frequencies of 608 cm^{-1} and 648 cm^{-1}. The band at 648 cm^{-1} is observed to increase in intensity on annealing of the matrix. There is no shoulder at 604 cm^{-1} present in these spectra as observed by previous workers in liquid phase spectra (117). Examination of these assignments indicate that there is a reasonable amount of the TTGG conformer present as well as the preferred TTTT conformer since there is no evidence for the presence of the TTTT conformer band at 604 cm^{-1} and the band at 648 cm^{-1} should contain quite a large contribution of the higher frequency TTGG conformer band.

The isotactic portion has bands present in this region at 622 cm^{-1} and 688 cm^{-1} which are assigned to contributions from TGTG and G'TTG conformers. Neither of these bands is seen to exhibit any intensity change on annealing of the matrix.

For the heterotactic isomer the C-Cl stretching bands are observed at 610 cm^{-1}, 628 cm^{-1} and 688 cm^{-1} and are made up of contributions from

TTTG and TTG'T conformers. Again no intensity change is observed for these bands on annealing of the matrix.

Examination of the 1430 cm^{-1} CH_2 deformation region of the matrix isolation spectra of each of the three isomers lends confirmation to the previous conclusion that this region of the spectrum in the case of P.V.C. has so far been oversimplified; since in each case there are at least three bands observed. In each particular case bands are observed at the following frequencies.

Taking the syndiotactic isomer first, bands are observed at frequencies of 1421 cm^{-1}, 1427 cm^{-1} and 1434 cm^{-1} of strong intensity.

The heterotactic isomer reveals bands in this region at frequencies of 1420 cm^{-1}, 1430 cm^{-1} and 1436 cm^{-1}, the 1430 cm^{-1} band is a shoulder and the other two are weak bands, there is also a band of strong intensity at 1446 cm^{-1}.

In the isotactic case bands are observed at 1417 cm^{-1} and 1431 cm^{-1} both of which are weak bands and a band of strong intensity at 1447 cm^{-1}.

In each case the rest of the spectrum examined in the matrix phase reveals no great differences to assignments in the liquid or solution phases. The only isomer which shows any change on annealing is the syndiotactic one and even in this case annealing does not result in very great changes in band intensities.

Examination of the matrix isolation spectra of all the above compounds would seem then to suggest that particularly in the case of the syndiotactic type of polymer polymerization at low temperatures may result in a greater proportion of energetically unfavourable conformational structure than was previously deduced.

The next section deals with the variable temperature infrared results.

In the case of 2-chlorobutane values of $\Delta H^\ominus$ were obtained in solution in CS_2 for two different equilibria;

(i) $S_{HH} \rightleftharpoons S_{CH}$ and

(ii) $S_{HH} \rightleftharpoons S_{HH'}$

where S_{HH}' and S_{CH} forms are high energy conformations. The value of $\Delta H^\ominus$ obtained for the equilibrium (i) was 2.24 ± 0.53 kJ mol^{-1} indicating that the S_{HH} conformation is more stable than the S_{CH} conformation by this amount. For the equilibrium (ii) the value of $\Delta H^\ominus$ was found to be 3.23 ± 0.77 kJ mol^{-1} which makes the S_{HH} conformation more stable than the S_{HH}' conformation by this quantity. These values are not particularly high and hence the presence of the high energy conformers in the solution phase in considerable quantities is likely to occur. The fact that the S_{HH} conformer is more stable than the S_{HH}' by a greater amount than it is when compared with the S_{CH} conformer is a sensible result when the structure of each conformer is examined; there being a much greater degree of steric hindrance in the case of the S_{HH}' conformer than for the S_{CH} conformer, since in the former case the three large substituents CH_3, CH_3 and Cl are in very close proximity, whereas in the latter only the two CH_3 groups are in such a position. This would indicate that the S_{HH}' is a much less energetically favourable conformer which is consistent with the $\Delta H^\ominus$ values.

These values fit in well in Table II.3 of chapter II on variable temperature and determination of energies between conformers, since it can be seen that previous workers (49) found the value of $\Delta H^\ominus$ to be larger for the equilibrium $S_{HH}' \rightleftharpoons S_{HH}$ than for the equilibrium $S_{CH} \rightleftharpoons S_{HH}$ in the liquid phase. The present values obtained in the solution phase in carbon disulphide for each equlibrium are a little higher than the liquid phase values, which might be due to a solvent effect.

A variable temperature Raman study was carried out on 2-chlorobutane liquid and it was possible to calculate values of $\Delta H^{\ominus}$ for the following equilibria:

(i) $S_{HH} \rightleftharpoons S_{CH}$ and

(ii) $S_{HH} \rightleftharpoons S_{HH}'$

For equilibrium (i) the value of $\Delta H^{\ominus}$ was calculated to be 2.27 kJ mol^{-1} and for equilibrium (ii) it was calculated as 3.67 kJ mol^{-1} which again fits in well in Table II.3 of Chapter II on variable temperature work. It can be seen that in the Raman case, as for the infrared conformer, stability lies in the order $S_{HH} > S_{CH} > S_{HH}'$.

Studies of the isotactic and heterotactic portions of 2,4,6-trichloroheptane by Raman spectroscopy have been carried out and assignments of bands in the C-Cl stretching regions of the spectra in each case agree well with the spectra of P.V.C. samples as studied by Robinson et al, bearing out all of their deductions concerning the amorphous region of the P.V.C. Raman spectra as discussed in Chapter IV.

Previous workers (119) have resolved the spectrum of P.V.C. between 600 - 700 cm^{-1} into seven component peaks and used the data in order to calculate a value of syndiotacticity by ratioing the sum of the areas under all the syndiotacticity peaks to the sum of the areas under all the peaks. In carrying out this calculation they have assumed that all the peaks have the same extinction coefficient. However, in the present study, values of extinction coefficients for some of the model compounds have been calculated using the infrared variable temperature measurements and values of $\Delta H^{\ominus}$ as described earlier. In the case of 2-chlorobutane for the three conformations S_{HH}, S_{CH} and S_{HH}' the values were found not to be equal, the S_{HH} conformer having a value of 19.2 m² mol⁻¹ and the S_{HH}' and S_{CH} conformers having values of 22.7 and 27.4 m² mol⁻¹, respectively. Although the results may not be readily transferable to the solid state spectrum of P.V.C. it would seem highly unlikely that the conformer bands in the case of the polymer would have equal extinction coefficients and the results for the model compounds would seem to add weight to this conclusion. Hence any calculation of concentrations of configurational and conformational isomers in the polymer situation ought not to make this assumption.

Variable temperature infrared studies were also carried out on the dl- and meso-2,4-dichloropentanes in solution in CS_2 and it was possible to calculate values of $\Delta H^{\ominus}$ for a conformer equilibrium in each case. For the dl isomer $\Delta H^{\ominus}$ was calculated for the equilibrium $S_{HH}\ S_{HH}$ (TT) $\rightleftharpoons$ $S_{HH}\ S_{HH}$ (TG) and was found to have a value of 0.89 kJ mol⁻¹. This indicates that there is only a small energy difference between these conformers and hence one would expect that this conformation is present in reasonable amounts at room temperature. In the case of the meso isomer, $\Delta H^{\ominus}$ was calculated for the equilibrium $S_{HH}\ S_{CH}$ (TG) $\rightleftharpoons$ $S_{HH}\ S_{HH}'$ (TG') and was found to have a value of 1.25 kJ mol⁻¹. This is a slightly higher value than that calculated for the equilibrium between the preferred conformer and a less favourable one in the dl system but is still a relatively low figure and so in this case one would expect that reasonable quantities of this high energy conformer might be present at room temperature.

Calculations of extinction coefficients were made from these $\Delta H^{\ominus}$ values for the conformations concerned and in each situation were found to be unequal, as for the previous compound discussed, 2-chlorobutane.

Values obtained for $\Delta H^{\ominus}$ between conformers in this work are summarised overleaf.

2-chlorobutane

I.R. (soln.)	$\Delta H^{\ominus}$ kJ mol^{-1}
$S_{HH} \rightleftharpoons S_{CH}$	2.24 ± 0.53
$S_{HH} \rightleftharpoons S_{HH}'$	3.23 ± 0.77

Raman (soln.)	$\Delta H^{\ominus}$ kJ mol^{-1}
$S_{HH} \rightleftharpoons S_{CH}$	2.27 ± 0.6
$S_{HH} \rightleftharpoons S_{HH}'$	3.67 ± 0.21

2,4-dichloropentane

I.R. (soln.)	$\Delta H^{\ominus}$ kJ mol^{-1}
dl	
$S_{HH}\ S_{HH}$ (TT) $\rightleftharpoons S_{HH}\ S_{CH}$ (TG)	0.89 ± 0.28
meso	
$S_{HH}\ S_{CH}$ (TG) $\rightleftharpoons S_{HH}\ S_{HH'}$ (TG')	1.25 ± 0.23

Allyl Chloride

I.R. (soln.)	$\Delta H^{\ominus}$ kJ mol^{-1}
gauche $\rightleftharpoons$ cis	1.129 ± 0.79

2-chlorobuta-1,3-diene

	$\Delta H^{\ominus}$ kJ mol^{-1}
s-trans $\rightleftharpoons$ s-cis	8.3 ± 0.6

These values can be related to Chapter II as follows; first of all in the case of 2-chlorobutane the values can be included in Table II.3. They can be included in this portion of the chapter because the structure of the molecule is such that rotation takes place about a C-C bond under the influence of three substituents, i.e. two methyl groups and a chlorine atom. The structure of this molecule is such that it is possible that it can exist in three different conformations (Fig. IV.1) as for other secondary butyl halides. The values obtained for $\Delta H^\ominus$ for this compound in solution are consistent with those found in the liquid (49).

The 2 isomeric forms of 2,4-dichloropentane have been included in Table II.6 of Chapter II since they are diastereo isomers of similar structure to the other compounds included in this table. The molecule possesses asymmetry at the C-3 carbon in this case. For this compound, as for other diastereo isomers included in the table, the conformational possibilities are different in the two forms and these possibilities are quite numerous. In the solution phase it was found that for the dl isomer the dl trans conformer is the low energy form and the value of $\Delta H^\ominus$ for the equilibrium studied between this conformation and the TG conformation is small but is of the order of liquid $\Delta H^\ominus$ values quoted in Table II.6 for similar compounds.

Studies of allyl chloride show that the gauche conformation is favoured in this case. This compound is included in Table II.11 under the heading of Substituted Propenes. In cases of this type studied it would appear that it can be concluded that the <u>gauche</u> form is predominant and exists in equilibrium with the high energy <u>cis</u> conformation. The value of $\Delta H^\ominus$ calculated for the <u>gauche</u> $\rightleftharpoons$ <u>cis</u> equilibrium in the solution phase for allyl choride is of the same order as that obtained for the liquid phase.

2-chlorobuta-1,3-diene would fit in with the results for other substituted 1,3-butadienes in Table II.12. The value of $\Delta H^\ominus$ for the s-<u>trans</u> $\rightleftharpoons$ s-<u>cis</u> equilibrium in this case has been calculated by usual statistical methods and was found to be 8.3 ± 0.6 kJ mol^{-1}. This value is a little higher than that found for 1,3-butadiene, indicating that the s-cis conformer is less stable in 2-chlorobuta-1,3-diene. This is probably because, as stated earlier, steric interactions at the 2,3 position could inhibit the formation of the s-cis conformer, and hence it would be expected that the value of $\Delta H^{\ominus}$ for the s-trans $\rightleftharpoons$ s-cis equilibrium would be quite high in the case of 2-chlorobuta-1,3-diene.

In all cases discussed above therefore, it is a useful exercise to collate the information calculated for conformational equilibria in this study with the information given in Chapter II as all the results are easily explained in relation to the discussions of the information in the tables.

In all cases, standard deviations are quoted for $\Delta H^{\ominus}$ values. These measure random errors. Additionally systematic errors may be present leading to inaccuracies which may be large enough to nullify any correlations between $\Delta H^{\ominus}$ and conformational or structural factors.

In the present work attempts to improve the accuracy by using interferometry as well as dispersive i.r. were unsuccessful. Nevertheless, the rate of advance of both dispersive and Fourier transform methods and the growth of computer handling of data suggests there may be significant improvements in either or both methods in the future.

It is conceivable that a complete spectrum is rapidly scanned, and weak bands enhanced for each of a series of temperatures. Band absorbance values can be collected and sorted according to temperature dependencies corresponding to high or low energy conformers or perhaps to both conformers. For a simple equilibrium a number of pairs of bands could lead to a rapidly computed $\Delta H^{\ominus}$ value based on a wider range of data than is currently available.

The present work suggests that the instrument refinements which are rapidly developing together with the on-line computing power of dispersive and Fourier transform i.r. could refine the accuracy of the $\Delta H^{\ominus}$ measurements listed to provide clearer correlations within the classes of compounds reviewed in Chapter II and in the model compound correlations considered in the later chapters.

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APPENDIX

Contributions to Scientific Meetings

INFRARED AND RAMAN DISCUSSION GROUP

The 87th meeting of the Group will be held in the Strand Building (Physics Departmen of King's College, London, on Tuesday, December 19th, 1978. The theme is the study of molecular interactions.

Programme

10.15 a.m.	Morning coffee.
10.50 - 11.20	Professor N. Sheppard (University of East Anglia). 'Recent I.R. Studies of the Structures of Molecules Chemisorbed on Metal Surfaces'.
11.25 - 11.55	D. Powell (University of East Anglia) 'Vibrational Spectra of Metal Cluster Compounds Containing Hydrogen and Organic Groups'.
12.00 - 12.30	A. Barnes (University of Salford) 'Intermolecular Interactions Studied by Matrix Isolation Vibrational Spectroscopy'.
12.45 p.m.	Lunch
2.00 - 2.30	R. Spragg (Perkin Elmer Ltd) Influence of weak interactions on spectra
2.35 - 2.55	R. Ferri (King's College, University of London) 'Interaction between chloroform and benzene'.
3.00 - 3.20	D. Steele (Royal Holloway College, University of London 'Investigations of Molecular Interactions in Organic Solutions by Vibrational Spectroscopy'.
3.25 - 3.45	Mrs J Goodfield (Polytechnic of Wales) 'Infrared and Raman Spectroscopy on Chlorinated Hydrocarbons in Relation to P.V.C.'.

Catering

Coffee and the annual Christmas Feast are available at a cost of £3.50 per head or £3.00 for students

Advance payment and reservation must be made by Monday, 11th December (reservation form attached).

Future Meetings

April 18th - 19th, 1979. Joint meeting with Chem. Soc. (Dalton Division) on Photochemistry, Lasers and Spectroscopy at Newcastle University.

Sept. 27th, 1979. Meeting at ICI Harrogate.

- -

Please reserve..........place(s) for morning coffee and Christmas Lunch on Tuesday, 19th December 1978.

A cheque for ....is enclosed (cost £3.50 per person or student £3.00)

Name....................Address..

Return to: Mr I Degen, Research Division, Kodak Ltd. Harrow, Middx. HA1 4TY.

POLYTECHNIC OF WALES

MEETINGS ASSOCIATED WITH THE DEPARTMENT OF SCIENCE

Thurs Oct 26 1978	The Liquid Scintillation Counter
Room J233 12.45p.m.	Dr. Graham White, University College, Cardiff.
* Mon Nov 6 1978	A Plenary Strategy for Chromatography
Room J132 6.30p.m.	Prof. J.H. Purnell, University College, Swansea.
Thurs Nov 23 1978	Infrared and Raman Spectra of Chlorinated Hydrocarbons in relation to P.V.C.
Room A112 1.00p.m.	Mrs. Jeanette Goodfield, Polytechnic of Wales.
+ Wed Nov 29 1978	Acetic Acid Manufacture - An Example of a Sophisticated Petro Chemical Process
Room G219 4.30p.m.	Dr. H.S. Green, B.P.Chemicals Ltd.
Thurs Dec 7 1978	Measurement of low pressures
Room A112 1.00p.m.	Dr. G.T.Roberts, Polytechnic of Wales.
* Fri Dec 8 1978	The Spectroscopy of Molecular Ions.
Room G219 5.00p.m.	Prof.A. Carrington FRS. University of Southampton.
Thurs Feb 8 1979	Pollen analysis and the history of British Vegetation
Room A112 1.00p.m.	H.M.Jones, Polytechnic of Wales.
Thurs Feb 22 1979	An Overview of Problems in Marine Biology in the Bristol Channel
Room G219 1.00p.m.	Dr. A. Nelson-Smith, University College, Swansea.
Thurs Mar 1 1979	Hydrogenated fats and heart disease
Room A112 1.00p.m.	L.H.Thomas, Polytechnic of Wales.
*Thurs Mar 15 1979	An Analytical Chemist Looks at the Environment,
Room G219 1.00p.m.	Dr. G. Nickless, University of Bristol.
† Tues Apr 10 1979	An Introduction to Patents
Room G219 10.00a.m.	M.P.Jackson,MA,CPA.The Wellcome Foundation Ltd. A.W.White, BSc.PhD.CPA. Beecham Group Ltd.
Thurs May 17 1979	Further progress in the use of NMR in the study of biological membranes.
Room A112 1.00p.m.	G.R.A.Hunt, Polytechnic of Wales.
Thurs June 21 1979	The regeneration problem in British forestry,
Room A112 1.00p.m.	R.M.Baker, Polytechnic of Wales.

* Refreshments provided forty-five minutes before lecture.
\+ Buffet available after lecture.
† Registration arrangements on request

THE POLYTECHNIC OF WALES
POLITECHNIG CYMRU

Director: J D Davies MSc PhD DSc CEng FICE FIStructE
Pontypridd
Mid Glamorgan *Telephone:* Pontypridd 405133
CF37 1DL

DEPARTMENT OF SCIENCE

Head: W O George BSc PhD DSc CChem FRIC FRSA

INTRODUCTION TO INFRARED SPECTROSCOPY EXPERIMENT AND INTERPRETATION

Tuesday 15th April - Thursday 17th April 1980

Fees on the detachable enrolment form are inclusive of accommodation (when requested), meals and refreshment.

The 91st meeting of the *Infrared and Raman Discussion Group* will be held on Wednesday 16th April 1980 at the Polytechnic of Wales.

A series of lectures by leading experts, related to the content of the practical course will be given. The programme of the meeting will be distributed to the Group and to those who register on the attached form.

The two days of practical work associated with the meeting will enable students to select up to eight 1½ hour experiments/demonstrations of a basic and/ or advanced nature.

The experiments will be supervised by tutors experienced in industrial problems and by technical staff from the instrument manufacturers.

An exhibition of books, films and various audio visual presentations will be held.

The course is made possible by the generous provision of equipment and technical representation by the Firms listed.

Residential accommodation on the Campus has been arranged to promote a corporate spirit.

Tuesday 15th April - Course Dinner
Wednesday 16th April - Tour of Welsh Mountains and
Valleys to include features of interest such as:
Sardis Road Rugby Ground to celebrate "The Decade of the Dragon". viz.
Pontypridd 1st XV v Llanelli 1st XV

TUTORS

P Pent	Yarsley Technical Centre
R A G Carrington	Shell Research Ltd.
J M Chalmers	ICI Plastics Division Ltd.
I A Degen	Kodak Ltd.
H Elliott	Polytechnic of Wales
A J Everett	Welcome Research Labs.
J E Goodfield	Polytechnic of Wales
H Hopkins	Polytechnic of Wales
W F Maddams	B.P. Co. Ltd.
R W Ward	B.P. Chemicals Ltd.
H A Willis	ICI Plastics Division Ltd.

FIRMS

B D H Chemicals Ltd.	Robert M Lenk
Beckman RIIC Ltd.	Keith Rutherford
Biorad Labs. Ltd.	Spencer J Levy
Foxboro Analytical Ltd.	Richard W Ramsey
Nicolet Insts. Ltd.	Graham V Fraser
Perkin Elmer Ltd.	Francis Dunstan
Pye Unicam Ltd.	David Parr
Specac Ltd.	William McCormack

Basic Experiments

Practical Manipulation of solids, liquids and gases. Choice of instrumental conditions for instruments with a range of performance. Interpretation in terms of qualitative and quantitative analysis.

Advanced Experiments

Sophisticated sample handling viz. multipath cells, variable temperature cells, microhandling techniques attenuated total reflectance, matrix isolation, computer handling of data, interferometry, on line gas-chromatography.

Further information will be sent to enrolled students including a form to obtain indications of the preferred selections from the Experiments on offer.

INTRODUCTION TO INFRARED SPECTROSCOPY - EXPERIMENT AND INTERPRETATION

NAME: ____________________ MALE/FEMALE (For Accommodation)

ADDRESS: ____________________
____
____

ORGANIZATION: ____________________ TELEPHONE NO. __________

REQUIRED ATTENDANCE:	Tues 15 April	Wednes 16 April	Thurs 17 April
TIME OF SESSION:	10.30 - 12.00 13.30 - 18.00	10.30 - 12.30 13.30 - 16.30	9.00 - 12.00 13.30 - 16.30
Please Circle as Required	Day Only £15 Overnight £10	Day Only £5 Overnight £10	Day Only £15 Cheque Enclosed £______

Please return with cheque made payable to IRDG, to Organizer:

Dr. W.O. George, Department of Science, Polytechnic of Wales, Pontypridd, Mid Glamorgan, CF37 1DL.