

"THE DETERMINATION OF TORSIONAL BARRIERS
BY FAR INFRARED SPECTROSCOPY."

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ABSTRACT.

The filtering problems and calibration of the far infrared vacuum grating spectrometer used in this research are briefly discussed along with the experimental techniques evolved for handling vapour, liquid and solid samples.

The far infrared absorption spectra of n-propyl chloride, bromide and iodide have been examined in the vapour, liquid and solid phases as well as the fluoride in the vapour phase. The spectra of n-propyl chloride isolated in a carbon tetrachloride matrix at 77°K has also been observed. These spectra confirm the existence of two isomers, trans and gauche, in the vapour and liquid and also the disappearance of the gauche in the crystal and indicate that the trans isomer is more favoured in going from vapour to liquid and in passing from chloride to iodide. The observed skeletal torsion frequencies correspond to triple cosine barriers of 4.29(3.57), 4.48(3.82) and 4.89(4.34) Kcals/mole for the trans(gauche) isomer of the chloride, bromide and iodide respectively.

The effect of environment on the absorption spectra of the allyl halides in the frequency range 425-60 cm^{-1} has been investigated. The spectra arise essentially from a single isomer which has been shown to be approximately the trans-Gauche form, its proportion again increasing from chloride to iodide. A complete vibrational assignment has been given for the range 100-1700 cm^{-1} . The skeletal torsion frequencies correspond to triple cosine barriers of 2.80, 3.18 and 3.13 Kcals/mole for the chloride, bromide and iodide respectively.

The skeletal torsion frequencies of the n-propyl halides are found to increase ingoing from vapour to liquid whereas the reverse is true for the allyl halides. An explanation is forwarded in terms of the asymmetry of the electron distribution in the molecule in a discussion on the origin of barriers to internal rotation and the effect of phase (solvent) on them.

General computer programmes have been developed to calculate the reduced moment of inertia, effective in the torsional motion, for any molecule.

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THE FAR INFRARED SPECTROMETER.

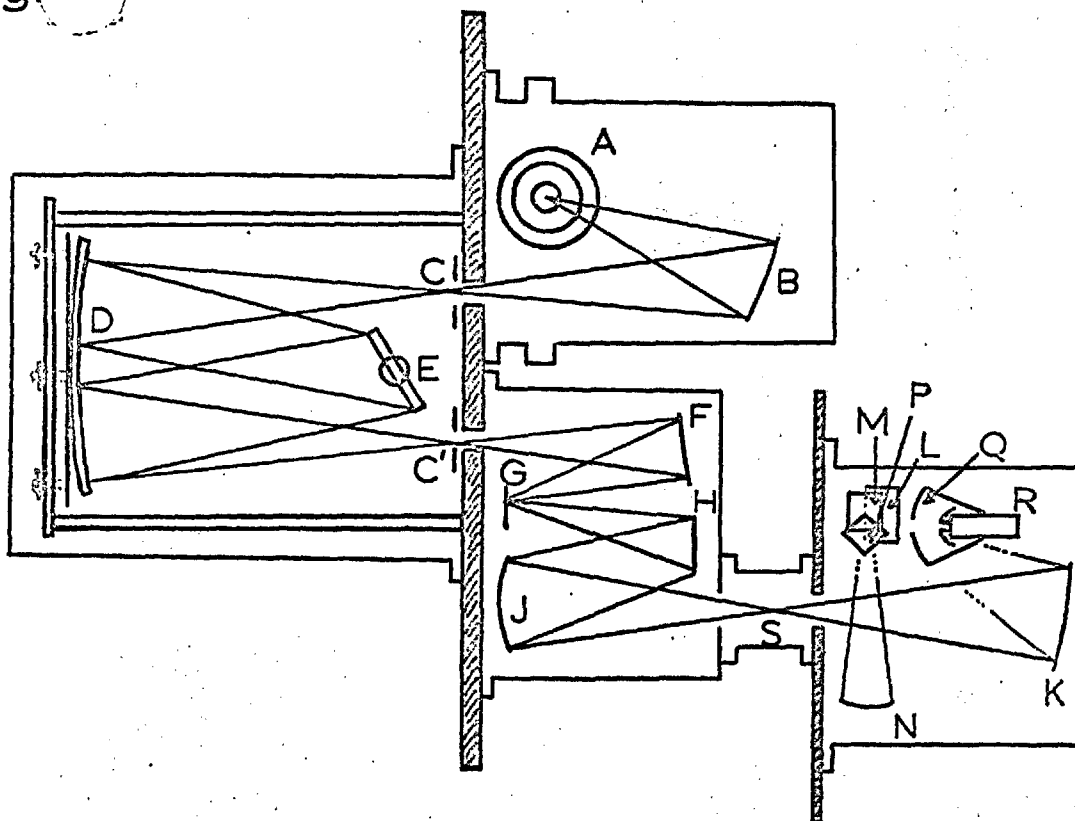
The far infrared spectra recorded during the course of this research were obtained on a single beam far infrared vacuum grating spectrometer designed and constructed in this laboratory by Wood, Taimsalu and Silver and covering the frequency range $60\text{--}425\text{ cm}^{-1}$. The salient features are shown in figure (1) and an excellent description of the instrument appears in the thesis of Taimsalu P. (Ph.D. London (1963)). A brief description is given below:

The spectrometer consists of separately evacuable monochromator and detector sections with sample area between. The radiation is produced by a fused quartz mercury lamp, is modulated at 10 c/s by a KBr crystal chopper and transmitted through one thickness of 500 gauge (0.125mm) black polythene: this combination of KBr chopper and black polythene is the basic filter used in all regions of the far infrared and transmits very little radiation of frequency higher than 450 cm^{-1} .

The monochromator employs $f/4$ Ebert optics to minimise aberrations and to pass as much radiation as possible by the use of long slits. Dispersion is by means of either an 80 lines/cm or 200 lines/cm echelette grating (70 X 70mm Bausch and Lomb, blazed at 91 cm^{-1} or 228 cm^{-1} respectively.) both of which are used almost entirely in the first order. A resolution of 0.6 cm^{-1} has been obtained at 150 cm^{-1} .

Elimination of higher order radiation is also effected by the use of one or two "crossed" reststrahlen reflection filters and often at lower frequencies also by the use of a Imm crystal quartz transmission filter.

Fig. 1.



- A Hg source, Cu cooling jacket & KBr chopper blades.
- B Spherical mirror.
- C Entrance slit. C' Exit slit.
- D Spherical Ebert mirror.
- E Echelette grating.
- F "Sliced" spherical mirror.
- G Plane "matchstick" mirrors.
- H Plane mirror.
- J Spherical mirror.
- S Sample cell.
- K Spherical mirror.
- L Plane mirror.
- M 1st reststrahlen "windmill".
- N Spherical mirror.
- P 2nd reststrahlen "windmill".
- Q Greenler image reducer.
- R Golay pneumatic detector.

The detector section employs a "Unicam" Golay pneumatic thermal detector, tuned only to detect radiation modulated at 10c/s. The amplified signal is finally recorded on a Honeywill-Brown strip chart recorder. Typical signal/noise ratios are 100:1 at 300cm^{-1} and 25:1 at 80cm^{-1} .

The spectrometer is evacuated to about 0.1mm Hg (Pirani gauge) - this being sufficient to remove the water vapour lines completely.

CALIBRATION OF THE SPECTROMETER.

The water vapour spectrum provides a very suitable and convenient means of calibration. The pure rotation spectrum of atmospheric water is often an unwelcome imprint superimposed on far infrared spectra. Accurate rotational energy levels have been tabulated (1) and can be used as the basis of the calibration. To record the spectrum the sample cell is merely left open to the atmosphere.

The standard diffraction formula for a grating is

$n\lambda = d (\sin\beta \pm \sin\gamma)$ where β and γ are respectively the angles of incidence and diffraction, d the grating constant and n the order.

If, as in this case, the spectrum is viewed by rotating the grating with fixed angles of incidence and diffraction, the above formula reduces to $n\lambda = 2d \sin\theta \cdot \cos\delta$ where 2δ is the angle between the incident and diffracted beams, which is a constant determined by the geometry of the mirrors and slits, and θ is the angle of rotation of the grating from the specular position.

In this particular spectrometer the equation reduces to

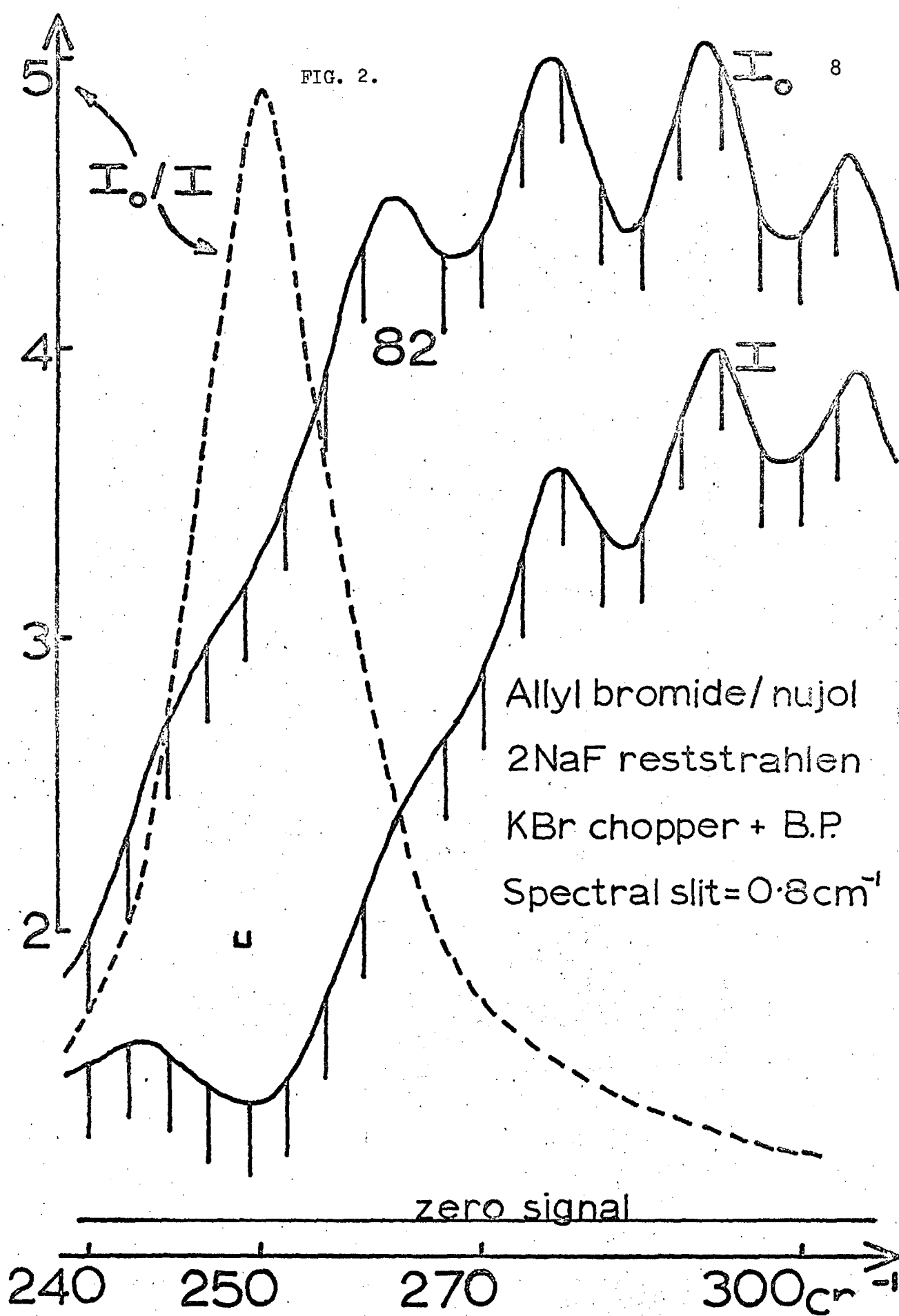
$\bar{\nu} \text{ (cm}^{-1}\text{)} = 100/0.974 \sin\theta$ and $\bar{\nu} \text{ (cm}^{-1}\text{)} = 40/0.974 \sin\theta$ for the 200 lines/cm and 80 lines/cm gratings respectively.

As the grating rotates a "pip mark" is superimposed on the spectrum for every 0.3 degree the grating revolves. Every twelfth "pip mark" is however missing in order to provide main reference marks -- (see figure 2).

Several of the strongest water vapour bands listed in Randall et al. (2) were identified on our spectra and the corresponding pip numbers read off as accurately as possible.

FIG. 2.

8



Substitution into the appropriate formula yielded values of θ . The frequency of any other pip mark can then be calculated if we know the relatively small angle $\Delta\theta$ between the two positions.

For example the 327.8 cm^{-1} band occurs on our spectra at exactly 80 (8) and was obtained using the 200 lines /cm grating thus $\sin\theta = 100/327.8 (0.974) = 0.3132$. Hence $\theta = 18^\circ 15'$.

Say we want to calculate the frequency at pip mark 80 (4) then $\Delta\theta$ will be four pip marks at 0.3 degree each i.e. $1^\circ 12'$. Thus at 80(4) $\theta = 18^\circ 15' - 1^\circ 12' = 17^\circ 3'$ and $\sin\theta = 0.2932$ hence $\bar{\nu} = 100/0.974 (0.2932) = 350.1 \text{ cm}^{-1}$.

In a similar manner the frequencies at every fourth pip mark were calculated using the following data as the basis;

WATER BAND (cm^{-1})	327.8	202.7	170.4	127.0	82.1
PIP NUMBER	80(8)	84(1.2)	85(11.4) or 29(5.1)	30(9.3)	33(10.1)
θ VALUE	$18^\circ 15'$	$30^\circ 25'$	$37^\circ 4'$ or $13^\circ 57'$	$18^\circ 52'$	$30^\circ 0'$

Thus most of the stronger water bands on our spectra could be identified with a band listed either in Randall et al. (2) or in Blaine (3). Hence a calibration graph of frequency against pip number was plotted and the frequency at every pip mark read off and tabulated to eliminate the need for continuous reference to the graph.

The calibration was found to drift slightly (see figures 3,4,5) due perhaps to wear in the gear rotating the grating and/or to slight changes in the position of the gratings in their holders.

Given below for each grating is a table of pip numbers, initial frequency ν_a when the spectrometer was first calibrated (Feb.1962), present frequency ν_b (July 1965) and calculated frequency ν_c obtained by numerical interpolation. (The frequencies ν_a and ν_b are, of course, read off from graphs.).

200-lines/cm Grating Calibration. (Frequencies in cm^{-1})

Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc
79 (6)	421			81 (6)	282.2	284.5		83 (6)	215.3	216.9	
7	410			7	278.5	280.6		7	213.2	214.8	
8	404	406	406.0 ^d	8	274.8	276.8	275.8 ^d	8	211.2	212.7	212.7 ^e
9	396	398		9	271.0	273.2		9	209.2	210.6	
10	388	390		10	267.8	269.7		10	207.3	208.7	
11	381	383		11	264.5	266.3		11	205.5	206.7	
80 (0)	374	376	375.8 ^d	82 (0)	261.4	263.0	262.2 ^d	84 (0)	203.7	204.8	204.9 ^e
1	367	369		1	258.4	259.9		1	201.9	203.1	
2	360.6	362.6		2	255.4	256.8		2	200.2	201.3	
3	354.5	356.0		3	252.6	253.8		3	198.5	199.6	
4	348.8	350.3	350.1 ^d	4	249.8	251.0	252.0 ^e	4	196.8	197.9	197.9 ^e
5	343.0	344.2		5	247.0	248.2		5	195.1	196.1	
6	337.3	338.6		6	244.2	245.5		6	193.6	194.5	
7	331.8	333.0		7	241.4	242.7		7	192.0	192.9	
8	326.6	327.8	327.8 ^d	8	238.8	240.0	240.6 ^e	8	190.4	191.3	191.4 ^e
9	321.0	323.0		9	236.2	237.6		9	189.0	189.8	
10	316.1	318.5		10	233.8	235.1		10	187.4	188.2	
11	311.3	314.0		11	231.2	232.8		11	186.0	186.8	
81 (0)	306.6	309.5	308.3 ^d	83 (0)	228.9	230.4	230.4 ^e	85 (0)	184.5	185.4	185.2 ^e
1	302.1	305.2		1	226.4	228.0		1	183.1	184.0	
2	298.0	300.9		2	224.1	225.8		2	181.8	182.6	
3	293.8	296.7		3	221.9	223.6		3	180.4	181.3	
4	289.8	292.6	291.2 ^d	4	219.6	221.3	221.2 ^e	4	179.1	179.9	179.7 ^e
5	285.9	288.5		5	217.4	219.1		5	177.8	178.6	

continued

80-lines/cm Grating Calibration. (Frequencies in cm^{-1})

Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc
28(9)	202.8	205.4		30 (9)	127.0	127.7		32 (9)	93.5	93.7	
10	197.7	200.4		10	125.2	125.7		10	92.4	92.7	
11	193.0	195.6		11	123.4	123.9		11	91.4	91.7	
29(0)	188.4	191.1	191.0 ^a	31 (0)	121.6	122.0	122.0 ^b	33 (0)	90.4	90.8	90.8 ^b
1	184.2	186.8		1	119.8	120.3		1	89.4	89.8	
2	180.0	182.6		2	118.2	118.6		2	88.4	88.9	
3	176.0	178.7		3	116.4	116.9		3	87.5	88.0	
4	172.2	174.6	174.5 ^a	4	114.8	115.3	115.3 ^b	4	86.5	87.1	87.0 ^c
5	168.7	170.8		5	113.2	113.7		5	85.6	86.3	
6	165.2	167.2		6	111.6	112.2		6	84.6	85.4	
7	162.0	163.6		7	110.1	110.8		7	83.8	84.6	
8	158.8	160.4	160.6 ^a	8	108.6	109.3	109.2 ^b	8	82.9	83.8	83.7 ^c
9	156.0	157.1		9	107.2	107.9		9	82.0	83.0	
10	153.0	154.1		10	105.9	106.5		10	81.2	82.3	
11	150.3	151.2		11	104.6	105.2		11	80.5	81.5	
30(0)	147.5	148.4	148.3 ^b	32 (0)	103.4	103.9	104.0 ^b	34 (0)	79.7	80.8	80.8 ^c
1	144.9	145.8		1	102.2	102.6		1	78.8	80.1	
2	142.4	143.3		2	101.1	101.4		2	78.0	79.4	
3	140.0	140.8		3	100.0	100.2		3	77.2	78.8	
4	137.6	138.4	138.2 ^b	4	98.9	99.1	99.1 ^b	4	76.6	78.1	78.0 ^c
5	135.3	136.2		5	97.8	97.9		5	75.8	77.4	
6	133.1	133.9		6	96.8	96.8		6	75.2	76.8	
7	131.0	131.7		7	95.7	95.7		7	74.5	76.1	
8	129.0	129.0	129.5 ^b	8	94.6	94.7	94.7 ^b	8	73.8	75.5	75.5 ^c

continued

200-lines/cm Grating Calibration. (Frequencies in cm^{-1})

Continued

Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc
85 (6)	176.4	177.2		86 (1)	167.8	168.5		86 (8)	160.5	161.0	161.1 ^e
7	175.1	175.9		2	166.6	167.4		9	159.8	160.0	
8	173.8	174.6	174.4 ^e	3	165.6	166.3		10	159.0	159.0	
9	172.6	173.4		4	164.4	165.1	165.0 ^e	11	158.2	158.0	
10	171.4	172.1		5	163.3	164.1		87 (0)	157.4	157.0	157.0 ^e
11	170.2	170.9		6	162.3	163.0					
86 (0)	169.0	169.6	169.6 ^e	7	161.4	162.0					

d (e) = calculated from the 327.8 (202.7) band as basis.

80-lines/cm Grating Calibration. (Frequencies in cm^{-1})

Continued

Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc	Pip.No.	Va	Vb	Vc
34 (9)	73.2	74.9		35 (7)	67.6	69.4		36 (5)	63.5	64.8	
10	72.6	74.3		8	67.1	68.9	68.9 ^e	6	63.2	64.4	
11	71.9	73.7		9	66.8	68.4		7	63.0	63.9	
35 (0)	71.4	73.2	73.1 ^c	10	66.2	67.8		8	62.8	63.5	63.7 ^c
1	70.8	72.6		11	65.8	67.4		9		63.1	
2	70.2	72.1		36 (0)	65.4	66.9	67.0 ^c	10		62.7	
3	69.8	71.6		1	65.0	66.5		11		62.3	
4	69.1	71.0	70.9 ^c	2	64.6	66.0		37 (0)		62.0	62.1 ^c
5	68.6	70.5		3	64.2	65.6					
6	68.0	69.9		4	63.8	65.2	65.3 ^c				

a (b) [c] = calculated from the 170.4 (127.0) [82.1] band as basis.

FIG. 3.

H₂O vapour spectrum(30-1-62)

1NaCl,(KBr+B.P.)

Spectral slit = 0.88cm⁻¹
(at 203cm⁻¹)

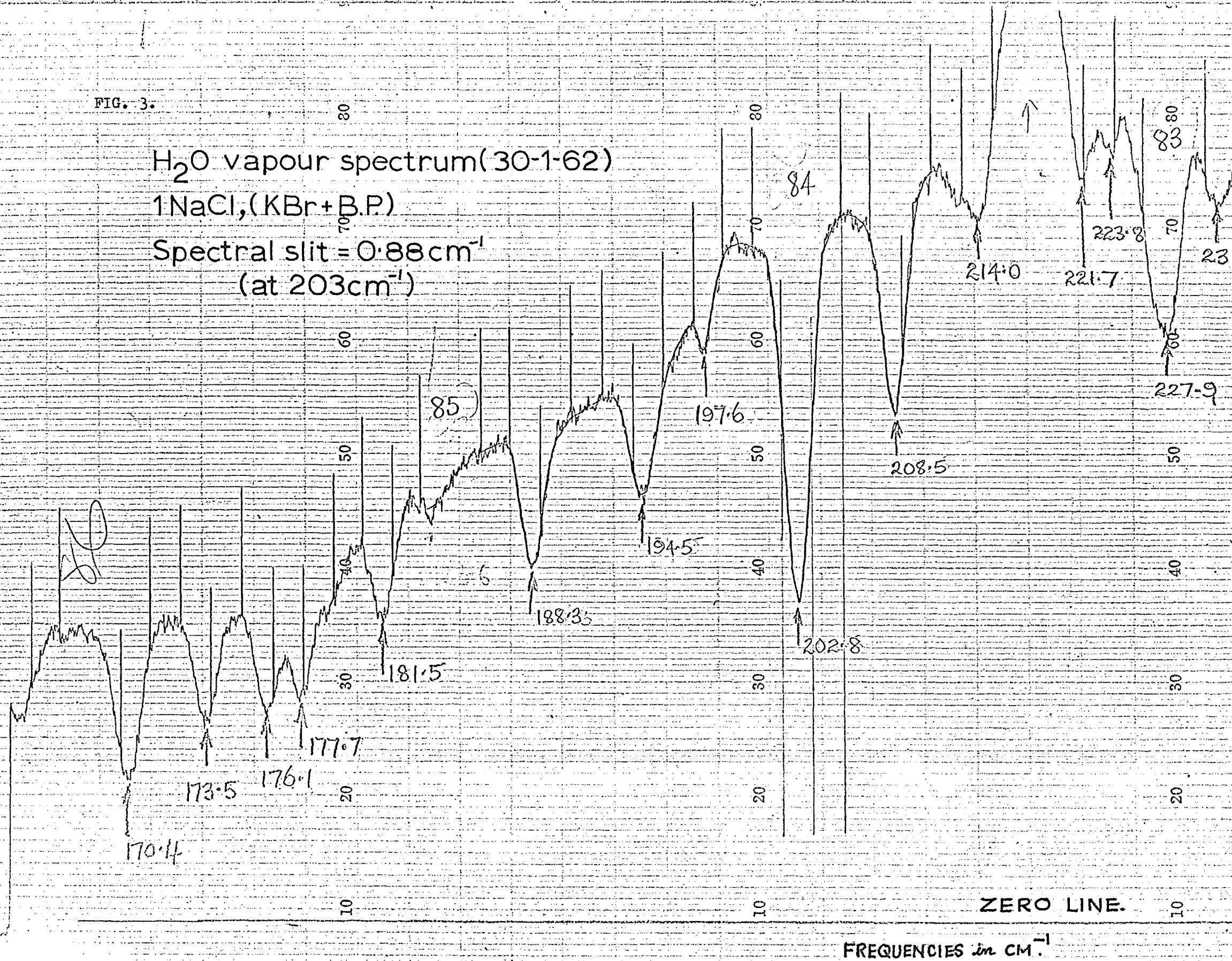


FIG. 4.

H₂O vapour spectrum (21-5-63)

1NaCl, (KBr + B.P.)

Spectral slit = 0.88 cm⁻¹
(at 203 cm⁻¹)

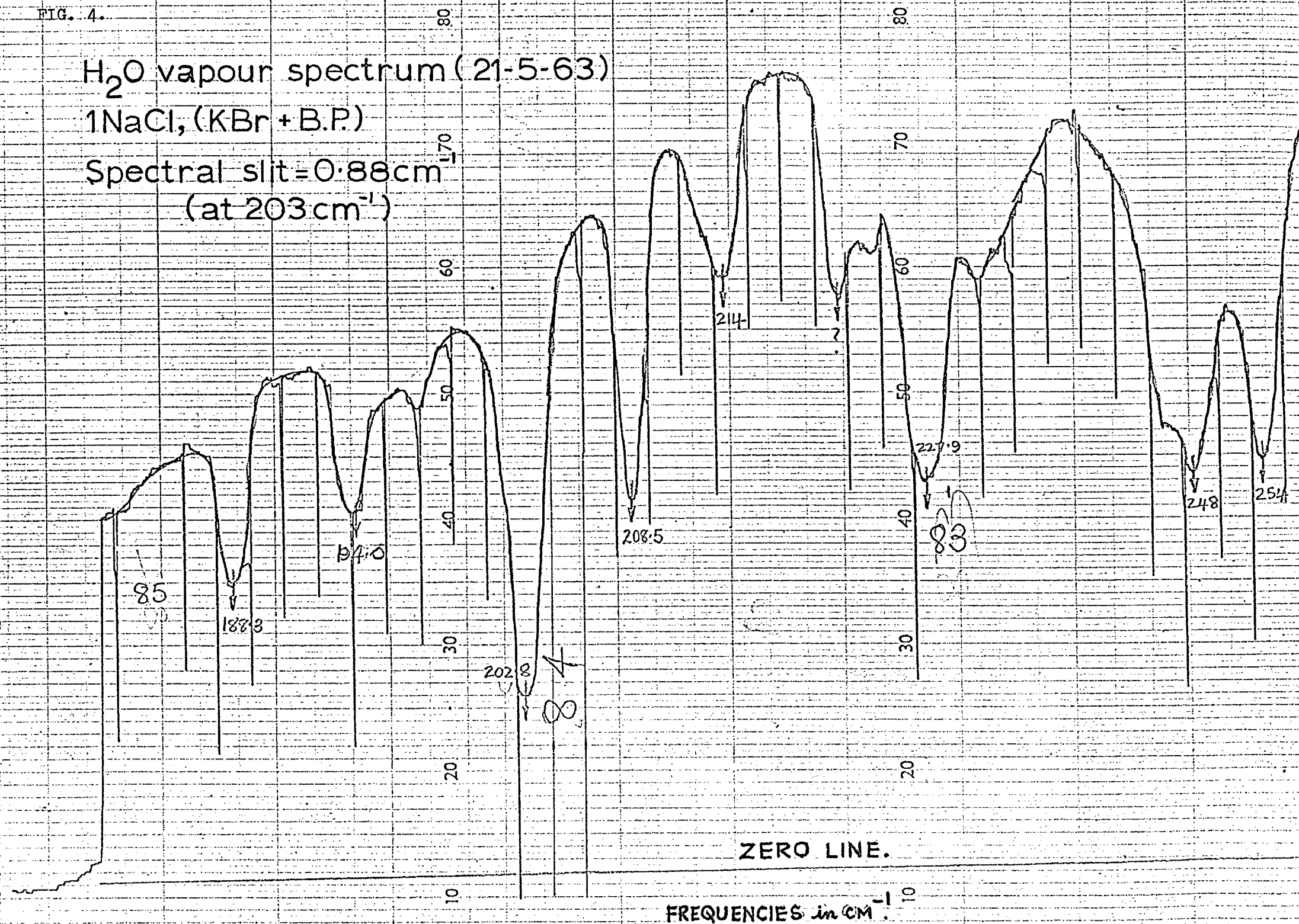


FIG. 5.

H₂O vapour spectrum (13-1-65)

2NaCl, (KBr+B.P.)

Spectral slit = 0.80 cm⁻¹
(at 203 cm⁻¹)

210.195

190

200.165

180

130.175

170

60

50

40

30

20

10

85

181.5 (67)

188.3 (68)

194.0 (103)

84

208.5 (260)

202.8 (330)

214.3 (100)

60

50

40

30

20

10

223.8 (115)

221.8 (115)

227.0

ZERO LINE.

FREQUENCIES in cm⁻¹

0

2

4

6

8

10

12

14

16

18

20

22

FILTERING.

The magnitude of the filtering problem in the far infrared has been discussed by Oetjen et al (4). If the spectral purity of the long wave radiation issuing from a monochromator is to exceed $\sim 95\%$, then the short wave energy must be attenuated by many orders ($\sim 10^7$) using some kind of filtering system.

A single sheet of 500 gauge (0.125 mm) black polythene, greatly attenuates the visible and near infrared radiation and transmits radiation of frequency less than $\sim 600 \text{ cm}^{-1}$.

The detection system requires the radiation to be chopped in order to be detected. If KBr is used then this only transmits radiation of frequency less than $\sim 400 \text{ cm}^{-1}$. (but does reflect $\sim 8\%$ of the relatively large amount of short wave radiation however). With this basic combination of KBr chopper and black polythene, very little radiation of frequency greater than $\sim 450 \text{ cm}^{-1}$ is detected.

To isolate actual first order radiation in the far infrared region one or two "crossed" reststrahlen selective reflection filters are used.

The two echelette gratings in operation at present are both blazed at 27° and are ruled at 200 lines/cm and 80 lines/cm. The useful working range of a grating is $3/2d$ to $2/3d$ where d is the grating constant. The 200 lines/cm grating is blazed at 228 cm^{-1} and has a range $350\text{--}150 \text{ cm}^{-1}$ while the 80 lines/cm grating is blazed at 91 cm^{-1} and covers the range $140\text{--}60 \text{ cm}^{-1}$.

The approximate reststrahlen frequencies (cm^{-1}) of the materials used on this machine are

LiF (380)	CaCO ₃ (340)	NaF (280)	NaCl (190)
KCl (160)	KBr (120)	KRS 5 (85)	Cs I (70)

During the four years of operation of the spectrometer the combinations of filters have continuously been checked and improved. Figures (6,7) show the background curves under typical conditions for the filter combinations used at present.

With the 200 lines/cm grating bands in the region $300 - 425\text{cm}^{-1}$ can be detected using one or two LiF reststrahlen but the amount of radiation at 400cm^{-1} is quite small.

Two reflections from NaF give a broad, spectrally very pure reststrahlen band covering the range $230 - 370\text{cm}^{-1}$. If only INaF is used then higher order radiation is present on the low frequency side ($250-230\text{cm}^{-1}$). CaF_2 , CaCO_3 and LiF have been used in this region but are definitely inferior to NaF.

It used to be thought that one reflection from NaCl gave a satisfactory peak since no second order water vapour bands were ever observed. However this is a poor criterion since the intensities are too low. Figure (6) shows the marked effect of introducing a second NaCl reflector. The blaze of the 200 lines/cm grating lies in the middle of the NaCl region and at the blaze the angular width is proportional to $1/n$ and the energy proportional to n^3 (n is the order) (4). Thus operation away from the blaze will only decrease the intensity of the first order radiation slightly but will greatly decrease the intensity of higher order spectra. In other words one must filter much harder on working through the blaze. Hence two reflections from NaCl are always used now. A 1 mm. crystal quartz transmission filter, which only transmits radiation less than $\sim 240\text{cm}^{-1}$, can also be used in this region with about 50% loss of signal at 200cm^{-1} .

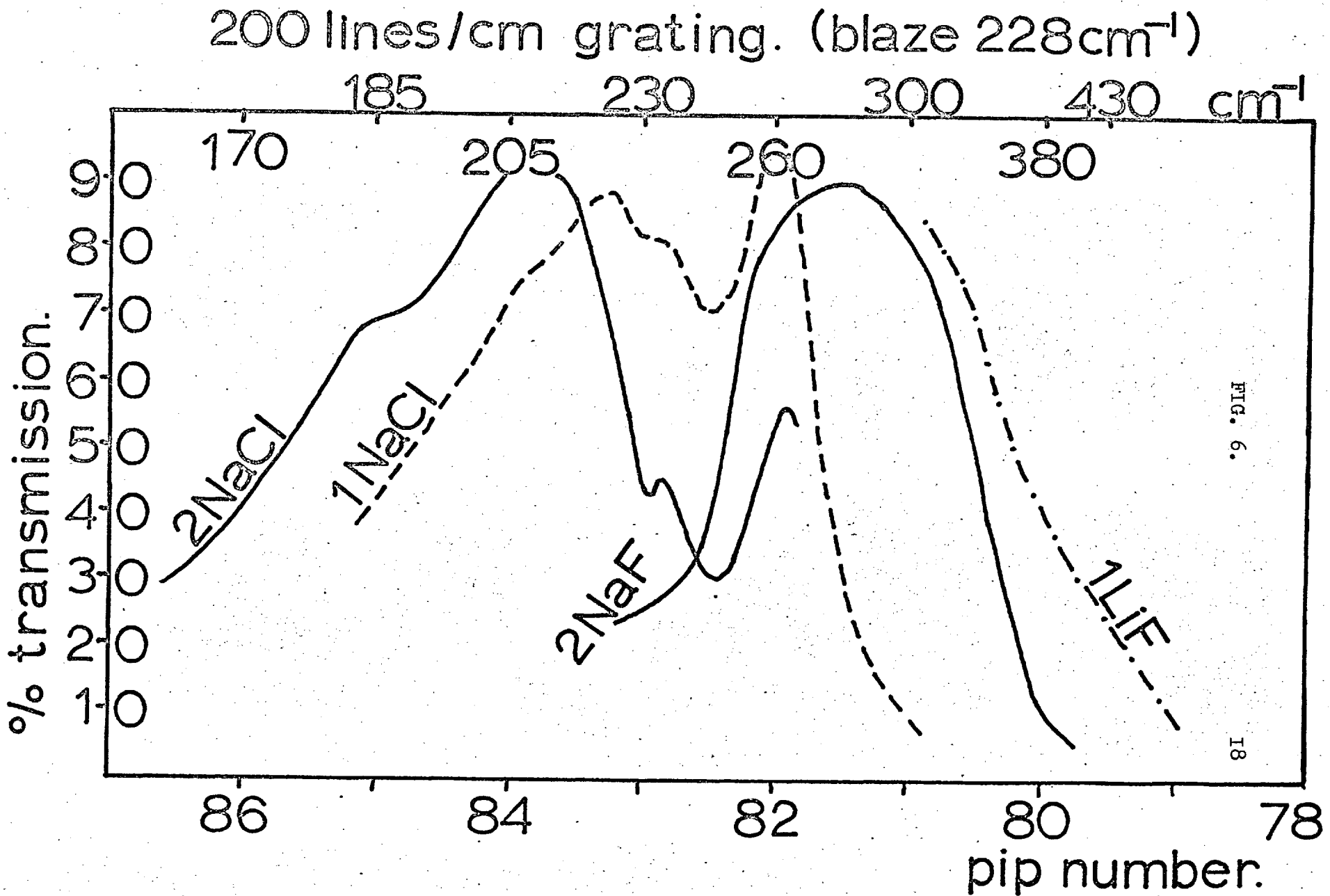


FIG. 6.

80 lines/cm grating. (blaze 91cm^{-1})

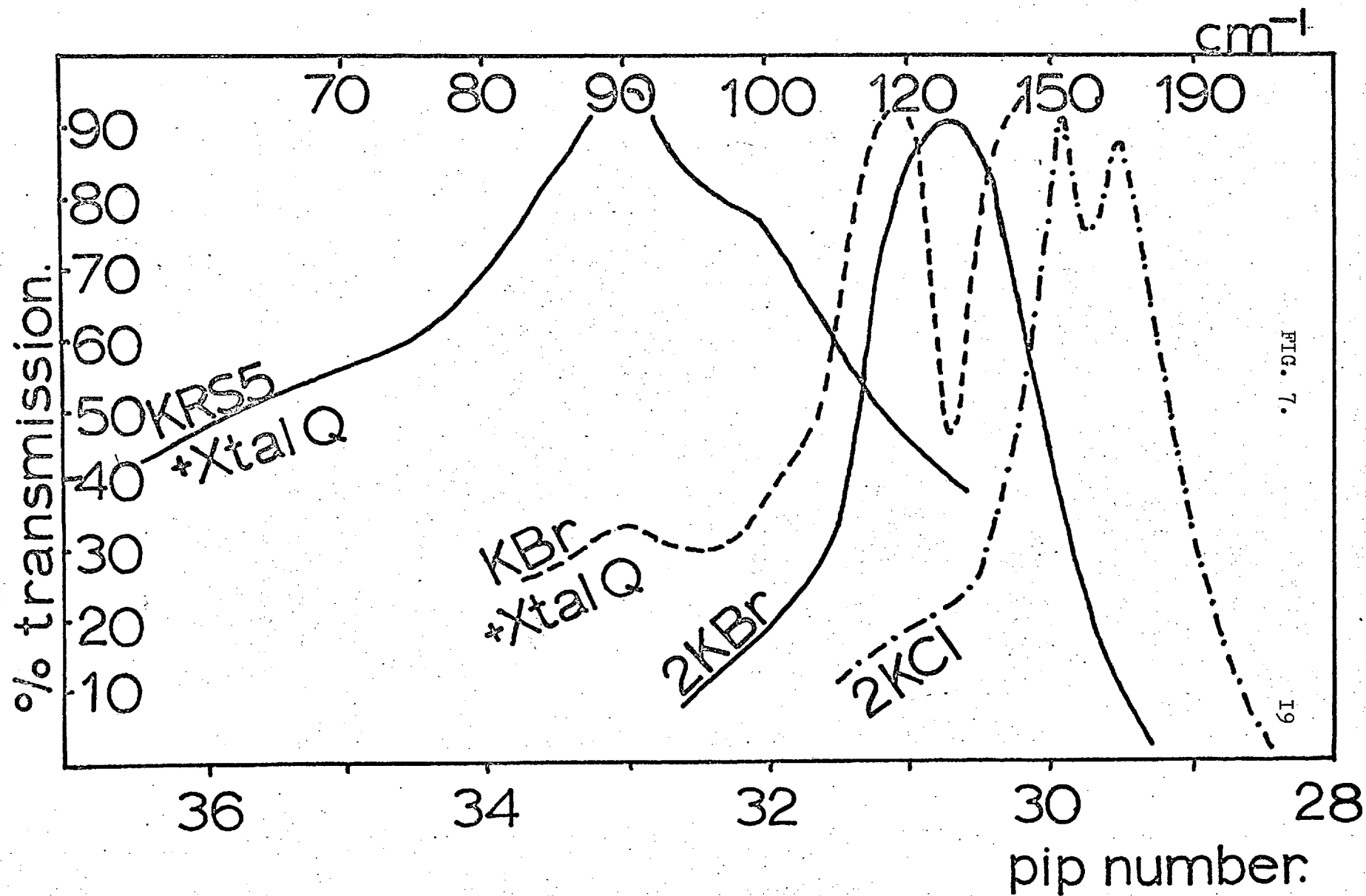


FIG. 7.

KCl has also been used on the 200 lines/cm grating but effectively only covers the same region as NaCl, and not quite so well.

Used in conjunction with the 80 lines/cm grating KCl and KBr give nice peaks which overlap considerably and cover the frequency range 200-100 cm^{-1} . However when the spectra of butadiene and acrolein were recorded in these regions the possibility of second order from bands about 300 cm^{-1} arose and hence 2KCl and 2KBr were employed. These runs showed that KCl and KBr contained appreciable higher order radiation, especially on the low frequency side. The spectral purity of the 2KBr and 2KCl regions were checked by running them in conjunction with the 1mm crystal quartz transmission filter which would eliminate the bands around 300 cm^{-1} . Exactly the same spectra were found with and without the quartz and these regions appear to be entirely first order radiation. Their only drawback is their relatively narrow width ($\sim 30\text{cm}^{-1}$). KBr plus crystal quartz extends the frequency range down below 100 cm^{-1} .

Below 100 cm^{-1} various filter combinations have been tried but 1 or 2 CsI, 1 or 2 KRS-5 and KRS-5/CsI all show an appreciable amount of higher order radiation. The crystal quartz is essential below 100 cm^{-1} since third order of 311 cm^{-1} in acrolein comes through quite strongly in 2KRS5 unless the quartz is present. At present IKRS-5 plus crystal quartz is used to cover the range 120-60 cm^{-1} but even then higher order radiation is definitely present. The cause is probably concerned with the blaze at 91 cm^{-1} .

To summarise, the filtering above 100 cm^{-1} is excellent but at present careful consideration has to be given to runs below 100 cm^{-1} .

N-PROPYL HALIDES - INTRODUCTION.

The n-propyl halides are the simplest members of the alkyl halides to exhibit rotational isomerism and accordingly they have received much attention in attempts to prove the existence of two isomers.

In an early study of torsional isomerism Mizushima (5) showed by Raman measurements that the spectrum of n-propyl chloride was much simpler in the solid state than in the liquid state and attributed this to the presence of rotational isomers in the liquid. The number of lines observed in the solid state spectrum could be accounted for by the presence of only one isomer. In a later work Mizushima (6) showed by comparing the behaviour of ethylene chlorhydrin, where there are also two forms in the liquid but only one form - the gauche - in the solid (7), with that of n-propyl chloride that the isomer present in crystalline n-propyl chloride was the trans isomer. Force constant calculations of the skeletal vibrations confirmed that the two isomers involved were in fact the trans ($\theta = 180^\circ$) and gauche ($\theta = 60^\circ$) forms and that the trans isomer alone remained in the crystal; θ is defined as the angle between the C-Me and C-X bonds on a plane perpendicular to the central C - C bond. Brown and Sheppard (8) examined the higher frequency infrared spectra and confirmed Mizushima's results for the chloride and also showed that the bromide and iodide similarly existed in both trans and gauche forms in the liquid, but as the trans alone in the solid.

Infrared intensity measurements by Mizushima's group in the temperature range 20 - 150°C for the gas and -60 to 10°C for the liquid indicated very little energy difference between the gauche and trans isomers of the chloride in either phase and the bromide in the gas phase.

$$\begin{aligned}\Delta E = E_g - E_t &= -50 \pm 150 \text{ cal/mole (gaseous chloride)} \\ &+50 \pm 60 \text{ cal/mole (liquid chloride)} \\ &-100 \pm 200 \text{ cal/mole (gaseous bromide)}\end{aligned}$$

These results agreed with the Raman results of Goubeau and Pajenkamp (9) and together with the results of Lamb (10) for the liquid bromide indicate that the trans form is favoured on passing from vapour to liquid. An electron diffraction study of n-propyl chloride by Morino (11) confirmed the presence of two isomers in the vapour phase with very little energy difference between them. The fraction of gauche form present was estimated as $81 \pm 5\%$.

Quite recently Sarachman (12) has identified lines of both isomers in the microwave spectrum of n-propyl chloride gas. Relative intensity measurements were consistent with an energy difference of magnitude no greater than 500 cal/mole. However lines arising from the excited states of the skeletal torsions of both forms and from the methyl torsion of the gauche form indicated that the assignment of these vibrations (Sheppard 1955) were incorrect. From intensity measurements the skeletal torsions were calculated to be $115 \pm 36 \text{ cm}^{-1}$ for the trans isomer and $100 \pm 40 \text{ cm}^{-1}$ for the gauche isomer. The methyl torsion of the gauche form was estimated at $200 \pm 50 \text{ cm}^{-1}$.

The microwave spectrum of n-propyl fluoride has been examined by Hirota (13) who confirmed the existence of two isomers and from relative intensity measurements found the gauche isomer to be more stable than the trans by $\sim 0.5 \text{ Kcal/mole}$. The dipole moments of the two forms were found to be similar (1.90D gauche and 2.05D trans) and to lie almost along the C - F axis. The methyl torsional barriers were calculated as 2.69 Kcals/mole and 2.87 Kcals/mole respectively for the trans and gauche forms using the method of line splitting.

From the less accurate method of intensity measurement the skeletal torsions were estimated as 160cm^{-1} (gauche) and 98cm^{-1} (trans).

The infrared spectrum of n-propyl fluoride has been examined by Sage and Klemperer (14) who kindly furnished us with their sample.

The Raman spectrum of liquid n-propyl fluoride was investigated by Goubeau (15) who also recorded the spectrum of liquid ethyl fluoride. However his results for ethyl fluoride are in conflict with those of Smith et al (16) who obtained satisfactory agreement between Raman and infrared data.

In order to clarify the problem of low frequency assignment the far infrared spectra of the chloride, bromide and iodide were examined in the gas, liquid and crystalline phases along with the spectra of the fluoride in the gas phase and the chloride trapped in a CCl_4 matrix at 77°K .

n-PROPYL HALIDES - EXPERIMENTAL.Materials

n-propyl fluoride - the sample used was part of that produced by Du Pont de Nemours for Hirota's microwave study (14) and was kindly provided by Klemperer. It was dried over 4A Linde molecular sieve and used without further purification.

n-propyl chloride, bromide and iodide were obtained as liquids from Messrs. Hopkins and Williams Ltd. They were fractionated and stored over molecular sieve. Refractive indices boiling points and vapour phase chromatograms were recorded for freshly distilled samples. No trace of any second component was evident for either compound and the samples were taken as being greater than 98% pure.

The table below compares the experimental and literature values of the boiling points and refractive indices:-

	Exptal.b.pt.	Lit.b.pt ⁽¹⁷⁾	Exptal η	Lit η ²⁰⁽¹⁷⁾
n-propyl chloride	47°C	45-47°C	1.3882	1.3886
bromide	71°C	70.9°C	1.4340	1.4341
iodide	103°C	102.4°C	1.5050	1.5051

Carbon tetrachloride was 'analar' grade Hopkins and Williams and was distilled and stored over P_2O_5 before use.

Apparatus70 cm. path length gas cell (Fig.8)

The stainless steel cell has a gold plated, kinematically mounted prism (A) and concave mirror (B) as optics. Brass flanges (CC') are bolted to the cell with 1,000 gauge polythene windows (DD') in between. A tap (not shown) on the main body of the cell facilitates filling and evacuation. Desiccant is contained in special aluminium foil 'boats' placed behind A or B, out of the radiation beam.

FIG. 8.

70cm path length gas cell.

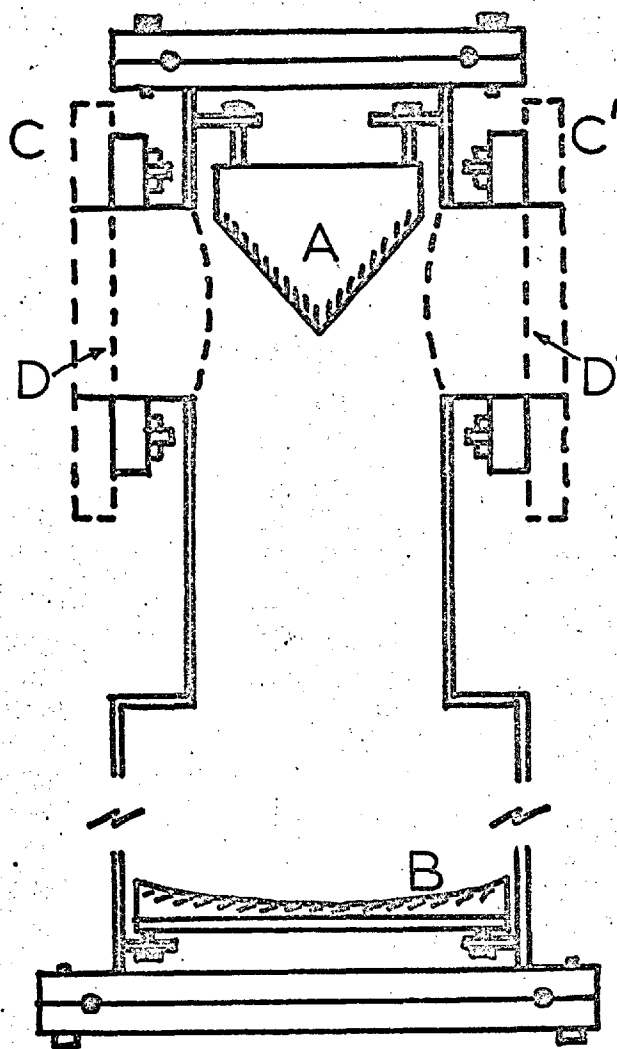
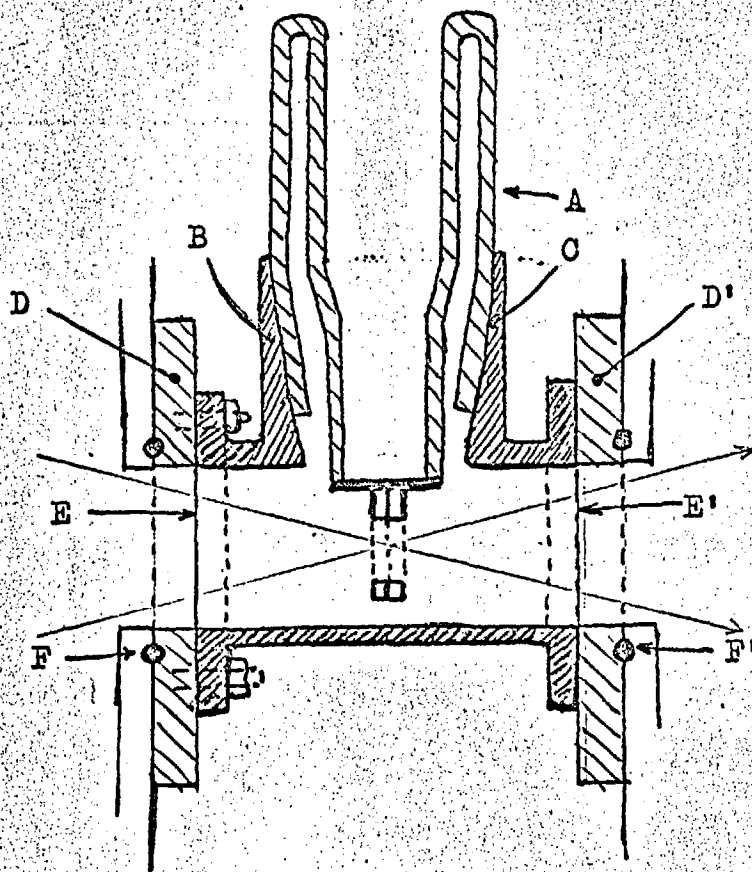
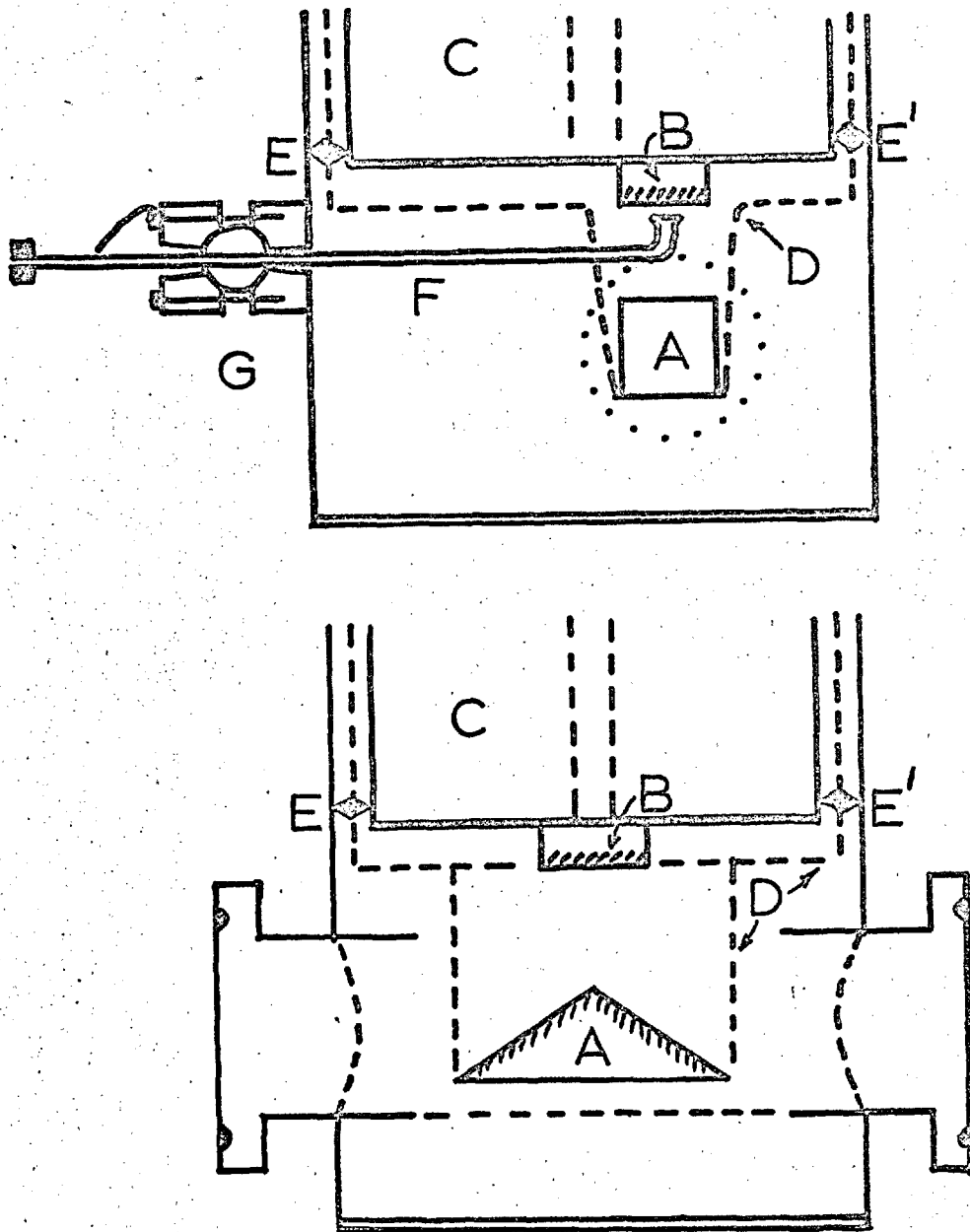


FIG. 9. 10cm. DEWAR CELL.





1:2 scale.

10 cm. dewar cell (Fig.9)

The simple stainless steel dewar (A) fits into the main body of the cell (B) via a conical joint (C). Brass flanges (DD) are bolted to the cell with 1,000 gauge polythene windows (EE') in between. Rubber O-rings (FF') prevent leakage when the cell is placed in position in the spectrometer and the latter evacuated.

Cryostat (Fig.10)

The cryostat is mainly constructed from copper, this having the required high conductivity and low emissivity. The prism (A) and deposition surface (B), having an area of ~ 5 sq.cm., are gold plated. The liquid helium tank (C) is surrounded by a copper radiation shield (D) which is attached to the liquid nitrogen tank (not shown) and is therefore at liquid nitrogen temperature. Teflon spacers (EE') prevent contact between surfaces at different temperatures. The gas inlet tube (F) enters the cryostat via a nylon ball joint (G) which is effective at the pressures attained by an oil diffusion pump. The tube can be withdrawn from the radiation beam whilst spectra are being recorded.

Methods.

Near infrared spectra were recorded on a Grubb-Parsons Spectromaster covering the range $400\text{--}5,000\text{ cm}^{-1}$. Gases were molecular sieve dried in a standard 10 cm path length cell with KBr windows while liquids were examined in a standard fixed path length cell. (experimental thickness used was 0.025 mm.)

The low frequency Raman spectra with associated polarisation data were recorded on the Cary-Model 81 Raman spectrophotometer at King's College, London. Samples were freshly distilled prior to use.

Far infrared spectra were recorded with the vacuum grating spectrometer constructed in the department and described previously. Gases were handled in a 70 cm. path length cell shown in figure (8) having gold plated optics and 1,000 gauge (0.25mm) polythene windows capable of withstanding three atmospheres and being quite clear throughout the far infrared. P_2O_5 was originally used as desiccant but this decomposed the propyl halide into the corresponding hydrogen halide whose pure [†] rotational spectrum was observed. Hence 4A Linde molecular sieve was used. The cell was filled to the required pressure by standard vacuum distillation procedure. The 'background' was recorded with the cell evacuated.

Liquids were examined either (a) in sealed polythene bags in a simple dewar cell (figure 9) in which the sample area was kept free of water vapour by P_2O_5 on the floor of the cell. With this cell the sample thickness cannot be rendered uniform due to the flexibility of the polythene and the action of some liquids upon it, or (b) in a modified near infrared variable pathlength cell (type SROIK) in which the KBr windows were replaced by crystal quartz windows wedged from 1.0mm to 0.9mm to avoid interference effects. (The 1.3mm crystal quartz transmission filter ($n = 1.55$) produces an interference pattern of spacing 2.5cm^{-1} noticeable at frequencies below 90cm^{-1}) Sample thicknesses of 0.1 - 3.0mm could be examined with this cell.

Backgrounds were recorded with a thinner sample of liquid for reasons explained below:-

When a spectrum of a relatively thick sample is compared with the spectrum recorded without sample in the beam by plotting the ratios of the two signals at corresponding pip marks, in theory the true absorption spectrum of the compound is obtained. However in practice interference in one of the polythene cell windows produces spurious bands which could be confused with weak genuine absorption bands of the compound.

This interference within a cell window is most noticeable in the 2NaF region and with one particular batch of polythene the effect was most marked (figure 2). The actual spacing of the pattern averages $13\text{--}14\text{cm}^{-1}$ which agrees well with that calculated ($12\text{--}13\text{cm}^{-1}$) if the refractive index of the polythene sample was assumed to be $1.51\text{--}1.52$. However as can be seen from figure (2) this effect is not too serious.

A much more serious effect is the interference which arises within one of the polythene sheets containing the liquid sample. Differences between the refractive indices of air and the liquid cause variations in the intensity of the superimposed interference pattern and this confuses the interpretation of the 'ratio plot'. To reduce the effect to a tolerable minimum the insides of the polythene bag are kept in contact with liquid in both thick and thin runs so that the effect is constant in both runs and should cancel in the ratio plot.

Solid samples were obtained following the procedure for liquids but using liquid nitrogen in the dewar (figure 9) and pumping on the sample area.

Extreme care must be exercised in filling the sample bag to have no bubbles in the beam otherwise evacuation will enlarge them and/or solidification with 'holes' in the solid will occur. Due to the low thermal conductivity of polythene the lowest attainable temperature with this system was about 120°K .

Matrix isolation - a specially designed helium cryostat (figure 10) was used to examine the spectrum of n-propyl chloride isolated in a carbon tetrachloride matrix. A gaseous mixture of 2 mole% n-propylchloride in carbon tetrachloride was deposited on a gold plated mirror at 77°K and appeared to form a satisfactory matrix. A pure carbon tetrachloride matrix deposited in the same manner was used as background. The deposition rate used was 1cc gas (NTP) per minute and sample thicknesses were of the order of 2mm .

Since the cryostat's sample area had an overall length of 20.4cms compared with the usual standard 10.0cm colls, mirrors J and K (figure 1) had to be replaced by mirrors of slightly longer focal length whenever the cryostat was being used.

n-PROPYL HALIDES - RESULTS

These are presented in tables (2 and 3) and are summarised in figures (11-21). The band centres were taken as the position of maximum absorption, the error involved being ± 1 or 2 cm^{-1} . The table (1) below indicates the appropriate spectroscopic slit width S_v in the various spectral regions.

$$S_v (\text{cm}^{-1}) = \frac{S}{2D} \sqrt{(4d^2 - 1)^{1/2}}$$

where S is the mechanical slit width in cms, D the distance between slit and grating ($= 53\text{cms}$ in this case) and d is the grating constant ($= 1/200$ or $1/80$)

TABLE (1)

Reststrahlen	Frequency Range (cm^{-1})	Mechanical Slit (cm)	$S_v (\text{cm}^{-1})$ limits.
2NaF †	370 - 230	0.15	1.86-0.68 ; 1.20 at 300cm^{-1} .
2NaCl †	260 - 160	0.30	1.77-0.57 ; 1.22 at 220cm^{-1} .
2KCl	200 - 120	0.30	2.76-0.96 ; 1.75 at 160cm^{-1} .
2KBr	150 - 105	0.375	1.92-0.90 ; 1.40 at 130cm^{-1} .
KBr+Xtal Q	150 - 90	0.40	2.04-0.68 ; 0.87 at 100cm^{-1} .
KRS5+Xtal Q	120 - 60	0.65	2.08-0.42 ; 1.40 at 100cm^{-1} .

For bands in the region $430 - 350\text{cm}^{-1}$ LiF reststrahlen is employed in conjunction with the 200 lines/cm grating. The theoretical slit width S_v is 2.3 cm^{-1} at 400 cm^{-1} but the small amount of energy present renders this figure meaningless.

† : 200 lines/cm grating used - otherwise 80 lines/cm.

INTERPRETATION OF SPECTRA.

The microwave spectra of n-propyl fluoride (13) and chloride (12) show that these exist in the gas phase as trans and gauche isomers and comparison with the vibrational spectra of related compounds (8) indicates that the liquid chloride, bromide and iodide consists of trans and gauche isomers, while the crystals are entirely trans. This is also supported by some force constant calculations of skeletal vibrations (6). The interpretation of the far infrared spectra confirms these views.

Several points of theory, relevant to the interpretation of the spectra are outlined below:

(1) Band contour considerations.

For a molecule having principal moments of inertia $A < B < C$ and reciprocal moments $a > b > c$ Badger and Zimmwalt (21) introduced a symmetry parameter $S = (2b-a-c) / (a-c)$ which takes the value +1 for a symmetrical planar molecule and -1 for a symmetrical spindle. The S values of the isomers of the n-propyl and allyl halides approximate to -1 and the molecules themselves approximate to accidental symmetric tops. Below is given the relevant theory of both symmetric and asymmetric tops.

For a symmetric top the change of dipole moment can be either parallel to the symmetry axis, perpendicular to it or have components both parallel and perpendicular to it. The resulting bands are termed parallel bands, perpendicular bands and hybrid bands. The contour of a parallel band of a symmetric top molecule has a strong central Q branch with P and R branches on either side (Pbranch on the low frequency side). The contour of a perpendicular band of a symmetric top is a single broad maximum. The hybrid band will, of course, be a compromise between the two.

For an asymmetric top ($A \neq B \neq C$) it is convenient to discuss the contours of bands in which the dipole moment change is parallel to one or other of the principal axes, even though in practice real band envelopes will often be a superposition of these theoretical contours. Depending on whether the change of dipole moment is in the direction of the axis of least, intermediate or largest moment of inertia we have bands of types A, B or C.

Herzberg (22) indicates that a type A band for small values of δ ($\delta = A/B$) approximates to a parallel band of a symmetric top. A type B band approaches in contour the perpendicular band of a symmetric top in that there is no strong Q branch for any value of δ . A type C band is practically the same as a type B band for very small δ values but a strong Q branch appears rapidly as δ increases.

Gerhard and Dennison (23) making reasonable approximations have calculated the band contours of symmetrical rotor molecules for a range of β values ($\beta = A'/C' - 1$ where C' is the odd moment of inertia) of $-\frac{1}{2}$ to 4.

Later Badger and Zumwalt (21) applied much the same considerations to the unsymmetrical rotor and plotted type A, B and C band contours for rather narrow ranges of the parameters $S = (2b-a-c)/(a-c)$ and $\rho = (a-c)/b$. The contours are plotted against $x = \Delta \bar{\nu} (2B/kT)^{\frac{1}{2}}/\pi$ rather than $\bar{\nu}$ so that they can be applied to molecules with any moments of inertia and to any temperature. It must be borne in mind that the actual band contour might be modified due to hot bands, degradation or resonance. However only in isolated examples is the distortion sufficient to cause ambiguity.

In table (4) are given the values of the principal moments of inertia (A, B, C in a.m.u. $\text{\AA}^2$), the reduced moment of inertia (I_m a.m.u. $\text{\AA}^2$) and the parameters S, ρ and β for the n-propyl and allyl halides. In the last two columns are given the P-R separations (in cm^{-1}) of the parallel (//) and of the perpendicular ($\perp$) bands calculated from Gerhard and Dennison (23)

assuming the molecules to be symmetric tops. In calculating the above, the parameters given in figures (22 and 23) were used.

(2) Position of hot bands.

(a) Methyl torsions.

Since very few methyl torsion frequencies have yet been observed in the far infrared, hot bands of methyl torsions are rare indeed. However the theory given by Fateley and Miller (24) and summarised later in the section dealing with "Barrier Information" may be used to predict the positions of the hot bands in a straightforward manner. (see later).

(b) Skeletal torsions.

The theory given by Fateley and Miller is strictly applicable only to the case of a 3-fold symmetric top attached to an unsymmetrical frame. Thus the solutions of the Mathieu equation listed by Herschbach (25) and Stejskal and Gutowsky (26) should only be applied to methyl torsions. However as a first approximation they may be applied to the case of an unsymmetrical top exhibiting a 3-fold potential upon rotation about the frame.

Graphs have been prepared of Δ b against Δ (see section on Barrier Information) by employing the data of Herschbach for Δ values between 2-100 and Stejskal and Gutowsky for Δ values between 100-205. The graphs have been plotted for A levels, E levels and 'unsplit' $(2E+A)/3$ levels and have been extrapolated to higher Δ values. The spacing between the curves for the different transitions $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$ etc. can be seen from this graph to become constant for Δ values of ~ 150 or more. The Δ values of the n-propyl and allyl halides are in excess of 200 and the position of the first hot band ($\nu = 1 \rightarrow 2$ transition) is predicted to be $\sim 3\text{cm}^{-1}$ from the $0 \rightarrow 1$ transition. In the harmonic oscillator approximation (large Δ) the hot bands lie on top of the fundamental. Hence the hot bands of the skeletal torsions of the

n-propyl and allyl halides would not be expected to lie far enough removed from the fundamental to be resolvable.

(3) Lattice modes.

In a crystal the degrees of freedom allotted to the rotation of an isolated molecule are expended in modes of vibration about an equilibrium orientation, just as the translation of a free molecule is transferred in the solid state into modes of vibration about an equilibrium position. These forms of vibratory motion in a crystal are known as lattice modes. The former are known as rotational or torsional lattice vibrations and usually occur in the range $30\text{-}200\text{cm}^{-1}$. The latter are known as translational lattice vibrations and are usually weak, in the range below 30cm^{-1} .

Providing that the unit cell's space group is known, then by methods in Bhagavantam and Venkatarayudu (27) the number of translatory and rotational lattice modes can be evaluated along with their Raman and infrared activity: Herzberg (22).

Unfortunately there is no reported crystal structure of the n-propyl or allyl halides in the literature, and there is no merit in guessing the crystal structure since the low frequency spectrum is quite sensitive to the actual choice. However if any lattice modes appear in the range of our spectrometer, they will be rotational in character due both to their intensity and frequency position.

Table 2 : Low frequency assignment and results : n-propyl halides (Frequencies in cm^{-1})

Assignment T = trans G = gauche		FLUORIDE		CHLORIDE					BROMIDE					IODIDE					
		Rliq ^A	IRgas	IRgas matrix ^M	Rliq ^B	Rliq	IRliq	IRsol	IRgas	Rliq ^B	Rliq	IRliq	IRsol	IRgas	Rliq ^B	Rliq	IRliq	IRsol	
C-C-C bend	T	374	n.i.	n.i.	365	365 [*]	365	363	362	n.i.	312 [*]	313	313	312	n.i.	288 [*]	286	290	288
	G	492	~472	n.i.	n.i.	425	428	426		n.i.	402	402	408		n.i.	390	388	396	
C-C-X bend	T	266	276) 262)	248) 237)	obs.	246 [*]	248	247	251	220) 208)	223 [*]	226	224	225	203) 193)	203 [*]	203	203	205
	G		321) 307)Q 294)	284	298	291	292	293		n.i.	272	270	273		n.i.	260	262	264	
Methyl torsion	T			217	obs.	212		215		197	200		205						
	G		222 213 Q 197 1→2 183	211	obs.					192									
Skeletal torsion	T		110) 97) 84)	132	127	141		140	147	127	131		151	130 ^g	127	131		133	146
	G		148) 139)Q 127	121	121			126		115			113	113 ^g	116			121	
Lattice modes								108 93 83						94 66		67°			82 66
										67°									

R = Raman IR = infrared
B = results of Nakamura (17)
M = 2 mole % in CCl_4 matrix
obs. = obscured

liq. = liquid sol. = solid
C = Raman of solid (17)
A = Raman of liquid by Garbeau (14)
Q = Q branch

g = glass formed
* = line also observed in Raman of solid (17)
n.i. = not investigated
1 → 2 = first upper stage band.

Table (3) : High frequency assignment and results : n-Propyl halides. All frequencies in cm^{-1}

Assignment Symmetry species and isomer		Chloride				Bromide				Iodide			
		IRsol	R liq	IR liq	IR liq	IR sol	R liq	IR liq	IR liq	IR sol	R liq	IR liq	IR liq
		B+S	N ⁺	B+S		B+S	N ⁺	B+S		B+S	N ⁺	B+S	
CH ₃ deformation	A'A''T	1460s	1460(4)		1453s	1460s	1456(4)		1456s	1460s	1456(4)dp		1456s
	G			1460s				1460s	1462sh			1460s	
CH ₂ scissors	A'T		1447(7)p?		1441s	1440s	1435(7)dp			1437s	1429(5)p?		
	G							1440s	1435s	1420m)		1425s	1425s
CH ₃ deformation	A'T	1375m	1384(1)			1376m	1384(1)			1372m	1378(2)p?		
	G			1378m	1378s			1378m	1379s			1375m	1379s
CH ₂ wag	A'T	1340m	1337(3)			1326m	1327(3)p?		1325w	1321m	1324(4)p		1321w
	G			1340m	1337m			1340w	1339w			1340m	1339m
	A'T	1262s	1255(4)	1262s	1255s	1222s	1226(6)p			1185s	1187(9)p		1181s
	G		1296(3b)	1306s	1302s			1286s	1280s		1274(4)p	1274s	1272s
CH ₂ twist	A''T	1291w	1296(3b)			1288w	1283(5)p					1195s	1188s
	G		1255(4)	1262s	1255s		1226(6)p	1228m	1222s				1140w
	A''T	1162m			1156w	1146m			1152w	1130w?			
	G		1211(3)	1208w	1208w		1196(2)	1200w	1199w				
CH ₃ i-p rock	A'T	1105m	1103(3)p			1103m	1109(2)		1099w	1093m			1085w
	G		1088(1)		1076w		1079(2)p?	1085m	1081w		1072(3)	1077m	
CH ₃ o-p rock	A''T	894s	896(5)p?			892s			896s	892m			894m
	G			894s	896s		888(4)p?	884s	886s		877(4)dp	875m	878m
C-C stretch	A'T	1062m	1063(3)		1063m	1040s			1037w	1013m			1010m
	G			1035m	1036m			1032	1031m			1011m	1010m
	A'T	1029m	1028(7)p		1029m	1025m	1026(7)p		1025w	1018m	1019(6)p		1017w
	G												

All frequencies in cm^{-1}

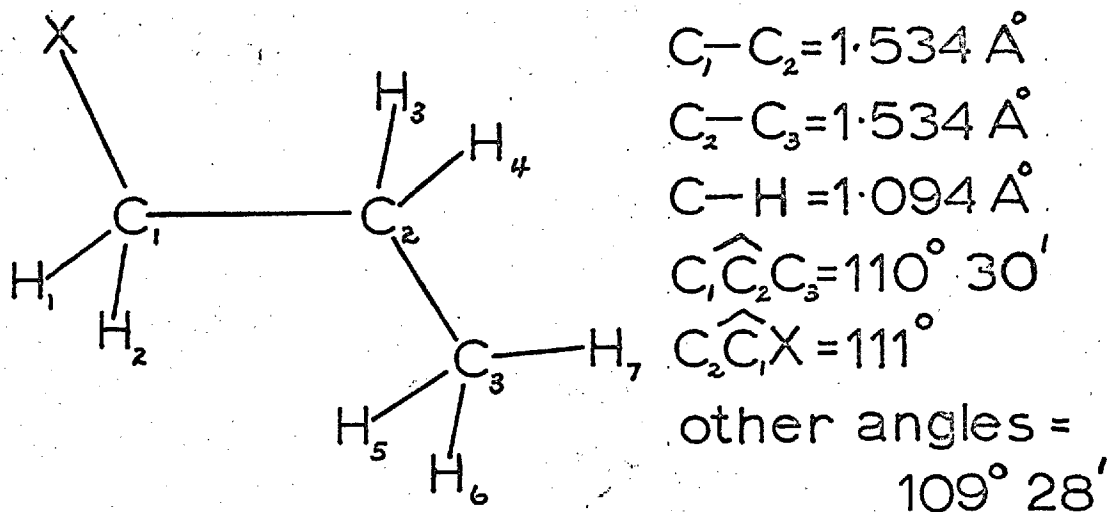
IR = Infrared R = Raman liq. = liquid sol = solid p = polarised dp = depolarised
o-p= out of plane i-p= in plane s = strong m = medium w = weak b = broad
sh = shoulder X = halogen T₊ = trans G = gauche
B+S = Brown and Sheppard (8) N⁺ = Frequencies by Nakamura (17), polarisation data by Kohlrausch or
Radinger and Wittek (18 or 19)
A'(A'') = symmetric (asymmetric) with respect to plane of symmetry.

Table (4)

see text for explanation

Molecule	A	B	C	I_m	S	ρ	β	//	$\perp^r$
Trans									
n-PrF	18.63	134.93	143.98	9.590	-0.981	6.3	6	14	broad
n-PrCl	19.63	211.85	221.91	13.051	-0.994	9.8	10	12	broad
n-PrBr	20.12	307.14	317.68	14.699	-0.995	14.2	14	10	broad
n-PrI	20.65	390.83	401.90	16.001	-0.999	17.7	18	9	broad
Gauche									
n-PrF	34.99	99.65	118.36	9.208	-0.841	2.0	2	21	36
n-PrCl	44.11	146.36	173.06	12.879	-0.874	2.4	3	18	31
n-PrBr	47.61	211.72	241.58	15.286	-0.927	3.4	3.5	17	27
n-PrI	50.32	271.60	303.90	17.061	-0.950	4.5	4.5	16	23
Trans allyl Cl	16.13	192.31	205.27	9.446	-0.990	11.0	11.5	11	broad
allyl Br	17.41	284.64	298.88	10.247	-0.994	15.4	16	9	broad
allyl I	18.77	357.42	373.02	10.696	-0.997	18.1	18	8	broad
T-Gauche allyl Cl	23.98	179.20	184.71	10.271	-0.990	6.5	6.5	12.5	broad
allyl Br	26.42	263.00	270.70	11.696	-0.996	9.0	9	10.5	broad
allyl I	28.51	330.32	339.89	12.510	-0.997	10.6	11	9.5	broad
C-Gauche allyl Cl	36.68	137.67	162.19	9.159	-0.896	2.9	3	16	31
allyl Br	40.29	205.58	233.23	10.543	-0.946	4.2	4.5	13	25
allyl I	42.99	262.25	292.15	11.336	-0.961	5.2	5.5	11.5	23
Cis allyl Cl	40.30	116.73	153.87	6.228	-0.774	2.1	2.5	18	32
allyl Br	43.48	177.52	217.84	6.578	-0.888	3.3	3.5	15	26
allyl I	45.92	228.99	271.74	6.824	-0.925	4.1	4.5	13	23

STRUCTURAL PARAMETERS for the n-PROPYL HALIDES. $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$.



	F	Cl	Br	I
$\text{C}_1-\text{X}(\text{\AA})$	1.379	1.775	1.94	2.18

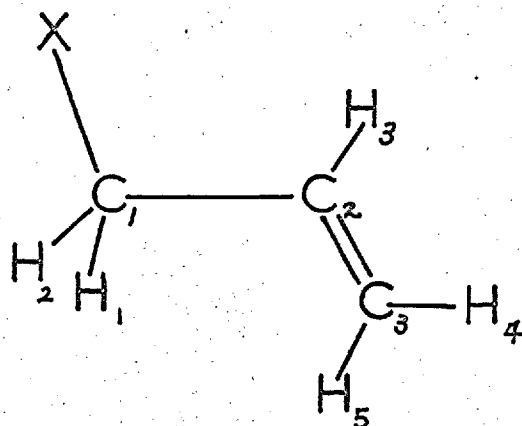
Data from:

HIROTA J.C.P. 37 283 (1962).

MORINO J.C.P. 28 175 (1958).

Interatomic Distances (1958).

STRUCTURAL PARAMETERS for the ALLYL HALIDES. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{X}$.



$$\text{C}-\text{H} = 1.09 \text{ \AA}$$

$$\text{C}_2-\text{C}_3 = 1.35 \text{ \AA}$$

$$\text{C}_1\hat{\text{C}}_2\text{C}_3 = 120^\circ$$

$$\text{C}_2\hat{\text{C}}_3\text{H}_{4(5)} = 120^\circ$$

$$\text{C}_2\hat{\text{C}}_1\text{X} = 109^\circ 28'$$

$$\text{C}_3\hat{\text{C}}_2\text{H}_3 = 120^\circ$$

other angles = $109^\circ 28'$

	Cl	Br	I
$\text{C}-\text{X}(\text{\AA})$	1.825	2.00	2.18
$\text{C}_1-\text{C}_2(\text{\AA})$	1.470	1.51	1.57

Data from SUTTON et al.

T. F. S. 51 1341 (1955).

INTERPRETATION OF SPECTRA - n-PROPYL FLUORIDE

Microwave intensity measurements suggest that the gauche isomer is more stable than the trans isomer by 0.47 ± 0.31 Kcals/mole (13). Thus the approximate isomeric composition in the gas phase will be approximately 85% gauche. The dipole moments of the two isomers have been evaluated by the Stark effect (28) and the results μ (gauche) = 1.90D and μ (trans) = 2.05D (both almost along the C - F axis) indicate that in liquid n-propyl fluoride a very similar isomeric composition will exist.

The only published spectral information in the "infrared" region for n-propyl fluoride apart from the unpublished work of Sage & Klemperer (14) is the Raman study by Goubeau (15) who also obtained the spectrum of ethyl fluoride. Smith et al. (16) also studied ethyl fluoride in gas and liquid phases by both infrared and Raman techniques and obtained a good correlation. However Goubeau's results for ethyl fluoride are not consistent with those of Smith and hence too much emphasis must not be placed on the figures published by Goubeau (15) for either compound.

The assignment of the skeletal bending frequencies is given in table (5) along with the results of a normal co-ordinate treatment performed by Hirota (29) in which the methyl group was taken as a point mass of 15.

TABLE (5)

$\bar{\nu}$ (cm ⁻¹)	c - c - c bend				c-c-x bend			
TRANS	n.i.	-	374(o)	384	276 262 321 307 294	277.5 263.5	266(o)	283
GAUCHE	472	430	492(2)	461		309	-	301
	This work	(13) Sage	(14) Goubeau	(28) Hirota	This work	(13) Sage	(14) Goubeau	(28) Hirota

The $c - c - c$ bend of the gauche isomer was observed in the near infrared but no reliable contour could be obtained at the low frequency end of the Grubb Parsons spectromaster. The band assigned to the $c - c - x$ bend of the gauche isomer has a PQR structure with P-R separation of 28cm^{-1} . Band contour considerations (23) predict the band to be a superposition of a parallel band of a symmetric top with strong Q branch and a P-R separation of 22cm^{-1} and a perpendicular band of a symmetric top with a P-R spacing of 36cm^{-1} .

The band assigned to the $c - c - x$ bend of the trans form has a doublet (B type) structure with a separation of 14cm^{-1} in excellent agreement with the figure predicted by theory (23).

The methyl torsion of the trans isomer is a pure C type band while that of the gauche isomer is a hybrid of types A, B and C. According to approximate band envelope considerations the gauche band would be expected to show sharp features while the transform will have a broad single maximum. Since the gauche form is 0.47 ± 0.31 Kcals/mole more stable than the transform one would expect the methyl torsion of the gauche form to be stronger than that of the trans. Hirota's microwave work (13) predicts the methyl torsions of the gauche and trans forms to be 210cm^{-1} and 213cm^{-1} respectively. The band observed in the far infrared in this region is assigned to the gauche methyl torsion with the Q branch centred at 212.7cm^{-1} and the R branch at 222.2cm^{-1} (i.e. a P-R spacing of $\sim 19\text{cm}^{-1}$ compared with the theoretical 22cm^{-1}). The peak at 197.2cm^{-1} is too sharp to be the P branch (which would be expected to occur at $\sim 203\text{cm}^{-1}$ where unfortunately a strong water band occurs) and is too far removed to be easily reconciled with the microwave limits of $213 \pm 6\text{cm}^{-1}$ as the trans methyl torsion. This peak is assigned to the first "hot band" ($1 \rightarrow 2$ transition), its frequency agreeing very closely with that

calculated (197.4cm^{-1}) using the theory of symmetric tops attached to an asymmetric frame (24). The position of the $2 \rightarrow 3$ transition is calculated to be 180.1cm^{-1} ; the weak absorption at 183cm^{-1} might be associated with this transition.

The strength of the band centred at 139cm^{-1} suggests a gauche origin. It is assigned as the gauche skeletal torsion Q branch with P and R branches at 127 and 148cm^{-1} (the separation being 21cm^{-1} compared with the theoretical 22cm^{-1}). The positions of the skeletal torsions predicted from microwave intensity work are 160cm^{-1} for the gauche isomer and 98cm^{-1} for the trans form. The very weak absorptions at 110, 97, 84cm^{-1} are tentatively assigned to the trans methyl torsion, these frequencies being much too far removed from the fundamental to be considered as hot bands of the gauche skeletal torsion ($V_1 \rightarrow 2 = 134\text{cm}^{-1}$).

n-PROPYL CHLORIDE.

Microwave intensity measurements (12) indicate very little energy difference between the isomers, so that the gas will be approximately 2/3 gauche. A similar isomeric composition would be expected in the liquid (30). The assignment of the skeletal bending frequencies (table 2) is the same as that proposed by Brown and Sheppard (8) on the basis of the Raman spectrum (18). The bands assigned to the skeletal bending of the trans isomer, which are weaker than their gauche counterparts, alone remain in the solid.

Considering the trans c-c-x bending mode: the band assigned to this mode has a B type contour in the gas at $237, 248\text{cm}^{-1}$, the P-R separation of 11cm^{-1} being in excellent agreement with theory (see table 5). In the liquid in this frequency ^{range} there is weak absorption at 231cm^{-1} as well as strong absorption at 247cm^{-1} suggesting possibly that there are two fundamentals in this range. Since at least one is due to the trans isomer and the skeletal bending will be the strongest trans band in this region, the assignment of 247cm^{-1} to the trans c-c-x band can be made with confidence and is further strengthened by the presence of an intense band at 251cm^{-1} in the solid. The presence of a shoulder at $\sim 237\text{cm}^{-1}$ on the strong band at 251cm^{-1} in the solid state spectrum is probably consistent with the presence of the weak shoulder at 231cm^{-1} in the liquid. Unfortunately the spectrum of the matrix isolated chloride is obscured in this region by the attenuation of the matrix. A tentative assignment of the band around 235cm^{-1} in the liquid and solid is to the trans methyl torsion.

The band at 211cm^{-1} in the gas with a shoulder on the high frequency side at 217cm^{-1} is considered to be composed of the methyl torsions of both the gauche and trans forms.

Neither peak can be the hot band of the other since calculation (24) yields a shift of some 14cm^{-1} from the fundamental. Band contour considerations (22) predict that the methyl torsion of the gauche form will be a hybrid band and have a pronounced Q branch while that of the trans isomer will be a pure C type band and have a noticeable Q branch. By consideration of the relative stability of the trans isomer in going from chloride to iodide, the proposed assignment of the two methyl torsions is the higher frequency to the trans isomer and the lower to the gauche. The barrier calculated for the gauche methyl torsion is in agreement with that obtained from microwave intensities (12).

This same work predicts the two skeletal torsional frequencies to be $115 \pm 30\text{cm}^{-1}$ for the trans form and $100 \pm 40\text{cm}^{-1}$ for the gauche. A band contour analysis indicates that the skeletal torsion of the gauche isomer will be a hybrid band while that of the trans isomer will be a pure C type band: both bands will have noticeable central Q branches (22) and a P-R separation of $\sim 12\text{cm}^{-1}$.

The far infrared spectrum of the gas in this region shows peaks at 121cm^{-1} and 132cm^{-1} with a high frequency shoulder at 139cm^{-1} which is probably the R branch associated with the 132cm^{-1} Q branch. The liquid spectrum shows a broad band centred at 140cm^{-1} with a pronounced low frequency shoulder at 126cm^{-1} . The solid state spectrum exhibits a strong band at 147cm^{-1} and a very weak band at 126cm^{-1} which is assigned to the gauche skeletal torsion and which would presumably disappear if the solid were completely trans. Thus the 147cm^{-1} band in the solid is confidently assigned to the trans skeletal torsion which follows through to 140cm^{-1} in the liquid and 132cm^{-1} in the gas. The gauche skeletal torsion is assigned to the 121cm^{-1} band in the gas, passing to 126cm^{-1} in the liquid.

It is evident from a consideration of the higher frequency spectra of the chloride, bromide and iodide that the stability of the trans isomer is increasing towards the iodide. Also from measurements of the energy difference between the trans and gauche isomers (6, 9, 10) the trans form appears to be favoured in going from vapour to liquid. The above assignment of the higher of the two skeletal torsion frequencies to the trans isomer and the lower to the gauche was made on this basis.

The bands observed at 108, 93, and 83cm^{-1} in the solid can only be plausibly ascribed to lattice modes. They are too far removed and too intense to be associated with the trans skeletal torsion and there are no bands observed in the liquid or vapour spectra below $\sim 110\text{cm}^{-1}$.

It is of interest to note that both forms of n-propyl chloride were trapped in the carbon tetrachloride matrix, the skeletal bendings and skeletal torsions of both isomers being observed.

n-PROPYL BROMIDE.

Near infrared intensity measurements (6) suggest approximately equal energies for the two isomers. The assignment of the four skeletal bending modes is straightforward, the gauche bands disappearing in the solid. This assignment again agrees with that given by Brown and Sheppard (8) and based on the Raman spectra (18). The trans c-c-x bending mode has a B type contour in the gas phase with a P-R separation of 12cm^{-1} agreeing closely with 13cm^{-1} in the fluoride and 11cm^{-1} in the chloride. The absence of any double maximum in the condensed phases removes the possibility of a second fundamental lying in this range. It is noticeable that the trans bands in both gas and liquid are relatively more intense than in the chloride, indicating increased stability of this form. The assignment of the torsional vibrations follows along similar lines to that of the chloride and again represents a revision of the previous assignment (8). The theoretical band contours of the methyl and skeletal torsions will be pure C type for the trans isomer and hybrid for the gauche isomer. Both bands will thus have a triplet structure with a noticeable Q branch. In the gas phase spectrum there are two sharp peaks at 197cm^{-1} and 192cm^{-1} , the intensities being almost equal. The lower frequency is not the $1 \rightarrow 2$ transition of the higher frequency since calculation yields a shift of some 14cm^{-1} whether the 197cm^{-1} band was the gauche or trans methyl torsion. By comparing the relative intensities of the two methyl torsions with the relative stability of the trans form throughout the series F $\rightarrow$ I, the band at 192cm^{-1} in the gas is assigned to the gauche form. The trans methyl torsion, assigned as 197cm^{-1} in the gas, is considered to occur as a weak shoulder at 205cm^{-1} in the liquid in fair agreement with the frequency reported in the Raman (18), but is thought NOT to be represented by the medium weak absorption at

184cm^{-1} in the solid. Little work has been done on the effect of phase on methyl torsions but it is thought more likely that they increase in the solid in an analagous manner to skeletal torsions.

The presence of two bands in the liquid in the skeletal torsion frequency range indicates that this mode of both trans and gauche forms is present. In the gas phase these bands appear to overlap (as in the chloride) but similar considerations as in the chloride indicate that the gas phase frequencies of 127cm^{-1} and 115cm^{-1} , corresponding to 131cm^{-1} and 113cm^{-1} in the liquid, are to be assigned to the skeletal torsions of the trans and gauche forms respectively.

The strong bands at 130cm^{-1} and 113cm^{-1} in the 'solid' state spectrum are considered to be the trans and gauche skeletal torsions. These frequencies are almost exactly the same as those observed in the liquid and since the other members of the series exhibit an appreciable increase of the trans skeletal torsion in the solid, it is suggested that a liquid-like glass was formed (in this particular run) instead of a crystalline solid.

In a different series of runs the "true" solid shows two low frequency bands at 94cm^{-1} and 66cm^{-1} , the latter agreeing well with the frequency reported from the Raman of the solid. The only plausible explanation is that these represent lattice modes since the vapour and liquid phase spectra exhibit no bands below 110cm^{-1} .

n-PROPYL IODIDE.

The assignment of the skeletal bending frequencies is slightly less straightforward in the iodide due to the possible near coincidence of the trans c-c-x bend and the gauche methyl torsion. The three remaining skeletal bending frequencies are assigned immediately, in conformity with reference (8) and, as expected, the trans c-c-c bend alone of the three remains in the solid. The tendency through the series F→I for the trans form to become increasingly stable is again evident.

The absorption around 200cm^{-1} in the gas phase spectrum undoubtedly contains both the trans c-c-x bending and the methyl torsional modes. By comparison with the other members of the series, the former would be expected to show a B type contour of P-R separation $\sim 12\text{cm}^{-1}$, while the latter, being hybrids, will exhibit triplet contour with appreciable Q branch and a P-R spacing of between 16 and 24cm^{-1} . However due to the very low vapour pressure of n-propyl iodide at room temperature ($\sim 3\text{cms Hg}$) even 70cms path of the gas does not absorb more than $\sim 15\%$ so that the gauche and trans methyl torsions, which are expected to be weaker than the trans c-c-x bend, will not show up appreciably especially if hidden under the stronger band.

The doublet at $193\text{-}203\text{cm}^{-1}$ is assigned to the trans c-c-x bending and since the higher frequency peak is considerably stronger than the lower, one or both of the methyl torsions might possibly be centred at 203cm^{-1} . The trans skeletal bending centred at 198cm^{-1} in the gas, becomes the strong band at 203cm^{-1} in the liquid and carries through to 205cm^{-1} in the solid. By comparison with the chloride and bromide the methyl torsions would be expected to be too weak to be observed in the liquid.

The only plausible assignment of the weak absorption at 190cm^{-1} in the solid would be to the trans methyl torsion. However since the resulting three fold barrier $V_3 = 1.89$ Kcals/mole is rather low when compared with the other members of the series the assignment is thought best left open.

The skeletal torsion modes of the two isomers appear to overlap in the gas phase. The band contours of both bands will be similar in having a triplet structure with appreciable Q branches. The bands at 127cm^{-1} and 116cm^{-1} in the gas become 133cm^{-1} and 121cm^{-1} in the liquid. The single band in the solid in this region (at 147cm^{-1}) is confidently assigned to the skeletal torsion of the trans isomer.

This band falls in the 2KCl region in which the filtering has been shown to be excellent and therefore the possibility of 147cm^{-1} being the second order of the strong band at 288cm^{-1} (also in the solid) is considered negligible. By comparison with the spectra of the chloride and bromide the most probable assignment is the higher frequency to the trans isomer and the lower to the gauche.

The Raman spectrum of solid n-propyl iodide (18) established a band at 67cm^{-1} . The present far infrared work confirms this band at 66cm^{-1} and also reports a band at 82cm^{-1} , both of which are considered to be lattice vibrations of the crystal for reasons given under the chloride or bromide.

n-PROPYL HALIDES - INTERPRETATION OF HIGHER FREQUENCY SPECTRA.

For the purposes of interpreting the higher frequency spectra the n-propyl halides will be discussed together, rather than separately, since the main purpose of this research is not the near infrared region.

The actual high frequency assignment of n-propyl chloride, bromide and iodide is given in table (3) along with the experimental data obtained from Raman and infrared studies. The assignment is essentially that due to Brown and Sheppard (8) which is based on a comparison of n-butane (31, 32) and the ethylene dihalides (33, 34). These authors only examined the liquid and solid phases and hence in the present work the vapour phase spectra were also examined in order to complete the experimental data.

Due to the large number of absorption maxima generally observed in the gas phase spectrum, the actual frequencies observed in the gas phase spectra of the chloride, bromide and iodide have not been tabulated. The gas phase spectra are discussed later.

Table (3) invites the following comments:

- (1) the $\nu_{\text{C-X}}$ Raman frequency of trans n-propyl bromide was misquoted as 694 (9b)p instead of 649 (9b)p by Brown and Sheppard (8).
- (11) the $\nu_{\text{C-C-X}}$ of trans n-propyl bromide, quoted by Brown and Sheppard from the results of Radinger (20) and Kohlrausch (19) to be possibly polarised (p?) has been shown to be definitely polarised.
- (111) Raman polarisation studies by the above two authors indicated that the $\nu_{\text{C-C-C}}$ of gauche n-propyl chloride and the $\nu_{\text{C-C-X}}$ of gauche n-propyl iodide were both depolarised. However since on theoretical grounds these results were not as expected, a polarisation study on the lower frequency bands of the n-propyl halides was undertaken with the result that the above two bands were found to be definitely polarised.

(iv) Brown and Sheppard considered the methyl torsion frequencies to be unobserved and assigned the two lowest bands observed in the Raman spectra to the skeletal torsions of the two isomers and arbitrarily assigned the lowest band to the trans isomer to conform with the behaviour of the other skeletal deformation modes. As is stated elsewhere the above is believed to be in error and the assignment given in table (2) is preferred.

Gas phase near infrared.

For the purposes of the discussion of the gas phase spectra the fluoride will be discussed separately from the other halides since its spectrum does not apparently resemble those of the chloride, bromide and iodide due to the near coincidence of the $\text{C-C}\nu$ and $\text{C-F}\nu$ modes and the extremely intense and broad absorption around $1,000\text{cm}^{-1}$.

As is evident from table (3) many corresponding fundamentals of the two isomers are almost coincident. Since in general in the gas phase the band width is greater and rotational structure appears the band contour resulting from a superposition of two or more bands would be rather complex and non-informative. This is exactly the situation in the n-propyl halides and band contours between 900 and $1,700\text{cm}^{-1}$ are too complicated to be used in assignment or to be correlated with the direction of change of molecular electric moment during the vibration. Due to the low vapour pressure of the iodide the bands were not strong enough for any definite conclusions to be drawn regarding the band contour. However in the chloride and bromide below 900cm^{-1} most bands show a triplet structure with P-R separations of 15cm^{-1} and 13cm^{-1} respectively. The only band in this region due to the trans isomer which is not superimposed by a gauche band is the $\text{C-X}\nu$; and this only in the bromide where a doublet structure is observed with a P-R separation of 10cm^{-1} in excellent agreement with theory (23).

This mode in the chloride is superimposed on the CH_2 rock also of the trans and the resulting contour is complicated. All other bands in this region ($900\text{--}400\text{cm}^{-1}$) are due either to the gauche isomer or to both isomers together, the P-R separations of 15 and 13cm^{-1} being rather less than those predicted from theory (18 and 16cm^{-1} respectively for the chloride and bromide.)

n-propyl fluoride: the main feature of the near infrared spectrum of gaseous propyl fluoride is the intense absorption between $900\text{--}1100\text{cm}^{-1}$ containing the C-C and C-F modes. This absorption is much more intense than the absorptions at ~ 1400 and $\sim 1470\text{cm}^{-1}$ which undoubtedly contain the CH_3 symmetric and asymmetric deformations and the CH_2 bending, twisting and wagging modes and are the strongest absorptions in the other members of the series.

The intense absorption around $1,000\text{cm}^{-1}$ is characteristic of the C-F of a monofluorinated alkane. Despite the gauche form being 0.47 ± 0.31 Kcals/mole more stable than the trans (13) the intensity of the C-F of the trans isomer will be appreciable and furthermore there will be extensive coupling in frequency and intensity between the two C-C and C-F of each isomer. Thus the broad complex absorption between $900\text{--}1100\text{cm}^{-1}$ contains six fundamentals, each having its own band envelope. The CH_3 rocking modes would be expected to occur $\sim 900\text{cm}^{-1}$ by comparison with the chloride, bromide and iodide and the medium strength absorptions at 866 and 912cm^{-1} can probably be assigned to these modes. Weak absns at 760 and 1252cm^{-1} would not be expected on a line through the other compounds but might result from fermi resonance shifts. The Raman spectrum of the liquid would be desirable, the reduced number of absorption maxima greatly aiding assignment.

ALLYL HALIDES: INTRODUCTION

The principal object of this work was to provide further data as a guide to elucidating the origin of the barrier hindering internal rotation. The majority of the data thus far has been for molecules in which the single bond is formed between two sp^3 hybridised carbon atoms. In molecules with an sp^2 hybridised carbon atom at one end of the torsion bond the question of equilibrium configuration is extremely important in discussing the relative importance of the dipole and quadrupole off-axis charge distributions (35).

The allyl halides are among the simplest molecules in which the single bond is formed between an sp^3 and an sp^2 hybridised carbon atom. They are also the unsaturated analogues of the first series studied (n-propyl halides) and hence seemed appropriate compounds for a detailed spectroscopic investigation.

The literature on the allyl halides is rather scant. An electron diffraction study on the chloride, bromide and iodide (36) provided a plausible set of molecular parameters with reasonable accuracy. Spectroscopic investigations are limited to three early Raman studies by Kohlrausch and Stockmair (1935)³⁷, Bacher and Wagner (1939)³⁸ and Kahovec and Kohlrausch (1940)³⁹ and a near infrared study by Thompson and Torkington (1945)⁴⁰. However no polarisation data was given in any of the Raman studies and a plausible assignment was not attempted even by the latter.

The question of which isomers are present and in what relative proportions is most important. The four most probable isomers are (a) trans (b) cis (c) trans-Gauche and (d) cis-Gauche, which have ϕ values of $180^\circ, 0^\circ, 120^\circ, 60^\circ$ respectively where ϕ is the angle between the $C=C-C$ and $C-C-X$ planes (see figure 23).

To give a plausible potential barrier curve in which the potential minima are reasonably separated the isomeric pairings would be expected as Trans with cis-Gauche or trans-Gauche with Cis.

Below are given the experimentally determined (36) and calculated values of the C_3 - halogen distances for the various isomers:-

$C_3 - X$ distance ($\text{\AA}$)

	Experimental	Trans	t-Gauche	c-Gauche	Cis
CHLORIDE	3.74 ± 0.02	3.99	3.730	3.145	2.808
BROMIDE	3.88 ± 0.02	4.18	3.905	3.295	2.940
IODIDE	4.08 ± 0.01	4.38	4.103	3.467	3.101

The figures in the table above indicate two possible situations:

- (a) $\sim 100\%$ t-Gauche and $\sim 0\%$ Cis
 (b) $\sim 70\%$ Trans and $\sim 30\%$ c-Gauche.

Sutton et al concluded that the weight of evidence of their electron diffraction investigation (36) of the allyl halides favoured the presence of a single form with $\theta \sim 120^\circ$. The number of bands appearing in the infrared spectrum of allyl iodide is also consistent with the presence of a single isomer.

However the electron diffraction technique is not as accurate as the errors quoted by Sutton and listed in the above table would lead us to believe. Thus we have the possibility of the % Cis or % c-Gauche being somewhat different to these quoted above, and in the limit one would not be able to decide between (a) and (b) purely from electron diffraction results.

If a 'planar' isomer existed (i.e. TRANS form) then certain vibrations would be asymmetric with respect to the plane of symmetry and hence would be depolarised or have a depolarisation ratio ρ of $6/7$ ($=0.86$). These vibrations are the skeletal torsion (expected $\sim 100\text{cm}^{-1}$), the vinyl CH_2 twist ($\sim 1000\text{cm}^{-1}$) and wag ($\sim 900\text{cm}^{-1}$), the $-\text{CH}=\text{CH}-$ o.p.wag ($\sim 500\text{cm}^{-1}$) and the methylene CH_2 twist ($\sim 1300\text{cm}^{-1}$) and rock ($\sim 800\text{cm}^{-1}$).

The skeletal torsion mode was too weak to be observed in the Raman but polarisation data on liquid allyl bromide in the range $200\text{--}1700\text{cm}^{-1}$ revealed that all bands were polarised with the possible exception of a single mode.

This polarisation data along with the electron diffraction results and the fact that only a few weak bands are observed in allyl chloride due to a second isomer concludes that the most probable explanation is the presence of a single major isomer which does not have a plane of symmetry and is most probably the *t*-Gauche (or a close approximation since the exact angle θ cannot be determined from infrared spectral data.)

Very recently Sharipov and Pentin (41) have studied the question of rotational isomerism in allyl bromide (and methallyl chloride) using temperature effect on band intensity. Attempts to obtain a reprint were unfortunately unsuccessful, so the full paper has not been consulted. They conclude that in the case of allyl bromide there are two isomers present: the 534cm^{-1} band belonging to one isomer and the 690cm^{-1} band to the other. They also quote that the actual orientation angles of the two isomers are closer to 30° and 150° than the ideal values of 0° (cis) and 180° (trans). If this were so then to correlate with the experimentally determined $\text{C}_3\text{-Br}$ distance (36), the relative proportions of the two isomers would have to be $\sim 15\%$ (30°) and $\sim 85\%$ (150°). The relative strengths of the 534 and 690cm^{-1} bands in the infrared spectrum seem inconsistent with Pentin's view. In view of the strength of the band due to the less abundant isomer it is rather surprising that no more than the expected number of fundamentals for a single isomer are observed in the frequency range below 1700cm^{-1} .

Considering the fact that I have not had a chance to study Pentin's paper and that I believe a complete study of the allyl halides to be a rather more searching test than the relatively inaccurate method of intensity temperature dependence I shall merely include the paper to complete the literature on the subject.

It might be noted here that the Raman polarisability data obtained in this research is not inconsistent with Pentin's view of two non-planar isomers.

The proposed configuration of the allyl halides is quite in line with the configurations of other molecules which have the torsion bond joining sp^3 and sp^2 hybridised carbon atoms i.e. acetaldehyde, acetyl fluoride and acetyl chloride have a C-H bond eclipsing the C=O bond rather than the C-halogen bond. Also, microwave work on isotopic propylene (42) shows that the double bond eclipses a methyl hydrogen. This can be understood in terms of forces between those parts of the electron distribution which are not out on the attached bonds any considerable distance if the net electron distribution in a double bond is represented by two "banana" orbitals. The electron distributions near the carbon atoms would then be staggered.

ALLYL HALIDES - EXPERIMENTAL

Allyl chloride and bromide were supplied as liquids by Messrs. Hopkins & Williams. The literature values and experimental values of fractionated samples of boiling point and refractive index are compared below:-

		(17)		(17)
	exptal. b.pt.	lit. b.pt	exptal. η	lit. η
allyl chloride	44° C	44.6°C	1.4149	1.4154
bromide	69.5° C	71.3°C	1.4651	1.4654

Vapour phase chromatography showed no other component present and the liquids were regarded as being >98% pure.

Allyl iodide was supplied as a dark red liquid by Messrs. Hopkins & Williams. The vapour phase chromatogram showed the presence of a second component (~15%) which normal fractionation failed to remove (first fraction b.pt. 86/88°C, main fraction 98°C pink). Near infra-red work showed that distillation had removed weak bands at 1083, 1238, 1309 cm⁻¹. However the spectrum of the first fraction showed a marked increase in the intensity of a band at 1692 cm⁻¹.

The main fraction from fractionation was dried overnight over KI and anhydrous Na₂SO₄ and then distilled under an atmosphere of dry N₂ gas. The vapour phase chromatogram of this distillate (b.pt 102°C - (17) lit.b.pt 103°) showed that the impurity level had dropped from 15% to <2%.

The near infra-red spectrum showed no sign of the band at 1692 cm⁻¹ which was quite strong in the first fraction of normal distillation. The impurity was probably an oxidation product since the allyl halides are extremely reactive

(~~αβ~~ unsat. aldehyde $\bar{\nu}$ c = o = 1705-1680 cm⁻¹ Bellamy (43)
 (~~αβ~~ unsat. acid $\bar{\nu}$ c = o = 1715-1690 cm⁻¹)

Near infra-red spectra were obtained with a Grubb Parsons Spectromaster covering the range 2 - 25 μ

Low frequency Raman spectra, including polarisation data, were recorded for freshly distilled allyl chloride and bromide samples on the Cary Model 81 Raman spectrophotometer at King's College London. (The iodide could not be obtained colourless.)

The far infra-red spectra ($425\text{--}60\text{cm}^{-1}$) were recorded using the vacuum grating spectrometer constructed in the department.

Gases were handled in the 70cm path length stainless steel cell depicted in figure (8), using either 1,000 gauge polythene or 1,000 gauge PTFE windows. The cell was filled to the required pressure by vacuum line procedures. Desiccant was also present in the gas cell.

At room temperature the liquids diffused quickly through the polythene sample bags. Thus most of the runs in the liquid phase were recorded on $\sim 40\%$ (v/v) solutions in nujol. The background was then pure nujol. A few runs were performed in which liquid nitrogen was used in the dewar cell (figure 9) to cool the sample somewhat in order to retard diffusion.

Solid samples were obtained by using liquid nitrogen in the dewar cell and evacuating the sample area. Due to the low freezing points of the chloride and bromide (-136°C and -119°C) and the low conductivity of the polythene, these liquids took several hours continuous cooling and pumping before they froze. Care was taken to avoid having bubbles in the sample.

RESULTS.

These are presented in tables (6-8) and summarised in figures (24-31). The position of maximum absorption is taken as the band centre, the resulting error being ~ 1 or 2cm^{-1} . Spectral slit widths are not given in the figures owing to the small frequency scale; However these are given in table (1) in the results section for the n-propyl halides.

INTERPRETATION OF RESULTS:

An electron diffraction study (36) and a near infrared investigation (40) of the allyl halides both concluded that the weight of evidence favoured a single isomer being present. The infrared spectrum was considered to arise from a single isomer, the excess bands being explained as overtones or combinations. The electron diffraction study concluded that the single isomer present was approximately the trans-Gauche in which the C-X bond is swung $\sim 60^\circ$ from the trans position.

A recent investigation of allyl-bromide (41) in which the temperature dependence of the intensity of infrared bands was studied, concluded the presence of two isomers.

Of the above methods the electron diffraction and temperature intensity studies are the least reliable and the presence of excess bands in the near infrared spectra of the allyl halides, which cannot be interpreted as overtones or combinations indicates strongly the presence of two isomers. Due both to the small number of excess bands and to their relative low intensity, one of the isomers is present in only small amount.

The near and far infrared spectra are interpreted on the basis that the chloride is mainly one form, the bromide almost entirely one form, while the iodide is apparently entirely in one form. Similarity of the spectra and the fact that the second isomer disappears in going from chloride

Table 6 : Low frequency assignment and results : allyl halides (Frequencies in cm^{-1})

Assignment a=trans-gauche b=second isomer		CHLORIDE					BROMIDE					IODIDE		
		IR gas	R liquid	R ^x liq.	IR liq.	IR solid	IR gas	R liquid	R ^x liq.	IR liq.	IR solid	R ^x liq.	IR liq.	IR solid
C = C-C bend	a b	~404	408(3)p	410	406	406	~390	392(9)p	390	390 N	396	375	381 N	386
C-C-X bend	a b	288) 280)	286(2)p	289	288N 292	292	253) 242)	253(6)p	253	251 N	266	226	229 N	248
		244?	243(1)p	243	244	248		210(0)	210	210 N	227			
Skeletal torsion	a b	127) 119)			120br	136	132) 120)			120 N	141		115N 112	~140 121?
Lattice modes						83 70					98 78			79 72

IR = infrared

R^x = Raman results of Kohlrausch (39) or Bacher (40)

br = broad

R = Raman

p = polarised.

liq. = liquid

N = nujol solution

TABLE (7) : liquid Raman and infrared results for the allyl halides

Mode	ALLYL CHLORIDE				ALLYL BROMIDE				ALLYL IODIDE		
	Raman (A)	Raman (B)	I.R. (C)	I.R. (A)	Raman (A)	Raman (B)	I.R. (C)	I.R. (A)	Raman (D)	I.R. (C)	I.R. (A)
1		1641(8)	1645	1639s	1640(12)p	1635(10)	1640	1634s	1625(3)	1640	1629 vs
2		1444(1)	1450	1445vs 1428sh	1448(1)	1440(1)	1445	1439vs		1440	1435 vs
3		1412(5)	1410	1410vs	1413(7)p	1406(6)	1410	1404vs	1402(1)	1405	1403 vs
4		1293(4)	1285	(1289w)	1294(6)p	1294(6)	1290	1290mw	1284(1)	1291	1290 m
5				1289m			1247	1244m	1219(0)		1200 s
6		1258(3)	1250	1256vs	1214(7)p	1211(7)	1208	1205vs	1150(5)	1153	1144 vs
7		1198(4)	1197	1199vw 1172	1194(7)p	1190(7)	1192	1190sh	1180(0)	1185	1186 vs
8		1100(0)	1098	1098w	1080(0)	1060(0)	1145 1071	1148vw 1070m		1049	1046 s 1016 vw
9		1034(0)	1040	1044vw							
10		988(0)	983	986vs	994(0)	984(0)	982	984vs		982	981 vs
11		934(3)	928	930vs	938(4)p	936(4)	922	923vs	932(2)	919	917 vs 874 vw 824 s
12	731(10)p	735(10)	735 700	734vs 688wgas	684(10)p	689(12)	762 690 655	687vs 649vw	663(5)	672	668 vs 606 vw

TABLE (7) : continued

Mode	ALLYL CHLORIDE				ALLYL BROMIDE				ALLYL IODIDE		
	Raman (A)	Raman (B)	I.P. (C)	I.R. (A)	Raman (A)	Raman (B)	I.R. (C)	I.R. (A)	Raman (D)	I.R. (C)	I.R. (A)
13	585(4)p	590(6)	594	590 ms	531(10)p	531(10)		535 s	490(6)	498	489 s
(a)	510(0)	517(0)	556	551 mw	463(0)	462(0)		457 vw			538 vw
14	408(3)p	410(4)	511	410 w	397(9)p	390(8)		390	375(6)		381
15	287(2)p	289(3)		288	258(6)p	253(7)		251	226(6)		228
(b)	243(0)	243(1)			210(0)	210(0)					
16		123(6)		120		120(5)		120			115

(A) = This work (B) = Kohlrausch (39) (C) = Thompson and Torkington (42) (D) = Bacher (40)

Table (8)

Assignment	Acrolein			Butene	Propylene				Vinyl Halides		
	CHO	CHO	CDO		*				Cl	Br	I
	A	B	B	C	D	E	F	F	G	G	G
C=C stretch	1625	1625	1621	1645	1649	1652	1652	1651	1610	1605	1593
C-C stretch	1158	913	877	(1068	920	920	920	887			
C-X stretch				(850					724	615	535
C=C-C bend	327	340	-	437					398	345	309
"C-C-X" bend	564	564	562	320	417	427	428	441			
C-C torsion	157	158 ^e	151 ^e	282	-	174 ^c					
V-CH ₂ torsion	993	993	993	623	990	578	991	982	622	497	435
V-CH ₂ wag	959	959	959	912	911	912	912	915	895	902	909
-CH=CH-wag	593	589	556	993	580	991	578	558	940	940	940
-CH=CH-bend	1275	1276	1275	1293	1294	1419	1298	1298	1280	1262	1229
V-CH ₂ rock	912	1159	1153	1166	1172	1229	1172	1150	1030	1008	990
V-CH ₂ scissors	1420	1422	1403	1416	1415	1298	1419	1431	1370	1377	1376
m-CH ₂ scissors				1450							
m-CH ₂ wag				1307							
m-CH ₂ rock				788							
m-CH ₂ twist				1257							

A = Harris (45)

D = Pitzer (48)

* = force constant calculation

B = Brand and Williamson (46)

E = Lord (49)

G = Thompson (51)

C = Sheppard (47)

F = Sverdlov (50)

c = from combination band

e = electronic spectrum

Table (8) : continued

Assignment	n-Propyl Halides			Allyl Halides		
	Cl	Br	I	Cl	Br	I
	H	H	H			
C=C stretch	(1029 (1062	1026 1040	1029) 1013)	1639	1634	1629
C-C stretch	(1035	1032	1011)-	1098	1070	1046
C-X stretch	(726 (649	649 564	593) 503)	734	687	668
C=C-C bend				410	390	381
"C-C-X" bend	(246 (291	223 272	203) 260)	286	251	228
C-C torsion	~140	~130	~130	~120	~120	~115
V CH ₂ torsion				986	984	981
V CH ₂ wag				930	923	917
-CH=CH- wag				590	535	489
-CH=CH- bend				1289	1290	1290
V CH ₂ rock				1199	1190	1186
V CH ₂ scissors				1410	1404	1403
m CH ₂ scissors	1444 1444	1435 1435	1429 1429	1445	1439	1435
m CH ₂ wag	1255 1337 1296 1337		1187 1324 1274 1340	1289	1244	1200
m CH ₂ rock	748 860 790 856		715 827 763 817	894	866	824
m CH ₂ twist	1162 1296 1211 1255		1130 1195	1256	1205	1144

H = Brown and Shepard (33)

to iodide indicates that this form is the same in each case and is trans or similar.

Low frequency assignment

For the purpose of discussion of the allyl halides, the low frequency region will be taken as below 800cm^{-1} , and is summarised below:-

Mode	Chloride	Bromide	Iodide
12	734S 688VW	687S 649VW	667S 606VW
13	590S 551M 512W	535S 457VW	489S 538VW
14	410S	390S	381S
15	288S 244W	251S 210W	228S

Frequencies in cm^{-1} .

As given in the high frequency assignment section (later) modes 12, 14 and 15 can confidently be assigned as $\text{c-x}\psi$, $\text{c=c-c}\delta$ and $\text{c-c-x}\delta$. Mode 13 has been assigned to the $-\text{CH}=\text{CH}-\text{o.p.}$ wagging mode.

Regarding the outstanding bands quoted above:-

- the series $688, 649, 606\text{cm}^{-1}$ is very weak and is assigned as a combination of the two skeletal bending modes 14 and 15.
- the two weak but definite far infrared bands at $244, 210\text{cm}^{-1}$ are confidently assigned as the $\text{c-c-x}\delta$ mode of a second, much less abundant isomer.
- the real problem lies in the assignment of the $551, 512\text{cm}^{-1}$ bands in the chloride, the 457cm^{-1} band in the bromide and the 538cm^{-1} band in the iodide.

The strongest band in the $800-400\text{cm}^{-1}$ region is the $\text{c-x}\psi$ of the predominant isomer. It would thus be expected that if any band due to the second isomer were to appear it would be the $\text{c-x}\psi$ of that isomer. In allyl chloride the 551cm^{-1} band (stronger than the 512cm^{-1} band) might seem to be too low in frequency to be assigned to a $\text{c-cl}\psi$ of a cis-type isomer in

view of the C-Cl frequency of gauche n-propyl chloride (649cm^{-1}) and gauche 1-chloro-2-hydroxyethane (662cm^{-1}). However the only alternative is that the C-Cl is obscured by the 590cm^{-1} band. It is however unlikely that all the second isomer bands lie under the series $590(\text{Cl}) - 535(\text{Br}) - 489(\text{I})$ and since nothing emerges on one side on traversing the series, it is more likely that the C-X of the second isomer is not hidden.

Thus the most plausible assignment is 551cm^{-1} (Cl) and 457cm^{-1} (Br) as the C-X of the second isomer and 512cm^{-1} (Cl) as the $-\text{CH}=\text{CH}-\text{op}$ wag of this isomer.

It is apparent from the strengths of these bands and to be expected on steric grounds that the abundance of the second isomer is decreasing towards the iodide. The very weak absorption at 538cm^{-1} in the iodide has however no stronger, higher frequency counterparts in the bromide or chloride and cannot be plausibly assigned. The possibility that any of the bands denoted as weak (w) in the previous table are due to impurities is extremely unlikely in the cases of the chloride and bromide since their vapour phase chromatograms showed no trace of any second component. There is the possibility that in the iodide the weak absorption at 538cm^{-1} could be due to an impurity since the vapour phase chromatogram showed the presence of a trace ($\sim 2\%$) of a second component.

Far infrared spectra

In view of the simpler nature of the spectrum of the iodide due to its being apparently entirely in one form, the order of the discussion below represents a reversal of the traditional order: chloride, bromide then iodide.

Allyl iodide: the far infrared spectrum of allyl iodide/nujol solution consists of three strong bands at 381, 228 and 115cm^{-1} , the former two agreeing well with Raman intervals of 375cm^{-1} and 226cm^{-1} respectively (40). Three fundamentals are expected in this frequency range for each isomer and thus the iodide appears to be entirely in one form. The assignment of the low frequency modes is given in table (6) and is clear cut. The strong band at 381cm^{-1} (386cm^{-1} in the solid state spectrum) is assigned to the c=c-c bending mode which occurs at 437cm^{-1} in but-1-ene and the c-c-c bend of n-propyl iodide (288cm^{-1}). Similar interpolation assigns the 228cm^{-1} band (shifted up 20cm^{-1} in the solid) to the c-c-x bending mode. The remaining band at 115cm^{-1} in nujol solution and 112cm^{-1} in the liquid is assigned to the c-c torsion as this is the only mode expected at such a low frequency. In the solid this mode appears as an intense absorption centred at 140cm^{-1} . Also present in the solid state spectrum are strong bands at 79cm^{-1} and 72cm^{-1} which are considered to be too far removed in frequency to be associated with the torsional mode and are assigned to lattice vibrations. The liquid phase spectrum (of each of the allyl halides) below $\sim 100\text{cm}^{-1}$ shows increasing absorption towards lower frequency but no bands are present which could be analogues of the 79cm^{-1} and 72cm^{-1} solid state bands.

Allyl bromide: the presence of four bands in the far infrared spectrum of the bromide when only three per isomer are expected confirms the existence of a second isomer. The assignment of the lower modes is again straightforward and is given in table (6). The strong band at 390cm^{-1} in nujol solution and found at 392cm^{-1} in the Raman spectrum of the liquid is assigned to the c=c-c bending mode of the predominant isomer, interpolating well with the c=c-c bend of but-1-ene (437cm^{-1}) and the c-c-c δ of n-propyl bromide

(312cm^{-1}). A similar interpolation between the c-c-c bend of but-1-ene (320cm^{-1}) and the c-c-Br bend of n-propyl bromide (223cm^{-1}) assigns the c-c-x bend of the predominant isomer of allyl bromide to the band, found at 251cm^{-1} in nujol solution and 253cm^{-1} in the liquid Raman spectrum. As with the iodide the c-c-c bending frequency rises only slightly in passing to the solid whereas the c-c-x bending frequency shows a considerable increase.

The relatively weak band at 210cm^{-1} in nujol solution (and quite definite at 210cm^{-1} in the Raman of the liquid) rises to 227cm^{-1} in the solid, behaving analogously with the 251cm^{-1} band. This band is hence assigned to the c-c-x bend of the second isomer.

Considering now the gas phase, a detailed discussion of the band contours of the allyl halides is deferred until a later section, but the important results may be stated here. All bands of the trans-Gauche isomers of the allyl halides would be expected to show a triplet structure. Hence the apparent doublet structure found experimentally for most bands of allyl halides is most unexpected. What is even more surprising is the fact that the P-R spacing of all the bands of a given allyl halide exhibiting this doublet structure is almost constant. This is not to be expected on theoretical grounds. Returning for a moment to the liquid phase, the broad band centred at 120cm^{-1} in nujol solution is almost certainly the c-c torsional mode of the predominant isomer by comparison with the iodide.

In the gas phase spectrum this band appears as a doublet at 119cm^{-1} and 131cm^{-1} ; the apparent P-R separation of 12cm^{-1} being rather close to that found for the c-c-x bending mode of the predominant isomer (253 - 242cm^{-1}). It is considered that this torsional vibration band would, under higher resolution than is regrettably attainable with the present far infrared spectrometer, show at least signs of a central Q branch in agreement with

theory.

The possibility of 119cm^{-1} being an upper stage band of 131cm^{-1} is excluded by calculation and the almost constant spacing ($\sim 12\text{cm}^{-1}$) between maxima of bands exhibiting this apparent doublet structure makes the assignment of 119cm^{-1} and 131cm^{-1} to the two skeletal torsions unlikely.

In the solid state spectrum the torsional mode of the predominant isomer is indubitably represented by the extremely intense absorption at 141cm^{-1} . A very weak absorption at 124cm^{-1} , also in the solid, might be interpreted either as the c-c torsion of the second isomer or as a weak lattice mode. The intense absorptions at 98cm^{-1} and 78cm^{-1} in the solid have no counterparts in the liquid state spectrum and are ascribed to lattice vibrations in line with the iodide.

Allyl chloride: in the chloride, as in the bromide, the presence of a second isomer is apparent from the far infrared spectrum and its presence is not incompatible with steric considerations since the chloride is more favourable for the existence of rotational isomers. The near infrared spectrum of allyl chloride in the frequency range $400-800\text{cm}^{-1}$ also provides strong evidence indeed for the existence of more than one isomer.

The assignment is once again straightforward and is made from table (9).

TABLE (9) (Frequencies in cm^{-1})

But-1-ene	Allyl Chloride	n-Propyl Chloride.
c=c-o δ 437	c=c-c δ 406	c-c-c δ 365
c-c-c δ 320	c-c-x δ 292	c-c-x δ 246

The c-c-c bending mode falls in a difficult part of the spectrum (for us) for determining the band contour but the c-c-x bending mode is extremely intense in the gas phase and shows an apparent doublet structure at $280, 288\text{cm}^{-1}$ in line with the bromide, but as stated before not to be expected on theoretical grounds. Here again high resolution studies of this c-c-x bending mode would be highly desirable.

A weak shoulder at 247cm^{-1} on the low frequency side of this intense gas phase absorption corresponds to a weak absorption in the liquid phase spectrum at 244cm^{-1} which was confirmed by a Raman study. In the solid state this band is quite pronounced at 248cm^{-1} and is assigned to the c-c-x bend of the second isomer.

At lower frequencies the broad band at 120cm^{-1} in the liquid is assigned to the skeletal torsional mode of the predominant isomer by comparison with the bromide and iodide.

In the gas phase as with the bromide the separation (8cm^{-1}) of the apparent doublet contour of this torsional mode is found experimentally to be very close to that of the c-c-x bending mode of the predominant isomer. Similar arguments as those put forward for the bromide render the assignment of 127cm^{-1} and 119cm^{-1} (in the gas) to the two skeletal torsions as unlikely. Calculation eliminates the further possibility of 119cm^{-1} being the first hot band of 127cm^{-1} .

In the solid the strong band at 136cm^{-1} represents the c-c torsional mode of the predominant isomer whilst the very weak absorption at 125cm^{-1} might arise from the same mode of the second isomer or be attributed to a weak lattice mode.

Since the liquid phase spectrum of allyl chloride shows ~~no~~^{no} bands below $\sim 110\text{cm}^{-1}$ the intense solid state absorptions at 83cm^{-1} and 70cm^{-1} are considered to be due to lattice modes.

Interpretation of higher frequency spectra.

All possible isomers of the allyl halides have the lowest possible symmetry (point group C_1) except for the trans and cis configurations which have a plane of symmetry (point group C_s). Thus all fundamental frequencies of any existing isomer will be active in the infrared and Raman spectra (Ref.22 pp 105, 252).

The CH stretching frequencies occur between $2800-3000\text{cm}^{-1}$; the more interesting region lies below 1700cm^{-1} where sixteen fundamentals are expected to be observed, three in the far infrared region (below 400cm^{-1}). In table (7) are given the experimentally determined infrared and Raman frequencies along with intensities and polarisation data where measured.

The sixteen bands assigned to fundamental modes are numbered 1→16 on the left of the table. The assignment has been made by consideration of the coincidences between the Raman and infrared frequencies, by a correlation of plausible variations as the mass of the halogen atom is changed, by studying any intensity variations and by taking into account the known magnitudes and intensities of vibration frequencies in other related molecules.

The array of sixteen fundamentals used in this assignment is essentially the same as forwarded by Thompson and Torkington (40). They however omitted modes 5 and 16 (of table 7) and included instead modes (a) and (b). Their reason for omitting mode 16 was that they postulated that such an improbably low frequency would have to involve a deformation of the skeleton and hence should change appreciably as the halogen mass changed. However at that time (1945), little was known about torsion and a low frequency mode $\sim 100\text{cm}^{-1}$ would be expected in these molecules and the explanation for its relative constancy is that in the torsional motion it

is the vinyl end of the molecule which moves while the halogen end being so much heavier remains more nearly stationary. The statement (40) that their array of fundamentals could explain satisfactorily, as overtones or combinations, all the remaining frequencies found in the Raman and infrared spectra cannot be accepted and for this reason the assignment given in the present work (believed to be the first attempted assignment of the allyl halides) is preferred.

In the following discussion concerning the actual assignment, all frequencies refer to the predominant trans-Gauche isomer.

Modes 1,2,3,12,14,15 and 16, can be confidently assigned to the following motions respectively:-

c=c stretch, CH₂ scissors, V-CH₂ scissors, c-x stretch, c=c-c bend, c-c-x bend and skeletal torsion.

The three out of plane (o.p.) deformation modes of the vinyl group: ν -CH₂ torsion, ν -CH₂ wag and -CH=CH o.p wag have not been definitely assigned in propylene and but-1-ene as is evident from table (8). Sheppard's early work on but-1-ene (46) was the first attempt to assign the three modes so later work is likely to be more reliable. From table (8) it can be seen that the three modes in question have to be allotted to two frequencies around 900cm⁻¹ and one frequency around 570cm⁻¹.

In acrolein, CH₂ = CH.CDO, but-1-ene, propylene and the vinyl halides each author has assigned the lower of the two 900cm⁻¹ bands to the ν -CH₂ wag. The more recent work on acrolein, CH₂=CH.CDO and propylene (Sverdlov 49) favour the assignment of the other 900cm⁻¹ band to the ν -CH₂ torsion and the 570cm⁻¹ to the -CH=CH-o.p. wag.

Regarding the earlier work on but-1-ene and the vinyl halides, as already mentioned, Sheppard's assignment of but-1-ene (46) was the

first assignment of a ν -CH₂ torsion while Thompson's paper (40) on the vinyl halides was more concerned with listing a plausible array of fundamentals than with actually giving a detailed assignment. For these reasons the ν -CH₂ torsion, ν -CH₂ wag and -CH=CH-o.p. wagging modes in allyl chloride have been assigned to the respective frequencies 986, 930 and 590cm⁻¹.

This is in agreement with a very recent study of the solvent effect on the ν -CH₂ torsional and wagging modes of various molecules by Cunliffe-Jones (51) who assume that these modes occur in allyl chloride at 985cm⁻¹ and 930cm⁻¹ respectively.

The six remaining unassigned fundamentals will now be considered. These are the c-c ν , ν CH₂ rock, -CH=CH- ν bend, CH₂ twist and CH₂ rock. Due to resonance the c-c ν frequency in acrolein would be expected to be appreciably higher than the 920cm⁻¹ in propylene, so the frequency of 913cm⁻¹ quoted by Brand and Williamson (45) is difficult to reconcile, and the 1158 cm⁻¹ quoted by Harris (44) is more in line. From a comparison of the c-c ν frequency of butene-1 and the n-propyl halides the c-c ν frequency of the allyl halides would be expected to be $\sim$ 1065cm⁻¹ and the series 1098, 1070, 1046cm⁻¹ is assigned to this mode.

The vinyl CH₂ rocking mode of the allyl halides would be expected to be $\sim$ 1165cm⁻¹ by interpolation within the series propylene, butene-1, allyl halide and acrolein. The series 1199, 1190, 1186cm⁻¹ is assigned to this mode in the allyl halides, the drop in frequency as the series (13cm⁻¹) is traversed would be expected to be less than in the vinyl halides (40cm⁻¹) where the substituent is attached directly to the double bond. This mode is very much lower, at 1030, 1008, 990cm⁻¹, in the vinyl halides, but this is not unreasonable in view of the considerable drop in the c=c ν frequency from allyl chloride (1639cm⁻¹) to vinyl chloride (1610cm⁻¹).

The methylene CH_2 rocking mode would be expected in the 800-900 cm^{-1} region by analogy with the n-propyl series, (where this mode is intense) and butene-1. The series of strong bands at ~~894~~, ~~866~~ and ~~824~~ cm^{-1} is confidently assigned to this mode.

The $-\text{CH}=\text{CH}-\text{i.p}$ bending mode would be expected to occur $\sim 1285\text{cm}^{-1}$ again by interpolation within the series propylene, butene-1, allyl halide and acrolein. By comparison of the spectra of the n-propyl halides with that of butene-1, the CH_2 wagging and CH_2 twisting modes would be predicted to occur around 1300cm^{-1} and 1260cm^{-1} respectively. Since these motions are similar, one would expect the same relative frequency change in both motions as the series is traversed. In the spectra of the allyl halides we have three series of bands occurring in this frequency range ($1200-1800\text{cm}^{-1}$): (a) $1289, 1290, 1290\text{cm}^{-1}$ (b) $1289, 1244, 1200\text{cm}^{-1}$ and (c) $1256, 1205, 1144\text{cm}^{-1}$. i.e. one constant series (a) and two series with a considerable decrease in frequency. Series (b) is assigned to the CH_2 wagging mode, series (c) to the CH_2 twisting mode and the constant frequency series (a) to the $-\text{CH}=\text{CH}-\text{i.p}$ bend. This latter mode in the vinyl series, drops in frequency somewhat from the chloride to the iodide ($1280, 1262, 1229\text{cm}^{-1}$) but as the halogen is removed further from the vinyl group, this mode would be expected to become less sensitive to substitution.

Band contours of the allyl halides.

Under low resolution the high frequency spectra of gaseous allyl bromide and iodide indicate that the great majority of bands have a doublet appearance with P-R separations of 11cm^{-1} and 10cm^{-1} respectively in the bromide and iodide. The chloride has more complex band envelopes but a P-R spacing of $\sim 13\text{cm}^{-1}$ is evident from several bands.

If the molecules are regarded as symmetric tops, then according to Gerhard and Dennison (23) a parallel band should have a triplet structure with P-R separations of $12, 10, 9\text{cm}^{-1}$ (chloride, bromide, iodide) while the perpendicular bands should be broad and have no appreciable Q branch.

If the molecules are not to be regarded as symmetric tops, then all bands will be hybrids of types A, B, and C. Type A has an appreciable central Q branch, type B has no Q branch while type C has a Q branch, the intensity of which increases with asymmetry. Thus most bands would be expected to exhibit a triplet structure.

The experimental P-R spacing of the bands is seen to be in good agreement with theory but the envelope is anomalous. Under high resolution the 590cm^{-1} band in the chloride and corresponding 535cm^{-1} band in the bromide both show evidence of a Q branch. The 687cm^{-1} band in the bromide however, exhibits no observable Q branch.

The apparent doublet appearance of the gas phase bands could be due to (1) hot bands - unlikely since hot bands would not be expected around 1200cm^{-1} .

(11) two isomers - again unlikely since the doublet separation is constant throughout a given compound.

(111) double potential minimum - the exact configuration of the allyl halides cannot be determined from infrared spectroscopy, but if this configuration is between the Trans and trans-Gauche forms then the potential energy curve would exhibit a double minimum (similar to ammonia) centred about the Trans position. The quantum mechanical splitting of the energy levels is smallest near the bottom of either minimum. i.e. the splitting of the bands would not be expected to be constant for a given compound (in NH_3 the splitting varies from 0.66cm^{-1} to 35.7cm^{-1}). One would also predict the splitting to remain in the liquid since the motion is internal. However in view of the constant splitting in each compound and the disappearance of the doubling in

pure liquid and dilute (3% molar) cyclohexane solution it is considered unlikely that the anomalous band envelopes arise from this consideration.

The most probable explanation is that under high resolution the band contours would be triplet but under normal, low resolution distortion has caused the envelopes to appear as doublets. Several factors could cause distortion of band contours - the $C=O$ stretch sometimes shows an apparent A type contour instead of the expected B type.

Distortion would seem to be evidenced in the band contour of the $C-C-X$ bending mode which has a doublet separation in the chloride (8cm^{-1}) less than in the bromide (11cm^{-1}) despite the rotational constant A being greater in the chloride.

BARRIER INFORMATION.METHYL TORSION.

The theory relating torsional energy levels and barrier heights for a single rotor with an n-fold barrier has been given by Herschbach (25) Its application to infrared torsional frequencies is summarised below.

The rotation of a methyl group relative to a reference framework is opposed by a threefold potential barrier, which reduces to a torsional oscillation if the barrier is sufficiently high. The torsional energy levels would be degenerate if it were not for the tunnelling effect which splits them into two sublevels, one of which is non-degenerate (A) and the other doubly degenerate (species E of the C_3 group). The A sublevel is alternately lower and higher than the corresponding E level. The splitting is greatest as the levels approach the top of the barrier and well above the barrier the levels go over into those for a freely rotating methyl group.

The model used is that of a rigid symmetric top attached to a rigid framework, which may be completely asymmetric. The potential energy hindering rotation may be expressed as a Fourier series:-

$$V(\alpha) = \frac{V_3}{2} (1 + \cos 3\alpha) + \frac{V_6}{2} (1 + \cos 6\alpha) + \text{etc.}$$

There is sound evidence (52) that the V_6 term is two orders of magnitude smaller than the V_3 term and thus terms after the V_3 term are neglected. When this potential is put into the wave equation for torsional motion, Mathieu's equation results. The energy solutions for each torsional quantum number ν give two sublevels A and E. The torsional energy is

$$E_{\nu\sigma} = 2.25 F b_{\nu\sigma} \text{ where } \sigma \text{ indicates either A or E levels,}$$

$$b_{\nu\sigma} = \text{an eigenvalue of the Mathieu equation}$$

$$F = h^2 / 8\pi^2 I_{\alpha}$$

$+I_\alpha$ = reduced moment of inertia for internal rotation.

$$= I_\alpha \left\{ 1 - I_\alpha \sum_g \frac{\lambda_g^2}{I_g} \right\} \quad (53)$$

I_α = moment of inertia of the top about its own symmetry axis.

λ_g = direction cosine between the axis of the top and the g^{th} principal axis of the entire molecule.

I_g = g^{th} principal moment of inertia of entire molecule.

The observed infrared frequency gives the difference between two of the energy levels which is $\Delta E_{\nu\sigma} = 2.25F \Delta b_{\nu\sigma}$. Hence if the absorption frequency is known and there is enough structural data to determine $F, \Delta b_{\nu\sigma}$ can be calculated. From $\Delta b_{\nu\sigma}$ a dimensionless parameter s can be determined, from tables of solutions for the Mathieu equation. The barrier height is then given by $V_3 = 2.25Fs$.

Tables of $b_{\nu\sigma}$ against s are given for s values between 2 - 100 in Herschbach's "tables for the Internal rotation problem" (54). For s values between 100 - 205 tables are given by Stejskal and Gutowsky (26) who however use a different terminology and this is explained below:

(a) Herschbach's $\underline{S} = \underline{16} \quad (S + \frac{1}{2} \text{ 's } \underline{\alpha})$
9

(b) The figures appearing in $S + \frac{1}{2}$'s appendix A have to be multiplied by $4/9$ and added to $S/2$ in order to obtain Herschbach's $b_{\nu\sigma}$.

(c) $S + \frac{1}{2}$'s A_1 values are for even ν ; their A_2 values are for odd ν .

Since continuous reference would be made to these tables it was thought desirable to prepare graphs of Δb against S for the fundamental and first three upper stage bands for the A and E sublevels and the 'unsplit' $(2E + A) / 3$ levels. With these graphs it is a formality to evaluate barrier height and hot band positions. If the A and E sublevels are so close together for any particular torsional quantum number, then the separate infrared transitions would not be expected to be resolved. In such cases we use the

'unsplit' $(2E+A)/3$ levels - in practice this is the case for S values greater than about seventy.

The barrier heights calculated from this procedure depend for accuracy upon the actual frequency chosen for the torsional vibration and upon the value of F which reflects the accuracy to which bond lengths and angles are known. In general the torsional vibration would be accurate to $\pm 2\text{cm}^{-1}$ for broad bands but the accuracy of F can only be estimated as between 2-10%. The barrier heights would thus be in error by $\sim 5\%$.

In order to determine the value of F we need to know the value of the reduced moment of inertia rI_x since the relationship between them is $F(\text{cm}^{-1}) = h/8\pi^2 rI_x$. Using accepted values of h, π and c

$$F(\text{cm}^{-1}) = 16.852/rI_x \text{ (a.m.u. } \text{\AA}^2)$$

In calculating the reduced moment of inertia rI_x the molecules fall into two classes (a) those with a plane of symmetry (i.e. trans n-PrX) and (b) those without (i.e. gauche n-PrX).

(a) Molecules with a plane of symmetry ('PLANAR' case).

With an arbitrary origin the centre of gravity was found, the origin moved to it and the sums over all atoms $\sum mx^2$, $\sum my^2$, $\sum mz^2$, and $\sum mxy$ calculated with respect to the centre of gravity. Transformation to new axes $x_0 = x \cos \theta + y \sin \theta$; $y_0 = y \cos \theta - x \sin \theta$ was made such that $\tan 2\theta = -2\sum mxy/(\sum my^2 - \sum mx^2)$. Then the principal moments of inertia are given by $I_{x_0} = \sum my_0^2 + \sum mz_0^2$, $I_{y_0} = \sum mx_0^2 + \sum mz_0^2$ and $I_{z_0} = \sum mx_0^2 + \sum my_0^2$.

For the top the z axis was taken as the torsion axis and x passed through the centre of gravity of the top. (y was chosen to keep the same sense of axes as those originally chosen). Referred to the top axes the following quantities were calculated

$$A = \sum m (x^2 + y^2)$$

$$C = \sum m yz$$

$$B = \sum m xz$$

$$U = \sum m x$$

where the summations extend only over the atoms constituting the top.

The direction cosine matrix λ_{tp} between the top and principal axes can be written down in this ('planar') case once the value of θ has been evaluated.

The components R_x, R_y, R_z of the vector, from the centre of gravity of the molecule to the origin of coordinates of the top, on $\lambda_{tp} =$ the principal axes can again be easily (or α_{tp}) evaluated in this case.

	X	Y	Z
x	λ_{Xx}	λ_{Yx}	λ_{Zx}
y	λ_{Xy}	λ_{Yy}	λ_{Zy}
z	λ_{Xz}	λ_{Yz}	λ_{Zz}

The values of β_x, β_y and β_z are then calculated, where

$$\begin{aligned}\beta_x &= \lambda_{Zx} A - \lambda_{Xx} B - \lambda_{Yx} C + U(\lambda_{Zy} R_y - \lambda_{Yy} R_z) \\ \beta_y &= \lambda_{Zy} A - \lambda_{Xy} B - \lambda_{Yy} C + U(\lambda_{Xy} R_z - \lambda_{Zy} R_x) \\ \beta_z &= \lambda_{Zz} A - \lambda_{Xz} B - \lambda_{Yz} C + U(\lambda_{Yy} R_x - \lambda_{Xy} R_y)\end{aligned}$$

The reduced moment of inertia for internal rotation is then given by

rI_α (or I_m) = $A - \sum_i \left(\frac{U_i^2}{M} + \frac{\beta_i^2}{I_i} \right)$ where M is the total mass of the molecule, I_i are the three principal moments of inertia of the entire molecule and the summation extends over these axes (X,Y,Z).

The above procedure was followed to evaluate rI_α for the skeletal torsion and eventually a completely general computer programme was developed to (a) check the first few hand-calculated examples and (b) to evaluate further rI_α values of various molecules. This programme is reproduced in the appendix. However to evaluate rI_α values for the methyl torsion the formula $rI_\alpha = I_\alpha \left(1 - \frac{I_\alpha \sum \lambda_g^2}{I_g} \right)$ (53) was used but since the direction cosines between the top axis and principal axes are obvious the calculations were performed by desk machine.

(b) Molecules with no plane of symmetry (SKEW case).

The centre of gravity having been found the origin was moved there and the matrix elements I_{ij} calculated referred to the centre of gravity of the molecule. i and j run from $x \rightarrow z$ and I_{xy} (for example) $= \sum mxy$ where the sum is taken over all atoms.

The matrix equation $I - \lambda E = 0$ was then solved (where E is the unit diagonal matrix) and the roots when taken in pairs give the principal moments of inertia. Each root was substituted back in turn into the simultaneous equations

$$(I_{xx} - \lambda) l_1^1 + I_{xy} l_1^2 + I_{xz} l_1^3 = 0$$

$$I_{yx} l_1^1 + (I_{yy} - \lambda) l_1^2 + I_{yz} l_1^3 = 0$$

and l_1^3 and l_1^2 found in terms of l_1^1 followed by normalisation according to $(l_1^1)^2 + (l_1^2)^2 + (l_1^3)^2 = 1$.

This procedure was performed for $i = x, y$ and z and the resulting elements formed the direction cosine matrix between the original and principal axes (λ_{op}). Knowing the centre of gravity of the top the direction cosine matrix between the top and original axes (λ_{to}) can be written down by inspection. The direction cosine matrix between the top and principal axes is then given by $\lambda_{tp} = \lambda_{to} \lambda_{op}$.

The components (r_o) of the vector from the centre of gravity of the molecule to the origin of coordinates of the top, on the original axes can easily be calculated and then $R_p = \lambda_{po} \cdot r_o$ where (R_p) are the components of this vector on the principal axes and λ_{po} is merely the transpose of λ_{op} .

The quantities A, B, C and U (defined previously) were calculated, followed by evaluation of $\beta_x, \beta_y, \beta_z$ and finally $rI\alpha$.

The above procedure was carried through by desk machine for the n -propyl halides and then a general computer programme for 'SKEW' molecules

was developed along similar lines to the procedure outlined above. Actually a special library routine evaluates the eigenvalues and eigenvectors of any reasonably sized square matrix (3x3 in this case) - these are the principal moments of inertia and the I_{op} matrix elements respectively. This programme is reproduced elsewhere along with that for the 'PLANAR' molecules (see appx.)

For the case of methyl torsion, the procedure used was exactly similar to that for 'PLANAR' molecules except that the I_{tp} matrix was evaluated as I_{to} . I_{op} . The matrix I_{to} is constant throughout the n-propyl series and is easily evaluated but the I_{op} matrix has to be obtained by computer.

The results for the reduced and principal moments of inertia of the various configurations of the n-propyl and allyl halides are given in table (10). As already pointed out, in calculating the positions of hot bands the theory outlined in the preceding pages can only be strictly applied to the case of methyl torsion but as a first approximation it may be extended to cover skeletal torsion. Listed in table (11) are the hot band positions for both methyl and skeletal torsions, calculated from the theory just given.

It is possible to calculate a torsional force constant $k_t = 4\pi^2 \bar{\nu}^2 I_m$ which in the harmonic oscillator approximation is related to a three-fold barrier parameter V_3 by the relation $2k_t = 9V_3$ and hence assuming standard values for the physical constants involved V_3 (Kcals/mole) = $\frac{1.89}{10^5} \bar{\nu}^2 (\text{cm}^{-1})$. I_m ($\text{amu}^\circ \text{A}^2$). Now from the theory previously outlined $V_3 = 2.25F_s (\text{cm}^{-1}) = 6.44F_s$ (Kcals/mole) where F is in cm^{-1} and remembering that $F.(\text{cm}^{-1}) = 16.85 / I_m (\text{amu}^\circ \text{A}^2)$ then $S_{H.O.} = 0.0495 \bar{\nu}^2 / F^2$. In the case of the skeletal torsions the values of S are above the range covered by my graphs (2-205) and the values quoted in table (11) are so-called "Harmonic oscillator S values" designated $S_{H.O.}$ and calculated from the above equation. The corresponding values of Δb_{1-2} have been extrapolated from the graphs.

Table (10)Calculated Moments of Inertia

Molecule and isomer		Principal			Reduced	
					Skeletal	Methyl
n-Propyl	T	18.63	134.93	143.98	9.590	2.761
Fluoride	G	34.99	99.65	118.36	9.208	3.059
n-Propyl	T	19.63	211.85	221.91	13.051	2.765
Chloride	G	44.11	146.36	173.06	12.879	3.131
n-Propyl	T	20.12	307.14	317.68	14.699	2.767
Bromide	G	47.61	211.72	241.58	15.286	3.161
n-Propyl	T	20.65	390.83	401.90	16.001	2.772
Iodide	G	50.32	271.60	303.89	17.061	3.177
Allyl	T	16.13	192.31	205.27	9.446	
Chloride	tG	23.98	179.20	184.71	10.271	
	cG	36.68	137.67	162.19	9.159	
	C	40.30	116.73	153.87	6.228	
Allyl	T	17.41	284.64	298.88	10.247	
Bromide	tG	26.42	263.00	270.70	11.696	
	cG	40.29	205.58	233.23	10.543	
	C	43.48	177.52	217.84	6.578	
Allyl	T	18.77	357.42	373.02	10.696	
Iodide	tG	28.51	330.32	339.89	12.510	
	cG	43.99	262.25	292.15	11.336	
	C	45.92	228.99	271.74	6.824	

Results are in amu. Å² and are calculated using the data given in figures (22, 23).

Table (11) : Positions of hot bands of skeletal and methyl torsions

	Molecule	n-Propyl Fluoride		n-Propyl Chloride		n-Propyl Bromide		n-Propyl Iodide		t-Gauche Allyl	
		Trans	Gauche	Trans	Gauche	Trans	Gauche	Trans	Gauche	Chloride	Bromide
Skeletal	$I_m(\text{amu.}\text{\AA}^2)$	9.590	9.208	13.051	12.879	14.699	15.286	16.001	17.061	10.271	11.696
	$F_m(\text{cm}^{-1})$	1.756	1.829	1.290	1.309	1.147	1.102	1.051	0.988	1.641	1.440
	$\nu_{O-1}(\text{cm}^{-1})$	100	139	132	121	127	115	127	116	127	132
	Δb_{O-1}	25.31	33.8	45.5	41.0	49.2	46.4	53.6	52.1	34.4	40.7
	S	174	(289)	(518)	(423)	(605)	(539)	(720)	(683)	(296)	(415)
	Δb_{1-2}	24.15	32.7	44.4	39.9	48.1	45.3	52.5	51.0	33.3	39.6
Methyl	$\nu_{1-2}(\text{cm}^{-1})$	95	135	129	118	124	112	124	113	123	128
	$I_m(\text{amu.}\text{\AA}^2)$	2.761	3.059	2.765	3.131	2.767	3.161	2.772	3.177		
	$F_m(\text{cm}^{-1})$	6.141	5.610	6.095	5.384	6.091	5.332	6.080	5.304		
	$\nu_{O-1}(\text{cm}^{-1})$	212.7	212.7	217	217	197	197	203?	203?		
	Δb_{O-1}	15.41	16.85	15.31	17.34	14.37	16.43	14.77	16.92		
	S	68.0	80.2	66.9	85.2	59.8	76.6	62.9	81.0		
	Δb_{1-2}	14.20	15.65	14.08	16.20	13.15	15.25	13.56	15.75		
	Δb_{2-3}	12.80	14.27	12.65	14.86	11.65	13.85	12.11	14.37		
	$\nu_{1-2}(\text{cm}^{-1})$	196.1	197.4	193.0	196.0	180.2	182.9	185.4?	188.0?		
	$\nu_{2-3}(\text{cm}^{-1})$	176.8	180.1	173.3	180.0	159.7	166.0	165.7?	171.5?		

* S values in brackets are harmonic oscillator values $S = 0.0495 \nu^2/F^2$.
H₂O.

Corresponding b_{1-2} values are extrapolated.

Table (12)

Methyl V_3 barrier parameters

Molecule		F cm^{-1}	$\bar{\nu}$ cm^{-1}	S	V_3 kcal/mole
n-Propyl Fluoride	T	6.14	212	68	2.69
	G	5.51	213	80.2	2.90
n-Propyl Chloride	T	6.095	217 (211)	71 (67)	2.78 (2.63)
	G	5.384	211 (217)	85 (89)	2.96 (3.09)
n-Propyl Bromide	T	6.091	197 (192)	60 (56.5)	2.36 (2.22)
	G	5.382	192 (197)	76.5 (75)	2.65 (2.60)
n-Propyl Iodide	T	6.086	203?	63	2.47?
	G	5.304	203?	81	2.77?

Table (13)

Skeletal V_3 barrier parameters

Molecule		$I_m \text{amu} \cdot \text{\AA}^2$	$\bar{\nu}$ cm^{-1}	V_3 kcal/mole	$K_t \times 10^{-12}$ dyne.cm
n-Propyl Fluoride	T	9.590	~ 100	1.82	
	G	9.208	139	3.36	1.05
n-Propyl Chloride	T	13.051	132 (121)	4.29 (3.61)	1.34
	G	12.879	121 (132)	3.57 (4.24)	1.11
n-Propyl Iodide	T	14.699	127 (115)	4.48 (3.68)	1.40
	G	15.286	115 (127)	3.82 (4.65)	1.19
n-Propyl Iodide	T	16.001	127 (116)	4.89 (4.07)	1.52
	G	17.061	116 (127)	4.34 (5.20)	1.35
t-Gauche allyl chloride		10.271	120	2.80	0.87
t-Gauche allyl bromide		11.696	120	3.18	0.99
t-Gauche allyl iodide		12.510	115	3.13	0.97

T = trans isomer.

G = gauche isomer,

DISCUSSION.

Introduction. In principle the energy of any molecular configuration is calculable from a quantum mechanical treatment and arises from the electrostatic interactions of the electrons and nuclei. In practice the mathematical complexity of such a treatment is so great that a rigorous computation is impractical. The same tractable approximations which have been developed for the general problem of molecular energies have been applied to this problem, but in view of the fact that the simpler task of predicting bond dissociation energies is unsatisfactory, it is not too surprising that the same crude approximations fail to predict the much smaller energies differences involved in barriers.

Although extensive studies have been made on a large number of molecules the reliability of the results leaves much to be desired. It is therefore difficult to evolve any satisfactory theory of the origin of the barriers or to predict the magnitudes of the barriers and equilibrium configuration in any molecules not so far studied.

In the following discussion the factors affecting the equilibrium configurations and the magnitude of the barriers to internal rotation in ethane-like and acetaldehyde-type molecules are reviewed.

A summary of the attempts to explain the origin of the barriers to internal rotation is given and a new theory, in terms of the electron asymmetry, is forwarded to explain the effect of phase (solvent) on the barrier height in different types of compounds.

Equilibrium Configuration:

If the electron distribution in the two orbitals forming a double bond may be represented as "bent" or "banana-shaped" as suggested by Pople (55) then the equilibrium configurations so far well established indicate that the

electron distributions near the atoms of the central bond tend to take up a staggered orientation. This accounts for the equilibrium configurations of ethane-like molecules, CH_3COX type molecules in which the $\text{C}=\text{O}$ bond is eclipsed by a methyl hydrogen and conjugated double bond systems such as acrolein or butadiene, although in this latter case conjugation is an important factor.

Barrier Magnitudes:

Regarding the factors influencing the barrier height, electrostatic and Van der Waals interactions may both be important in molecules containing two or more strongly polar or large groups but neither seem to be dominant in many simpler molecules. Thus the barriers in ethane, methyl silane and methyl germane (2.90, 1.70, 1.24 Kcals/mole respectively) fall off more slowly than predicted from Van der Waals forces whilst on the electrostatic approach they require bonds with unexpectedly high dipoles.

Considering molecules with only hydrogen atoms off the central bond: Libby has shown that the lack of sensitivity of the barrier height in ethane (56) to isotopic substitution is a strong argument that steric repulsion between hydrogens is not the principal cause of the barrier. Similar behaviour has been observed for CH_3NH_2 (57)/ CD_3ND_2 (58), for $\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$ (59) and for the isotopic acetaldehydes (60).

Karplus and Parr (61) considering only nuclear-nuclear repulsion energies ΔE_{nn} , have shown that for molecules with only hydrogens off the torsion axis the calculated barriers are consistently greater than the experimental barriers by a factor of 5/3. The offsetting of this ΔE_{nn} term is considered to be due to the sum of an electron-electron and an electron-nuclear interaction term: $\Delta E_{\text{ee}} + \Delta E_{\text{en}}$.

Considering now molecules with other substituents off the torsion axis: the effect of substituting other atoms for hydrogen in ethane-like or

acetaldehyde-type molecules seems to be quite small as long as substitution is confined to one end of the central bond. Thus the barriers of the compounds $\text{CH}_3\text{CH}_2\text{X}$ ($\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CN}$) lie in the range 3200 ± 400 cal/mole while those of the compounds CH_3COX ($\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CN}$) lie in the range 1200 ± 150 cal/mole. This led Wilson (62) to conclude that at least where one of the groups concerned is a methyl group, the barriers to internal rotation must in some way be "an inherent property of the axial bond itself and not due in any substantial measure to direct forces between the attached atoms or those parts of the electron distributions which are out on the attached bonds any considerable distance."

When large or polar atoms are present at both ends of the central bond, the barrier is raised considerably in consequence of Van der Waals and/or electrostatic interactions, i.e. 12.4 Kcal/mole in $\text{CCl}_3\text{CH}_2\text{Cl}$ (35) and 3.92 Kcal/mole in CF_3CF_3 (63).

However although the effect of substitution at one end of the central bond is quite small it is also rather irregular. Thus substitution of hydrogen by fluorine in methyl silane progressively lowers the barrier; CH_3SiH_3 1.70, $\text{CH}_3\text{SiH}_2\text{F}$ 1.56, CH_3SiHF_2 1.26, CH_3SiF_3 1.20 Kcal/mole respectively.) whereas the same substitution in ethane causes the barrier first to rise and then fall (CH_3CH_3 2875, $\text{CH}_3\text{CH}_2\text{F}$ 3306, CH_3CHF_2 3180, CH_3CF_3 3040, CH_2FCF_3 4200, CHF_2CF_3 ?, CF_3CF_3 3920 cal/mole respectively.)

With larger substituents (say chlorine) the irregularity is still evident: $\text{CH}_3\text{CH}_2\text{Cl}$ has a barrier of 3.56 Kcal/mole compared with CH_3CH_3 and CH_3CCl_3 , both of which have a barrier of 2.90 Kcal/mole.

Similar irregular effects are observed in acetaldehyde-type molecules. The barrier heights for CH_3CHO , CH_3COF , CH_3COCl and CH_3COCN are

respectively 1.16, 1.04, 1.30 and 1.21Kcals/mole and are difficult to correlate.

Ward (64) has investigated the barrier heights in the three series $\text{CH}_3\text{CH}_2\text{X}$, $\text{CF}_3\text{CH}_2\text{X}$ and $\text{CF}_3\text{CF}_2\text{X}$ ($\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) to see if they threw any light on the origin of the barriers to internal rotation but had to conclude that steric effects, either alone or in combination with polarizability differences cannot account for the observed changes in the barrier heights of even relatively simple halogen substituted molecules.

The table below summarises the V_3 barrier parameters of the trans n-propyl halides and the t-Gauche allyl halides (studied in this research) along with those of some related compounds for comparison:

V_3 BARRIER PARAMETERS (KCAL/MOLE.)

$\text{CH}_3.\text{CH}_3$	2.87	(65)	$\text{CH}_3\text{CH}_2.\text{CH}_2\text{Br}$	4.48	(70)
$\text{CH}_3.\text{CH}_2\text{CH}_3$	3.30	(66)	$\text{CH}_3\text{CH}_2.\text{CH}_2\text{I}$	4.89	(70)
$\text{CH}_3.\text{CH}_2\text{F}$	3.33	(67)	$\text{CCl}_3.\text{CH}_2\text{Cl}$	12.4	(35)
$\text{CH}_3.\text{CH}_2\text{Cl}$	3.56	(68)	$\text{CH}_2=\text{CH}.\text{CH}_3$	1.98	(71)
$\text{CH}_3.\text{CH}_2\text{Br}$	3.57	(68)	$\text{CH}_2=\text{CH}.\text{CH}_2\text{Cl}$	2.80	(70)
$\text{CH}_3.\text{CH}_2\text{I}$	3.22	(69)	$\text{CH}_2=\text{CH}.\text{CH}_2\text{Br}$	3.18	(70)
$\text{ClCH}_2.\text{CH}_2\text{Cl}$	4 (calc.)		$\text{CH}_2=\text{CH}.\text{CH}_2\text{I}$	3.13	(70)
$\text{CH}_3\text{CH}_2.\text{CH}_2\text{Cl}$	4.29	(70)	$\text{CH}_2=\text{CH}.\text{CCl}_3$	3.20	(35)

In line with what has been said in the above discussion it can be seen from the table that as long as substitution is confined to one end of the torsion bond then the barrier parameters are not greatly different from the parent molecules. Van der Waals and electrostatic interactions are evident in 1,2 dichloroethane and 1,1,1,2 tetrachloroethane and result from substitution at both ends of the central bond. Since no Van der Waals interactions is expected in either the trans configurations of the n-propyl halides or the trans-Gauche allyl halides, the relatively large barrier parameter increase

of these molecules would seem to arise from electrostatic interactions.

However while the barrier parameter increases smoothly across the n-propyl halides it is irregular for both the allyl and ethyl halides.

Summary:

Thus all one can conclude is that unless Van der Waals or electrostatic interactions become important (as in CX_3CH_2Y for example) then the barrier heights of many simple substituted molecules will not be greatly different from the parent molecule.

Finally it may be noted that the barrier parameters for internal rotation about a torsion bond joining an sp^3 and an sp^2 hybridised carbon atom are significantly smaller than the parameters for internal rotation when the torsion bond unites two sp^3 hybridised carbon atoms i.e. the V_3 values of the allyl halides are smaller than the V_3 values of their saturated analogues, the n-propyl halides.

Origin of the barrier and the effect of phase (solvent).

The origin of the internal rotation barriers has long been an elusive problem in chemistry and despite great recent experimental progress theoretical explanations of the origin of the barrier have been diverse and inclusive. A brief summary of these attempts follows:

Eyring (71) attributed the effect to direct nuclear repulsions but his calculated barrier values were much smaller ($\sim 10\%$) than found experimentally. Recent refinements of repulsive forces still do not give reasonable behaviour (Mason and Kreevoy 72, Van Dranen 73). Wilson (74) has stated strong arguments against direct repulsion being the main source of the barrier.

In many approaches to the problem, a localised orbital charge distribution is assumed. A classical electrostatic model was employed by

Lassetre and Dean (75) and Oosterhoff (76) who based their calculations on the coulomb interactions among dipole and higher moments of the C-H bonding electrons. Oosterhoff found that too ionic a C-H bond was required and since the replacement of hydrogen by fluorine does not change the barrier significantly, direct coulomb interaction cannot be the main source of the barrier.

Pauling (77), by introducing d and f orbitals into the localised contributions of the C-H and C-C bonds, proposed that the barrier was due to exchange interactions of the electrons in the carbon orbitals of the C-H bonds. However he neglected electron-nuclei interactions which would favour an eclipsed configuration in disagreement with experiment (78).

Eyring (79) refined the localised contribution by the inclusion of spin correlation among the bonds (deviation from perfect pairing). A similar treatment has been forwarded by Harris and Harris (80). Karplus and Parr (61) assumed a delocalised cylindrically symmetric charge distribution.

Of the variety of causes suggested above none have been demonstrated to be dominant and so the problem is still largely unanswered.

Regarding now the effect of phase (solvent), since the crystal structure, and hence the forces operating, of the n-propyl and allyl halides are not known, the crystalline phase will be omitted from this discussion which will therefore only apply to vapour and liquid (solvent).

For easy reference the values of the skeletal torsion frequencies of the trans n-propyl and trans-Gauche allyl halides in liquid and vapour phases are tabulated below:

cm ⁻¹	trans n-propyl			trans-Gauche allyl		
	chloride	bromide	iodide	chloride	bromide	iodide
$\bar{\nu}$ vapour	132	127	127	123	126	--
$\bar{\nu}_t$ liquid	140	131	133	120	120	112 115 nujol

The points to notice are the increase in the torsion frequencies of the n-propyl halides in going from vapour to liquid and the corresponding decrease in torsion frequencies of the allyl halides. Why the difference?.

Given below is an explanation which is in agreement with the above experimental data.

Electrostatic interactions of the bare protons in ethane give a barrier of about 5Kcals/mole (depending critically on the molecular parameters employed). Now if the sum of the electron distributions in the C-H bonds on one carbon atom was equivalent to cylindrical symmetry about the C-C axis then the bare proton interaction would represent the only contribution to the barrier provided the electron distribution is not distorted from cylindrical symmetry during the torsional motion.

The decrease of the barrier to the experimental value of 2.87 Kcals/mole would then represent the tendency of the electrons to concentrate along the classical tetrahedral bond directions and offset the proton-proton interactions, rather than be cylindrically symmetrical about the torsion axis.

The nature of solvent effects are not yet fully understood, especially in a pure liquid, but in comparison with vacuum all effects of the environment will reduce interactions between charges. Hence in the liquid phase the electron distribution will be less concentrated in the bond directions and the offsetting of the proton-proton interactions will decrease. The barrier will thus rise towards the bare proton value.

The above argument is applicable to any ethane-like molecule (i.e. one in which the torsion bond and all adjacent bonds are saturated). If one of the adjacent bonds is a double bond (i.e. $\text{CH}_3\text{-CH=CH}_2$, CH_3COX ($\text{X}=\text{H}, \text{F}, \text{Cl}$) and the allyl halides) then the observed equilibrium configuration is one in which the double bond is eclipsed by a single bond on the other carbon atom

and furthermore is less energetically favoured than the staggered configuration if only the bare proton interactions are considered. Thus the departure from cylindrical symmetry of the electron distribution is sufficient to favour the eclipsed form energetically (this is not unreasonable since a bare proton calculation on acetaldehyde indicates the staggered form only 0.51Kcals/mole more stable than the eclipsed). In the liquid phase the decreased asymmetry of the electron distribution means that the factor stabilising the observed eclipsed form becomes less important. Hence the decrease in torsion frequency in the liquid is understandable in such molecules.

The above "theory" when applied to molecules with conjugated double bonds about the torsion axis (i.e. butadiene and benzaldehyde) predicts the observed configuration but the effect of solvent predicts that the barrier should fall in conflict with experiment. However the solvent will promote delocalisation of charge and impart rather more double bond character to the torsion bond than exists in the vapour. The observed rise in the potential barrier in going from vapour to liquid is therefore understandable.

Furthermore the torsion frequency of a given compound (i.e. acrolein), and hence the V_3 parameter, will be higher the more polar the solvent.

Hence the behaviour of the three different types of molecule have been accounted for in terms of the one factor, the asymmetry of the electron distribution.

While the above arguments are not the last word on the origin of torsional barriers it is suggested that similar arguments would have to be incorporated into any detailed theory.

APPENDIX.

Given in the first part of the appendix are the general computer programmes developed during this research for the determination of the reduced moment of inertia, I_m , for a planar or skew molecule.

In the second part of the appendix are listed the actual charts or "runs" for each compound. Not every run actually performed is listed since many runs were performed as checks on previous ones. In every run listed the basic filter combination of black polythene and KBr chopper was used. Given in the third column of the following tables are the reststrahlen filters employed in each particular run, column two gives the frequency range covered and column four the bands observed, if any. The following symbols are used:

XQ = crystal quartz transmission filter

Vac = vacuum BG = background

s = strong w = weak vw = very weak

sh = shoulder

Also given in the second part of the appendix are the actual spectra, for each compound, in diagrammatic form with % absorption plotted against a linear frequency scale. (The various numbers represent frequencies in cm^{-1} .)

Spectral slit widths are too small to be easily represented in these figures but can be obtained from table (I).

title
reduced moment for planar molecule
chapter 0

a2

a>30

b>30

c>30

d>30

e>30

f>30

g>30

h>50

u>30

v>30

w>30

x>30

y>30

z>30

π >30

>> in this program c. of g. of top must be +ve on y0 axis

s=1

i) read(n)

i=i(1)n

read(wi)

read(xi)

read(yi)

read(zi)

repeat

dn=0

en=0

fn=0

gn=0

i=i(1)n

ai=wixi

bi=wlyi

ci=wizi

dn=ai+dn

en=bi+en

fn=ci+fn

gn=wi+gn

repeat

dn=dn/gn

en=en/gn

fn=fn/gn

>> centre of gravity of molecule, total mass

newline

print(dn),4

print(en),4

print(fn),4

print(gn),4

>> -change origin to c. of g. of molecule

i=i(1)n

gi=xi-dn

vi=yi-en

ni=zi-fn

repeat

d=0
e=0
f=0
g=0

a3

```
i=i(1)n
ai=wigigi
bi=wivivi
ci=wipipi
ui=wigivi
d=ai+d
e=bi+e
f=ci+f
g=ui+g
repeat
>> the sums mxx, myy, mzz, mxy.
newline
print(d)0,4
print(e)0,4
print(f)0,4
print(g)0,4
h1=e-d
>> tan20
h2=-2g/h1
h3=1+h2h2
h4=sqrt(h3)
>> cos0cos0, sin0sin0.
h5=0.5+0.5/h4
h6=0.5-0.5/h4
h7=dh5+eh6+gh2/h4
h8=eh5+dh6-gh2/h4
h9=h8+f
h10=h7+f
h11=h7+h8
>> tan20, ix, iy, iz.
newline
print(h2)0,4
print(h9)0,4
print(h10)0,4
print(h11)0,4
read(r)
d=0
e=0
f=0
g=0
i=i(1)r
ai=wixi
bi=wiyi
ci=wizi
d=ai+d
e=bi+e
f=ci+f
g=wi+g
repeat
d=d/g
e=e/g
f=f/g
```

>>- centre of gravity of top z, x, y.

```
newline
print(d)0*****,4
print(e)0,4
print(f)0,4
```

a4

```
a=0
b=0
c=0-
i=i(1)r
di=wiyyi+wizizi
ei=wiyixi-wiyid
fi=wiyi
a=di+a
b=ei+b
c=fi+c
repeat
```

>> a, b, u.

```
newline
print(a)0,4
print(b)0,4
print(c)0,4
h12=sqrt(h5)
h13=sqrt(h6)
>> cos0, sin0.
```

```
newline
print(h12)0,4
print(h13)0,4
h14=d-dn
```

```
h15=-en
jump2,0>h2
```

```
h16=h13
h17=-h13
h18=h13
h19=-h13
```

```
jump3,h2>0
```

```
2) h16=-h13
```

```
h17=h13
h18=-h13
h19=h13
```

```
3) h20=h12h14+h18h15
```

```
h21=h19h14+h12h15
```

```
h22=ah12-bh16+ch21
```

```
h23=ah17-bh12-ch20
```

```
h24=a-cg/h22h22/h9-h23h23/h10
```

>> rx, ry, bx, by, im.

```
newline
print(h20)0,4
print(h21)0,4
print(h22)0,4
print(h23)0,4
print(h24)0,4
```

```
s=s+1
```

```
read(k)
```

```
jump1,k>s
```

```
end
close
xxx
```

title
reduced moment for skew molecule-i

routine 925

a5

chapter 0

a>10

b>40

c>30

d>30

e>30

f>30

g>30

h>30

u>10

v>10

w>30

x>30

y>30

z>30

u>30

s=1

1) read(t)

j=i(1)t

read(wj)

read(xj)

read(yj)

read(zj)

repeat

a=0

b=0

c=0

d=0

j=i(1)t

cj=wjxj

dj=wjy

ej=wjz

a=cj+a

b=dj+b

c=ej+c

d=wj+d

repeatxxxx

a=a/d

b=b/d

c=c/d

newLine

print(a)0,4

print(b)0,4

print(c)0,4

print(d)0,4

j=i(1)t

fj=xj-a

gj=yj-b

hj=zj-c

repeat

an=0

bn=0

cn=0

```

dn=0
en=0
fn=0
j=i(1)t
cj=wjffj
dj=wjggj
ej=wjhjhj
rj=wjfggj
fj=wjfhjhj
gj=wjgjhjhj
an=cj+an
bn=dj+bn
cn=ej+cn
dn=rj+dn
en=fj+en
fn=gj+fn
repeat
newline
print(an)0,4
print(bn)0,4
print(cn)0,4
print(dn)0,4
print(en)0,4
print(fn)0,4
n=3
i=1
m=3
e=0.00001
a0=an
a1=dn
a2=en
a3=bn
a4=fn
a5=cn
jump down (n925)
newline
j=i(1)3
print(uj)0,4
repeat
newline
j=i(1)3
print(vj)0,4
repeat
newline
j=4(1)6
print(vj)0,4
repeat
newline
j=7(1)9
print(vj)0,4
repeat
read(r)
an=0
bn=0
cn=0
dn=0

```

```

j=i(i)r
aj=w jxj
bj=w jyj
cj=w jzj
an=aj+an
bn=bj+bn
cn=cj+cn
dn=w j+dn
repeat
an=an/dn
bn=bn/dn
cn=cn/dn
en=bn/cn
newline
print(an)0,4
print(bn)0,4
print(cn)0,4
print(en)0,4
xn=-a+an
yn=-b
zn=-c
newline
print(xn)0,4
print(yn)0,4
print(zn)0,4
s=s+1
read(k)
jumpi,k>s

```

end

close

```

11
19 -0.482 -0.6445 -1.115
1 -0.367 1.037 0
1 -0.367 -0.518 0.90
12 0 0 0
12 1.550 0 0
1 1.914 0.518 0.90
1 1.914 0.518 -0.90
12 2.114 -1.433 0
1 3.203 -1.395 0
1 1.750 -1.947 0.90
1 1.750 -1.947 -0.90
3
10

```

title
reduced moment for skew molecule-2
chaptero

a8

```
a>10
b>10
c>10
d>10
e>10
f>10
g>10
h>10
w>10
x>10
y>10
z>10
S=1
1) read(dn)
i=1(1)4
read(ai)
repeat
i=1(1)9
read(bi)
repeat
i=1(1)3
read(ci)
repeat
d1=b1c1+b2c2+b3c3
d2=b4c1+b5c2+b6c3
d3=b7c1+b8c2+b9c3
read(k)
i=1(1)k
read(wi)
read(xi)
read(yi)
read(zi)
repeat
an=0
bn=0
cn=0
un=0
i=1(1)k
fi=ay1+a2z1
gxi=a3y1+a4z1
hi=xi-dn
an=wififi+wigigi+an
bn=wifihi+bn
cn=wigihi+cn
un=wifi+un
repeat
newline
print(an)0,4
print(bn)0,4
print(cn)0,4
print(un)0,4
e1=a1b2+a2b3
e2=a1b5+a2b6
e3=a1b8+a2b9
e4=a3b2+a4b3
```

e5=a3b5+a4b6

e6=a3b8+a4b9

e7=b1

e8=b4

e9=b7

newline

j=i(i*)5

print(ej)0,4

repeat

newline

j=**6(i)9

print(ej)0,4

repeat

xn=ane7-bne1-cne4+une6d2-une5d3

yn=ane8-bne2-cne5+une4d3-une6d1

zn=ane9-bne3-cne6+une5d1-une4d2

read(wn)

read(en)

read(fn)

read(gn)

v=an-unun/wn-xnzn/en-ynyn/fn-znzn/gn

newline

print(xn)0,4

print(yn)0,4

print(zn)0,4

print(v)0,4

s=s+i

read(t)

jumpi,t>s

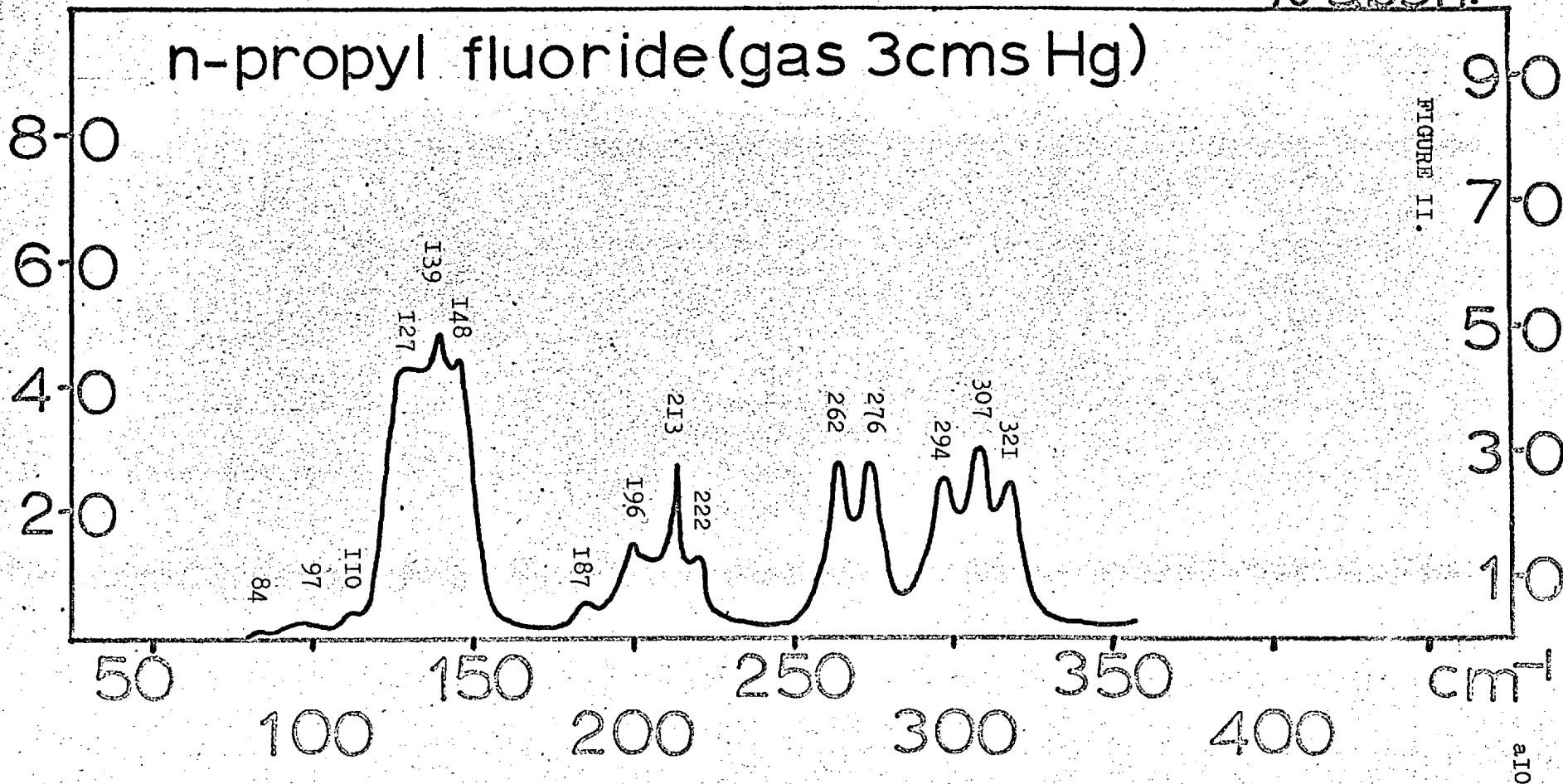
end

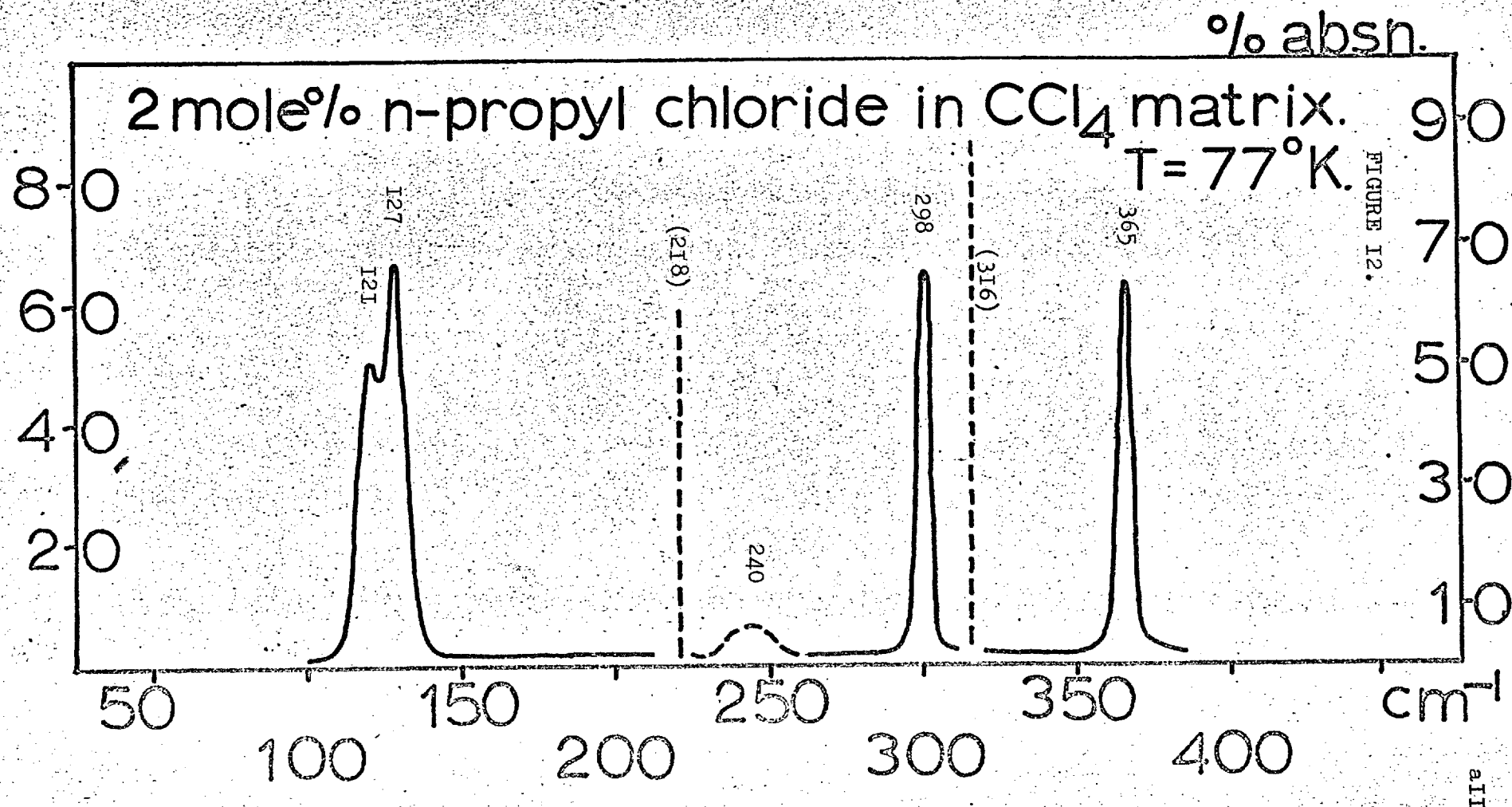
close

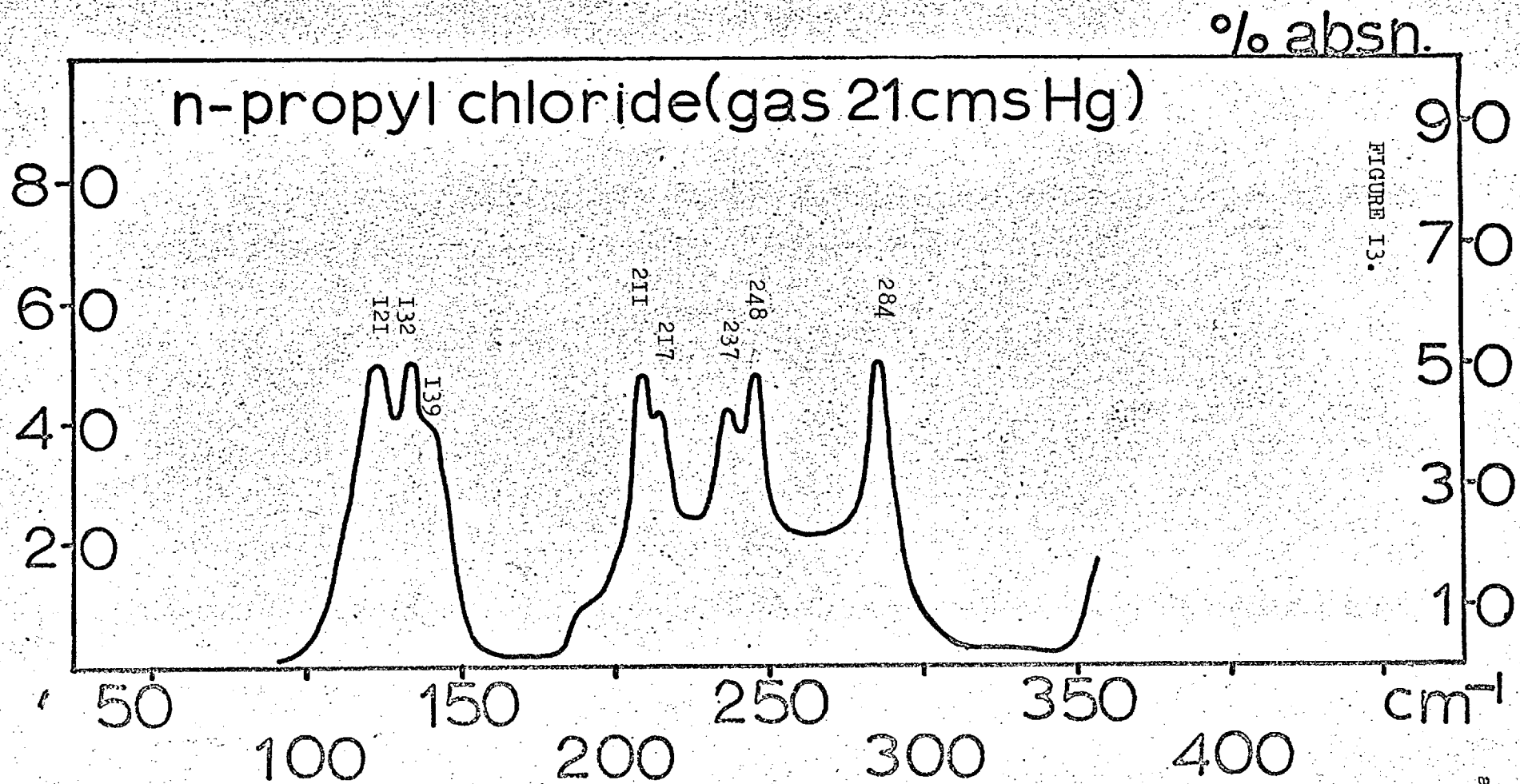
-0.47105 -0.50047 -0.86572 0.86572 -0.50047
0.92339 -0.21784 0.31608 0.03528 0.86806 0.49521
-0.38225 -0.44612 0.80924
-1.1905 0.53509 0.32718
3
19 -0.482 -0.6445 -1.115
1 -0.367 1.037 0
1 -0.367 -0.518 0.90
62.0
35.055 99.116 . 117.797
10

n-propyl fluoride(gas 3cms Hg)

% absn.







n-propyl chloride (liquid)

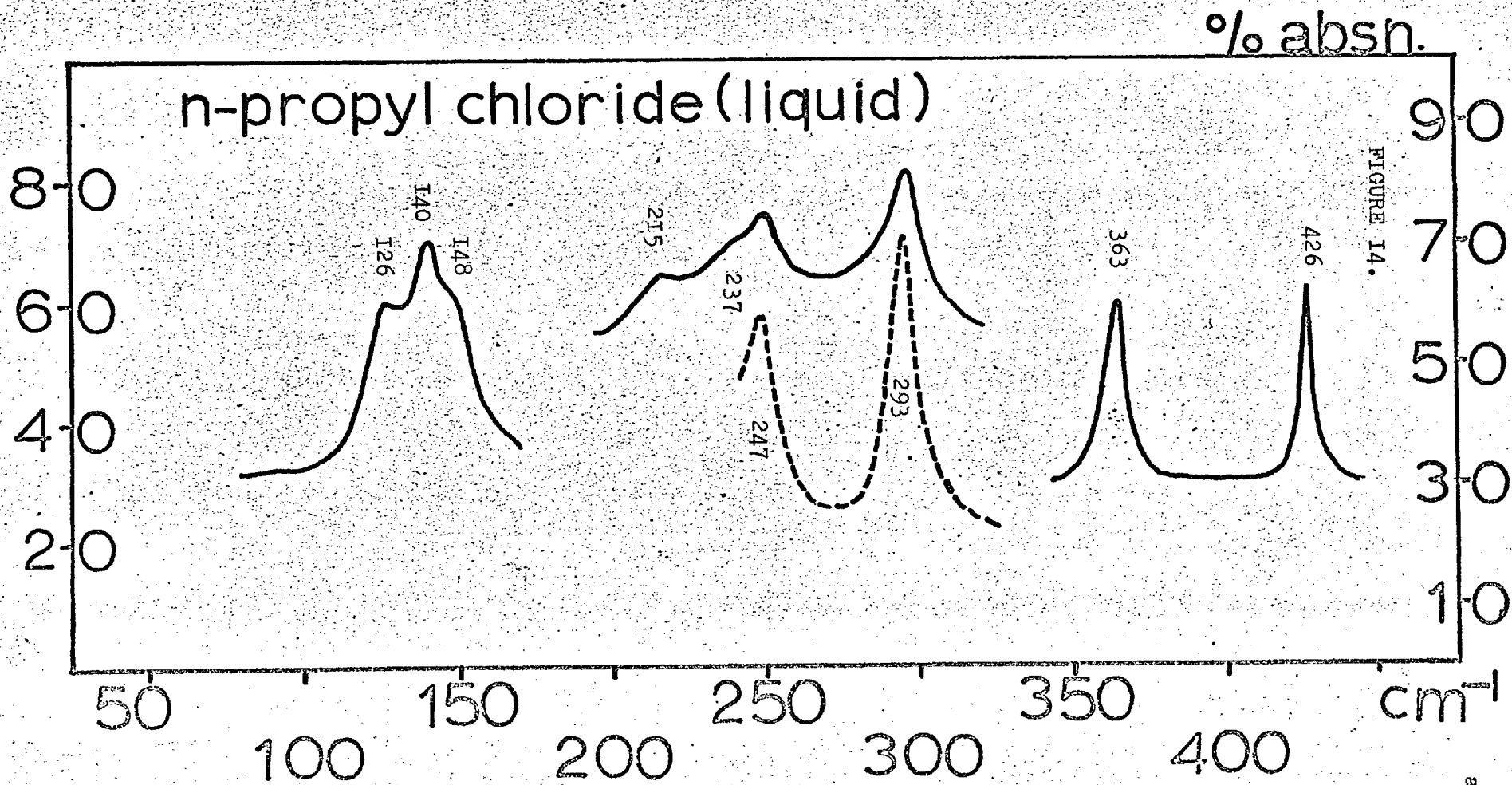


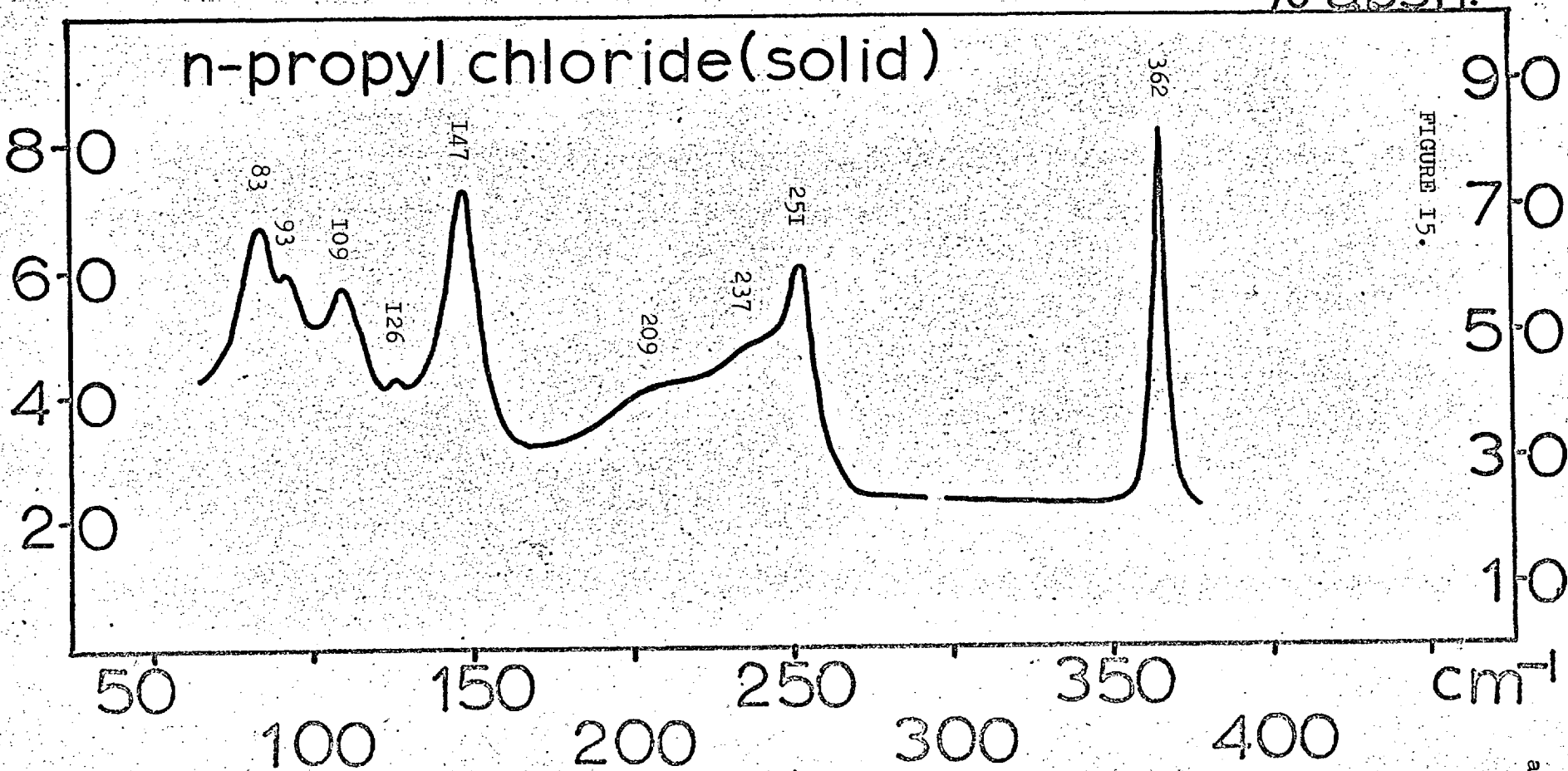
FIGURE 14.

n-propyl chloride(solid)

% absn.

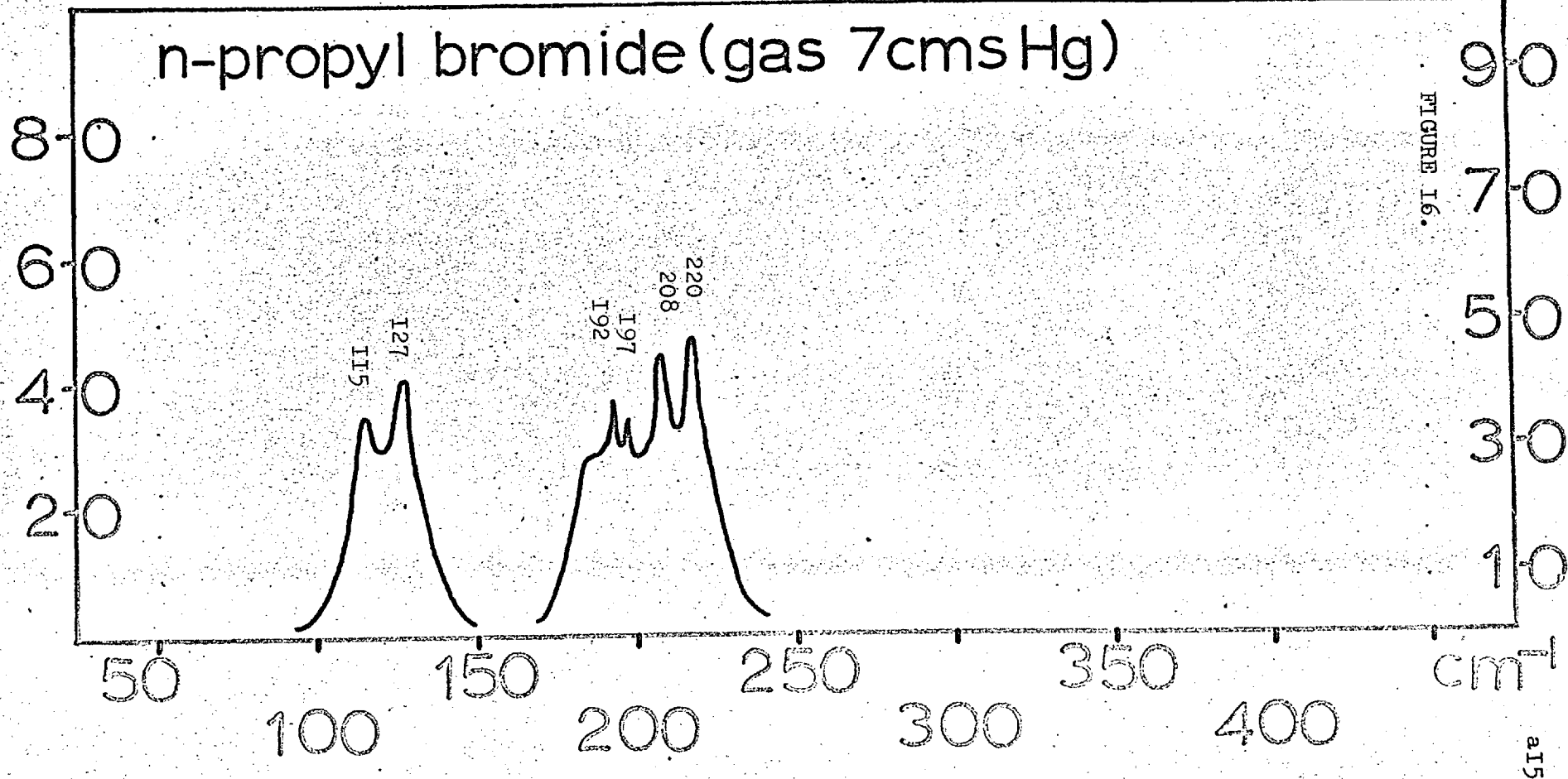
FIGURE 15.

a14



n-propyl bromide (gas 7cms Hg)

% absn.



n-propyl bromide (liquid)

% absn.

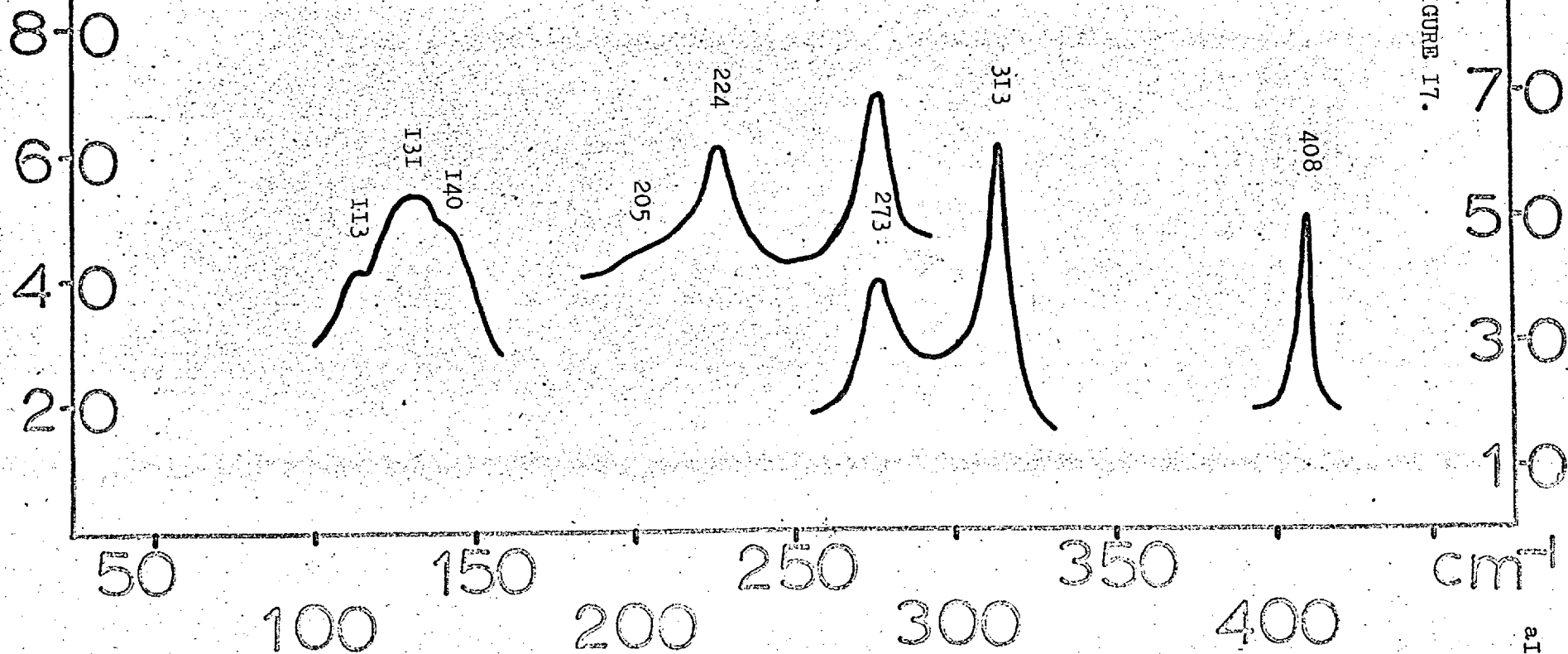
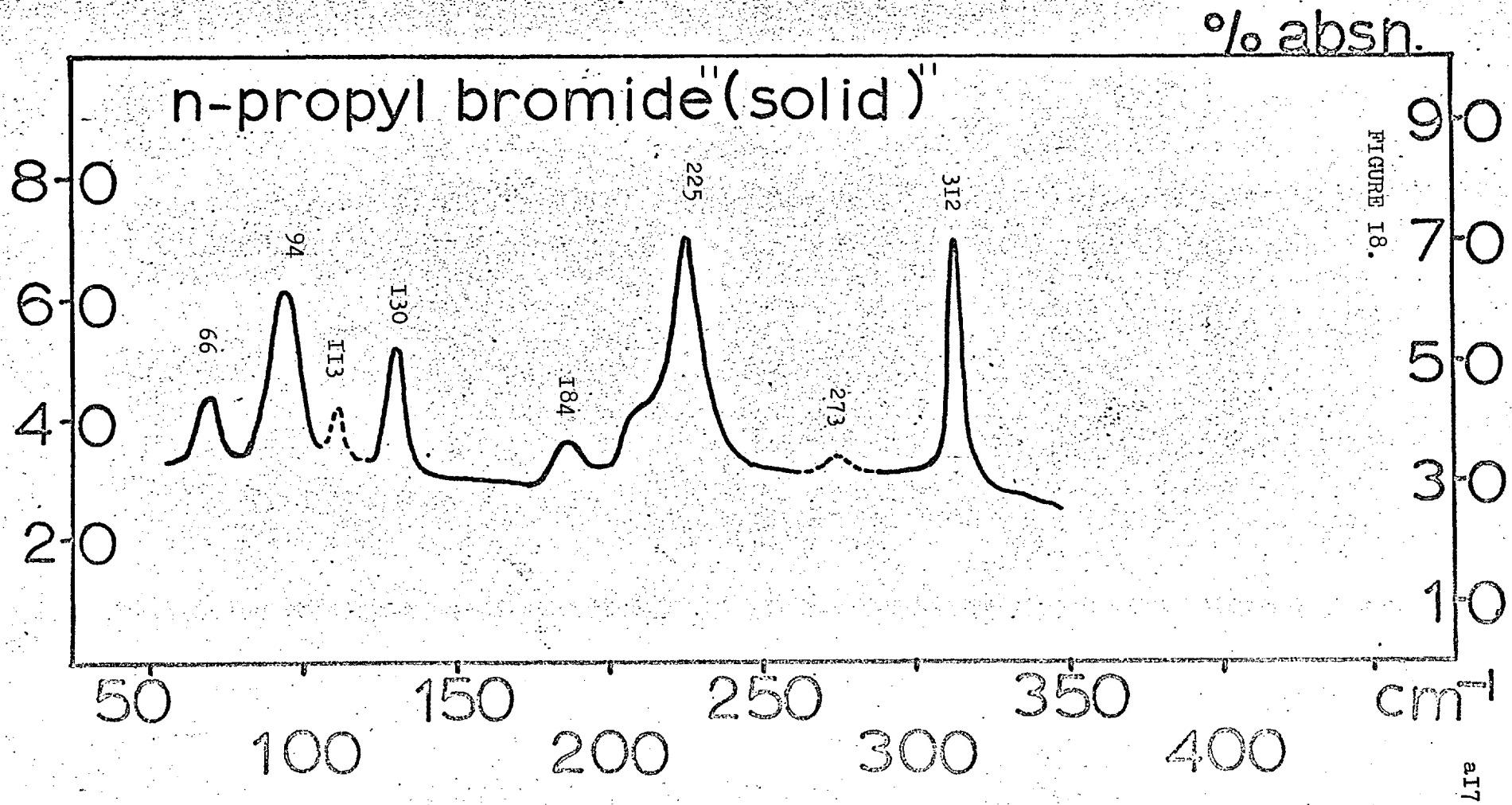


FIGURE 17.



n-propyl iodide(gas 3cmsHg)

% absn.

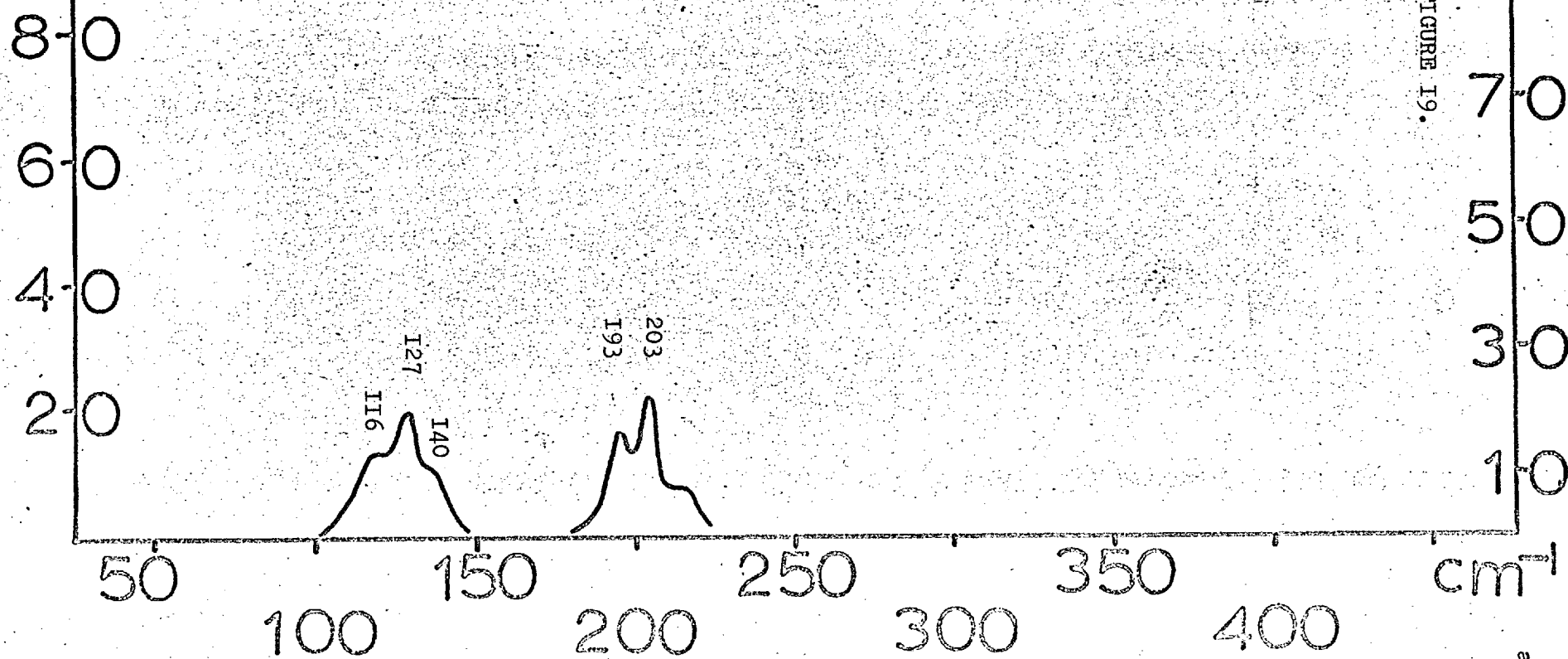
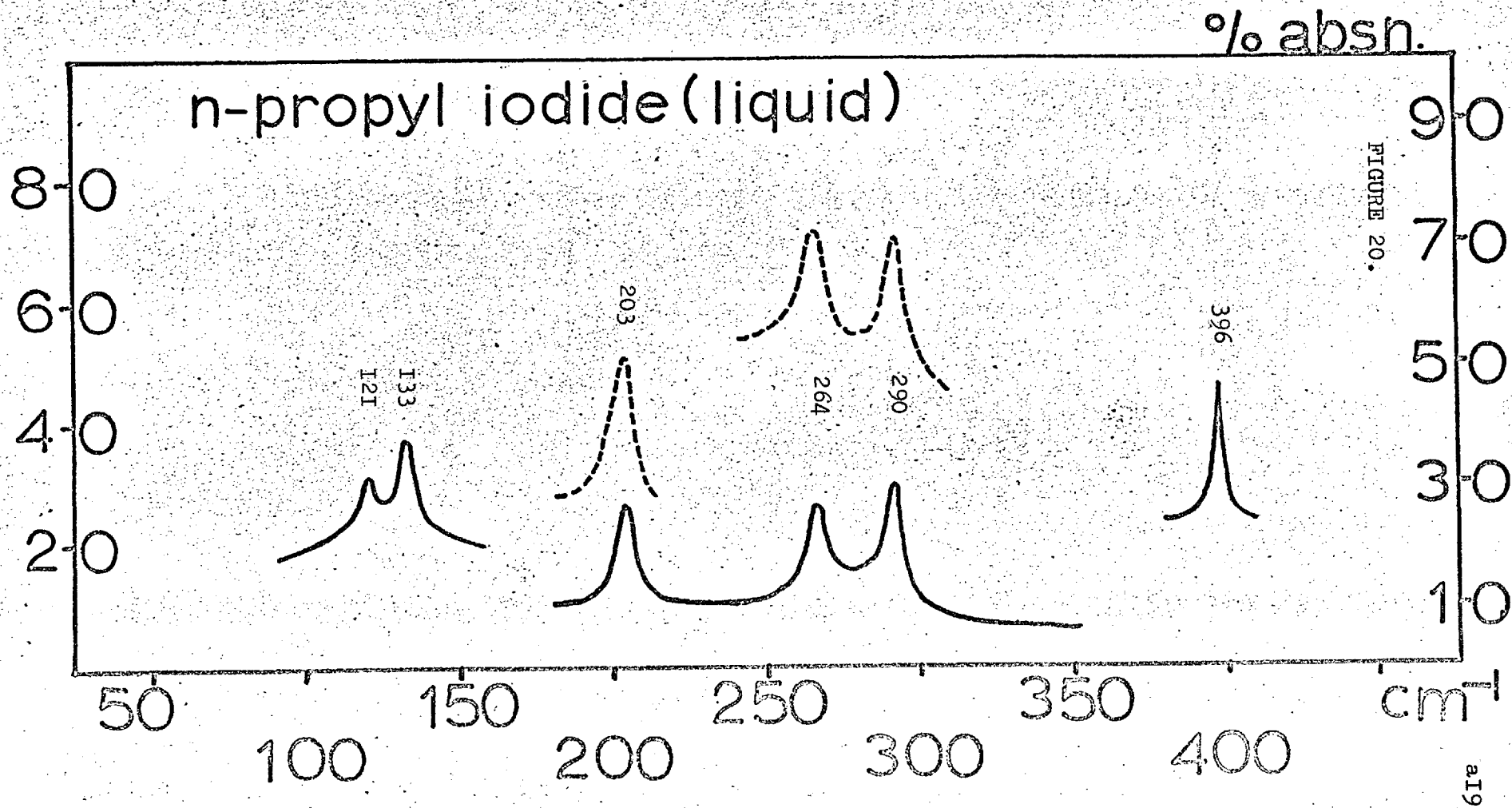


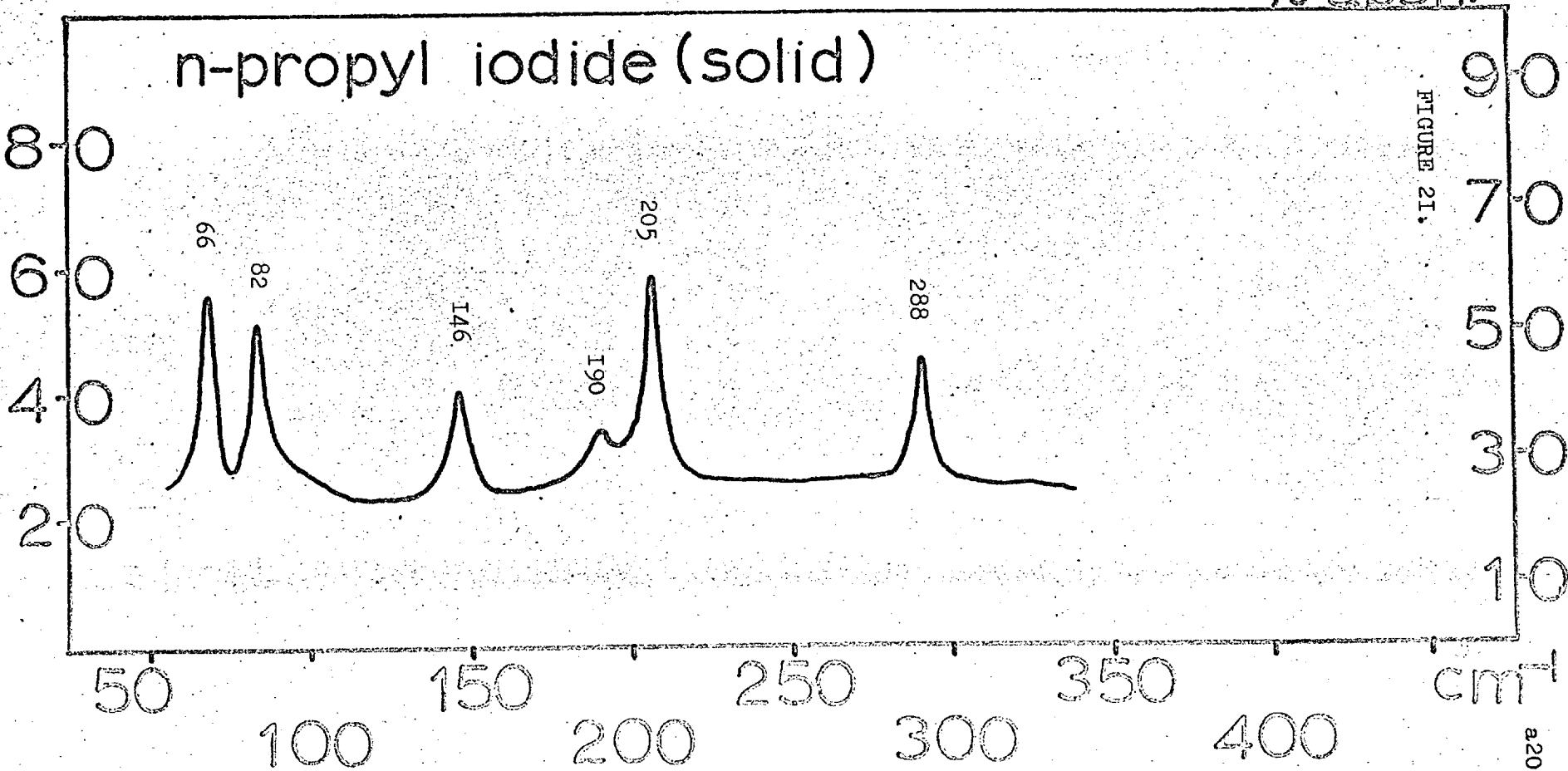
FIGURE 19.

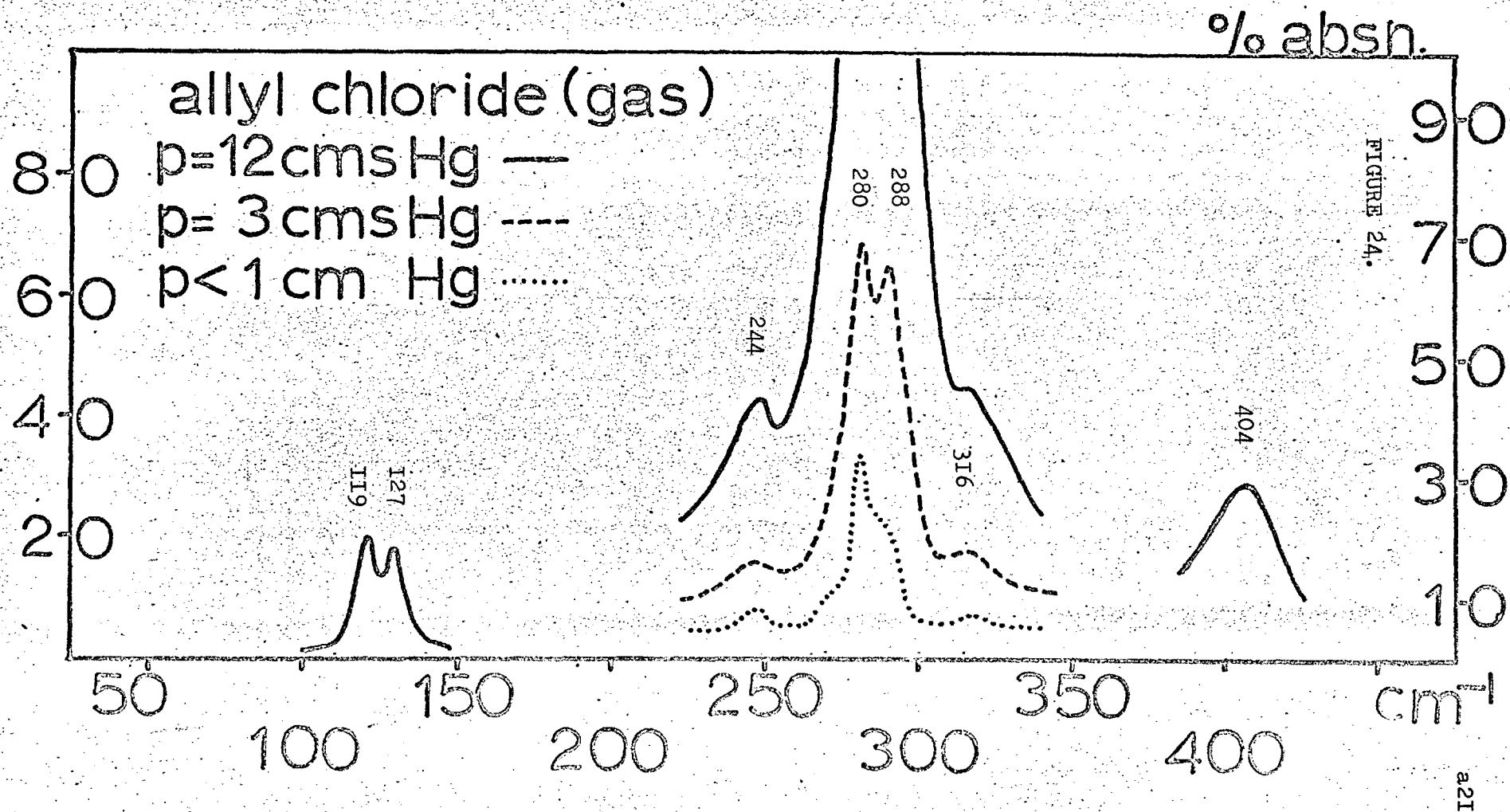


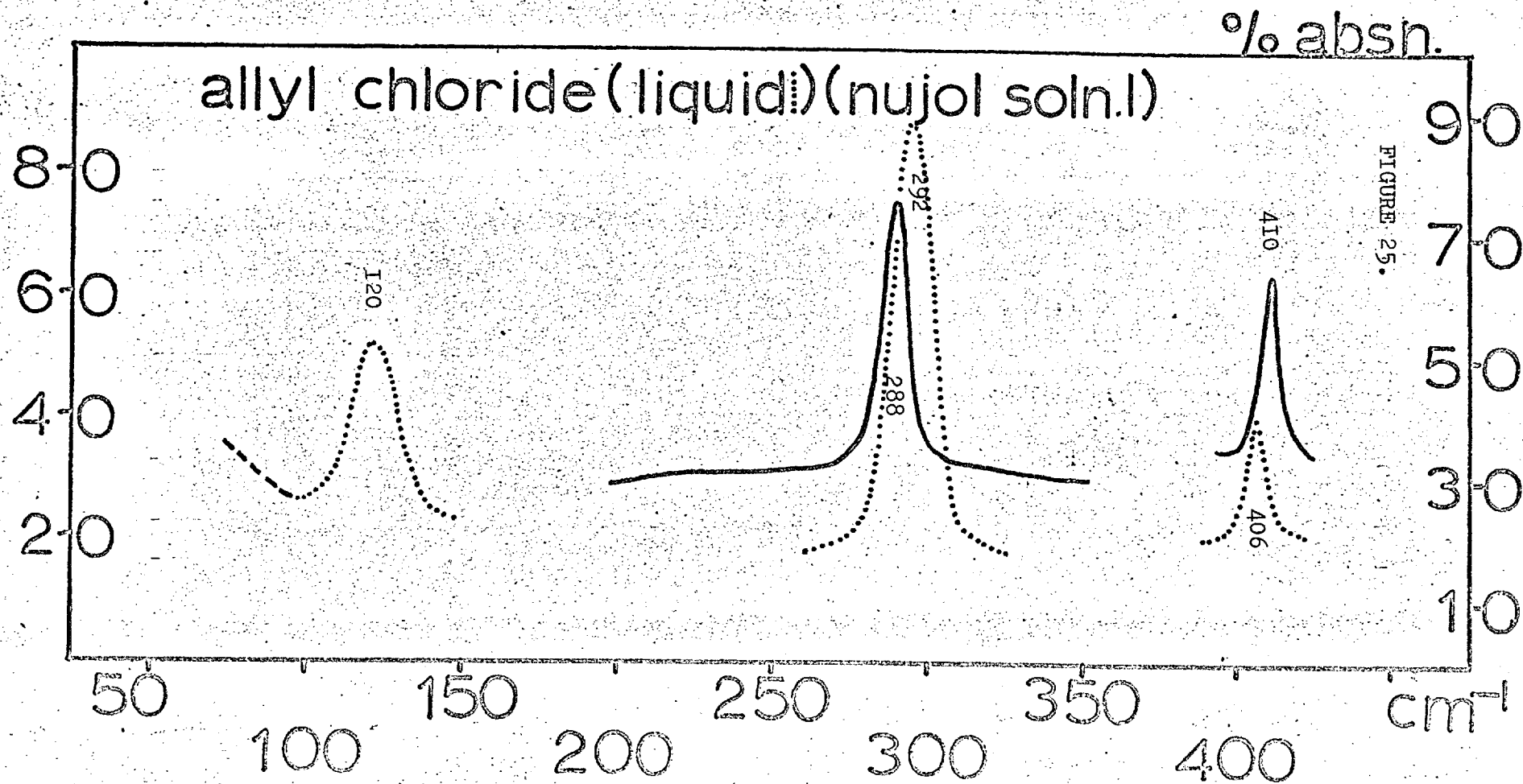
n-propyl iodide (solid)

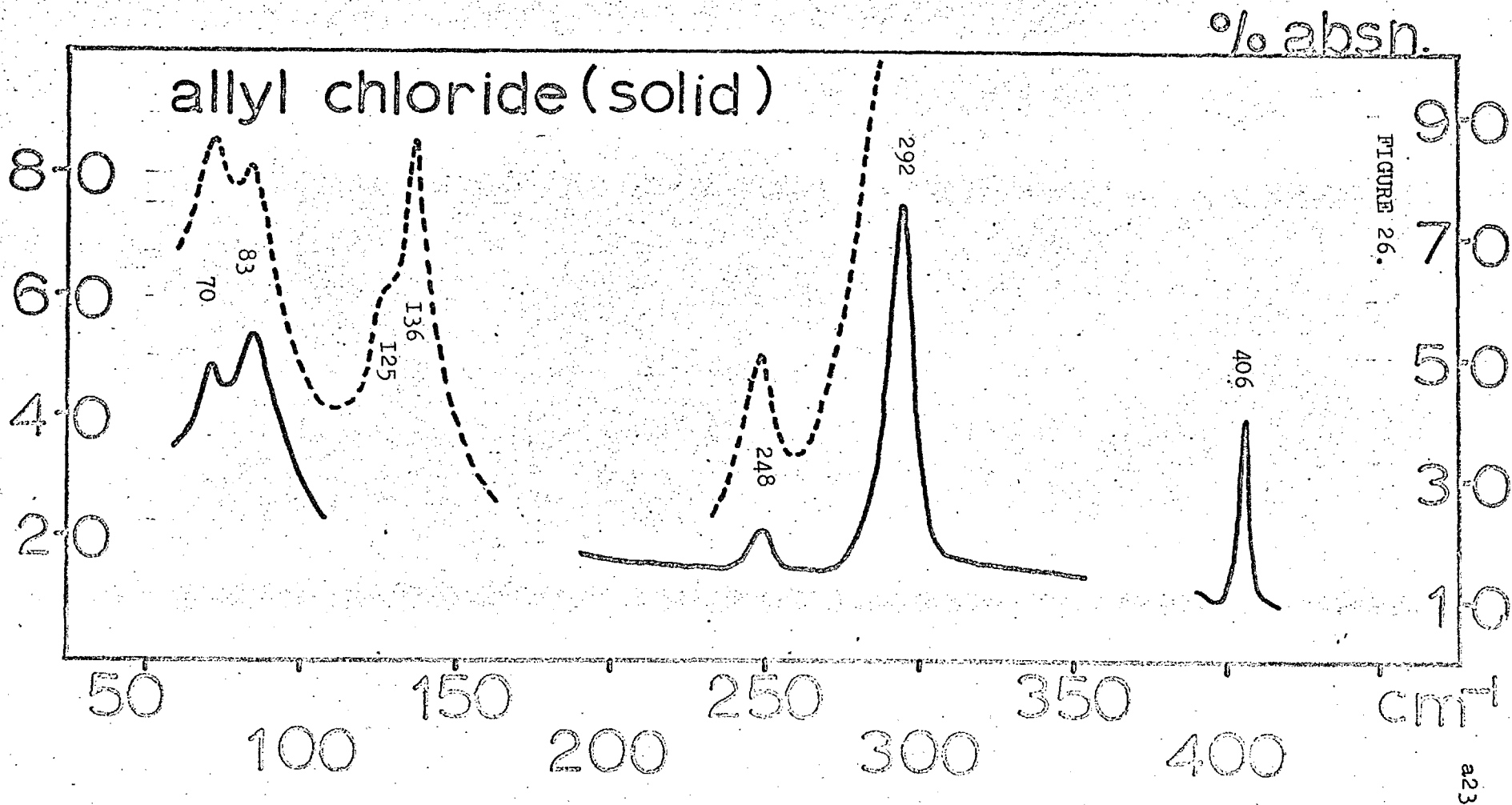
% absn.

FIGURE 21.









allyl bromide (gas 5cms Hg)

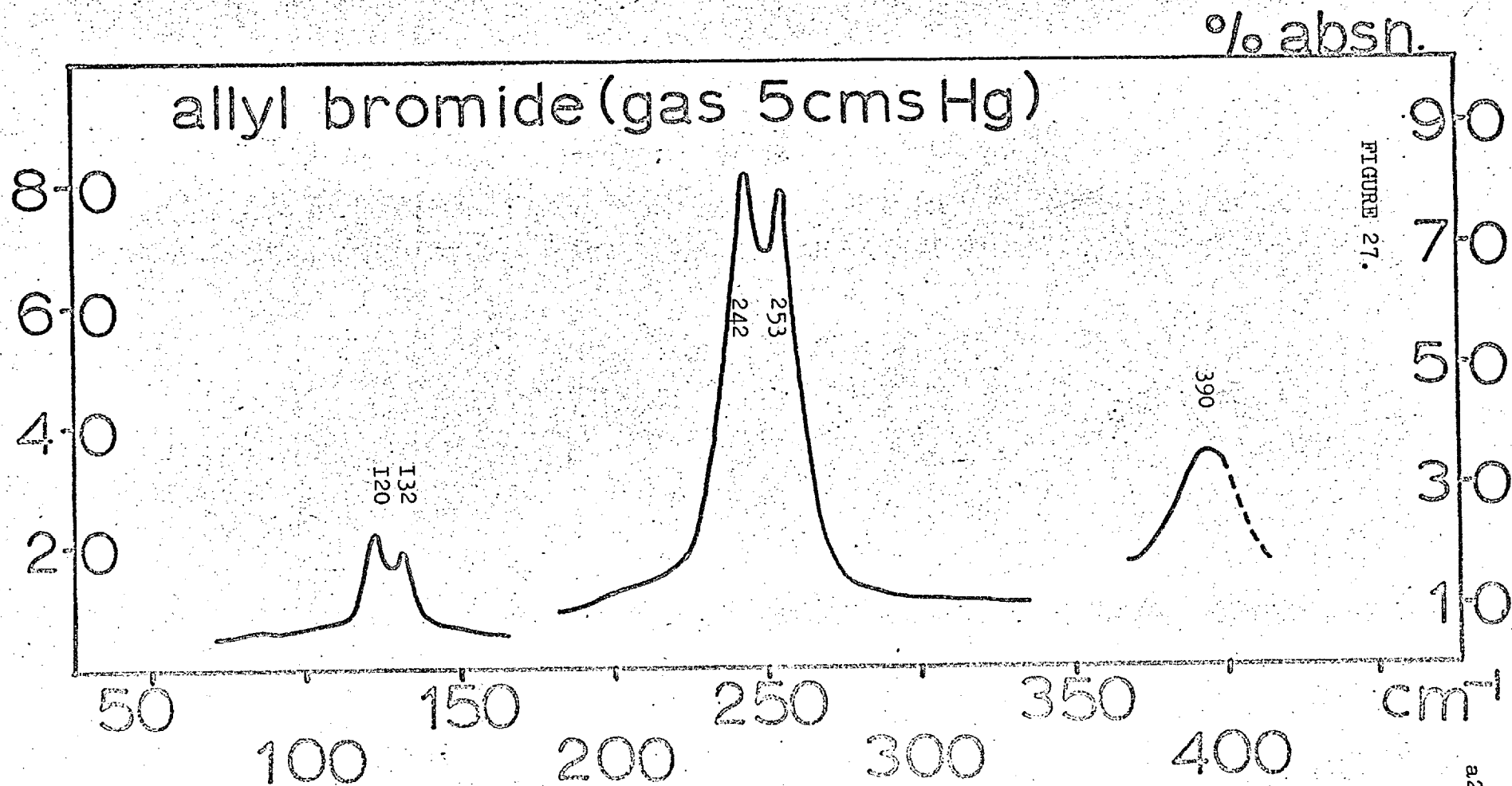
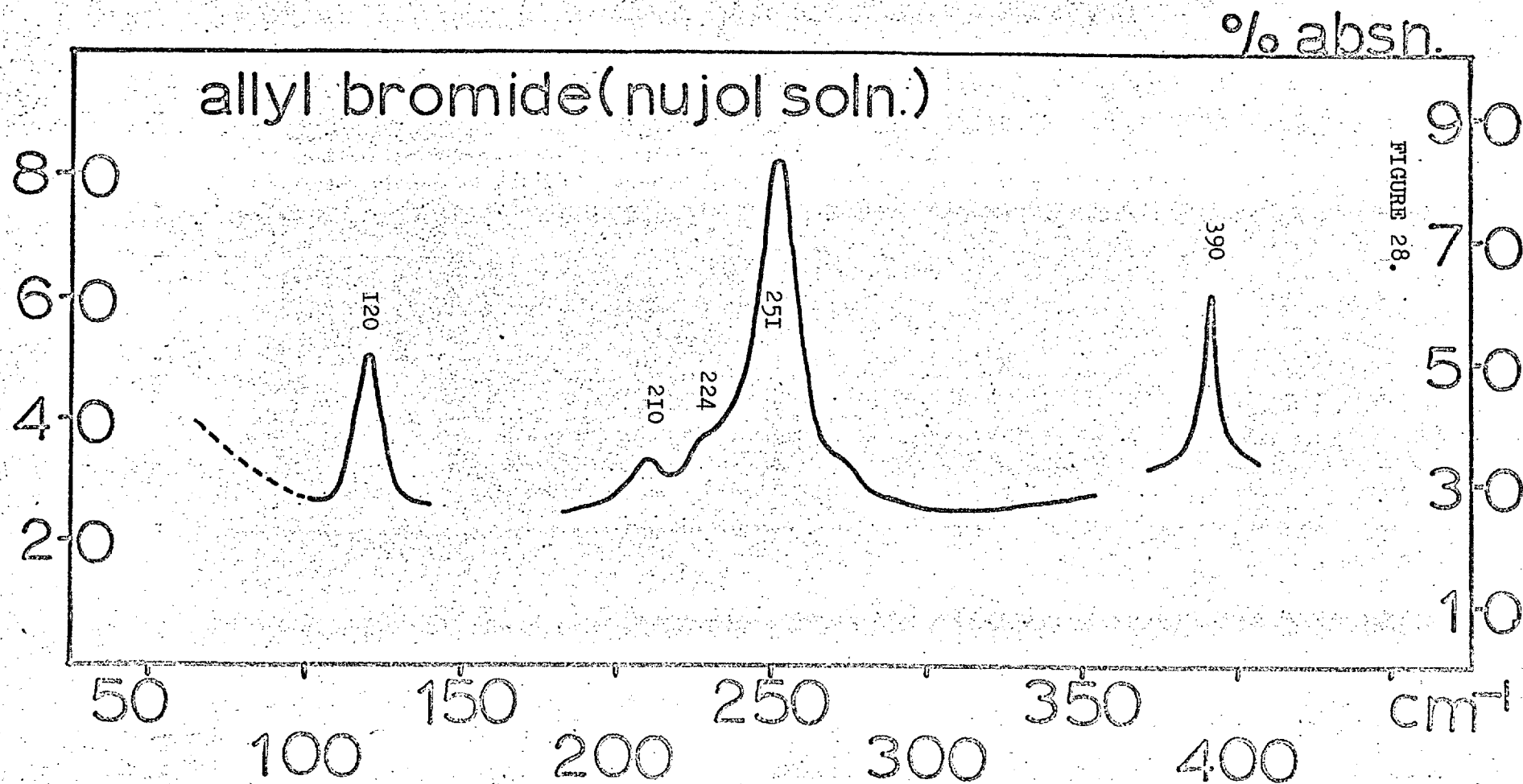


FIGURE 27.



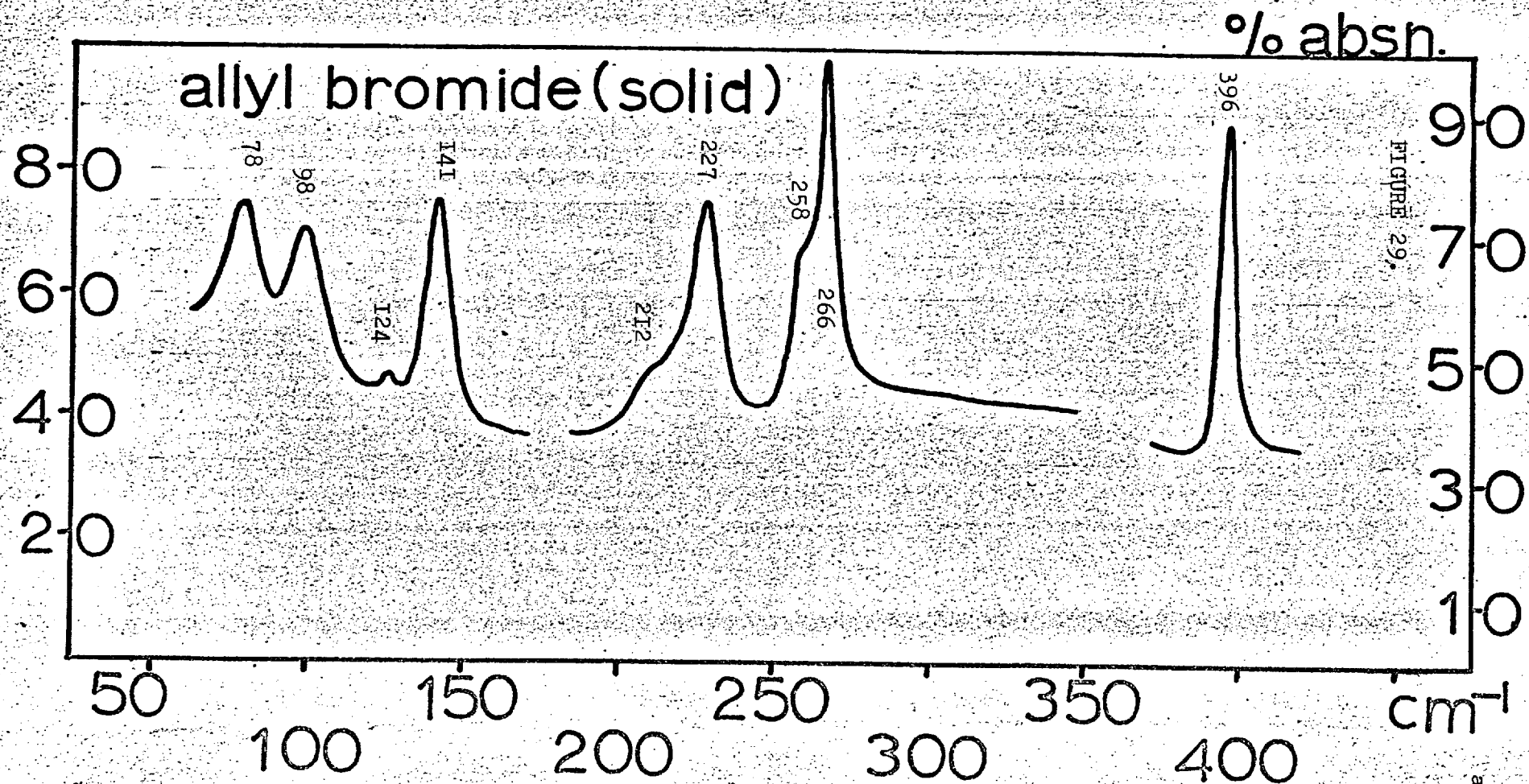


FIGURE 29.

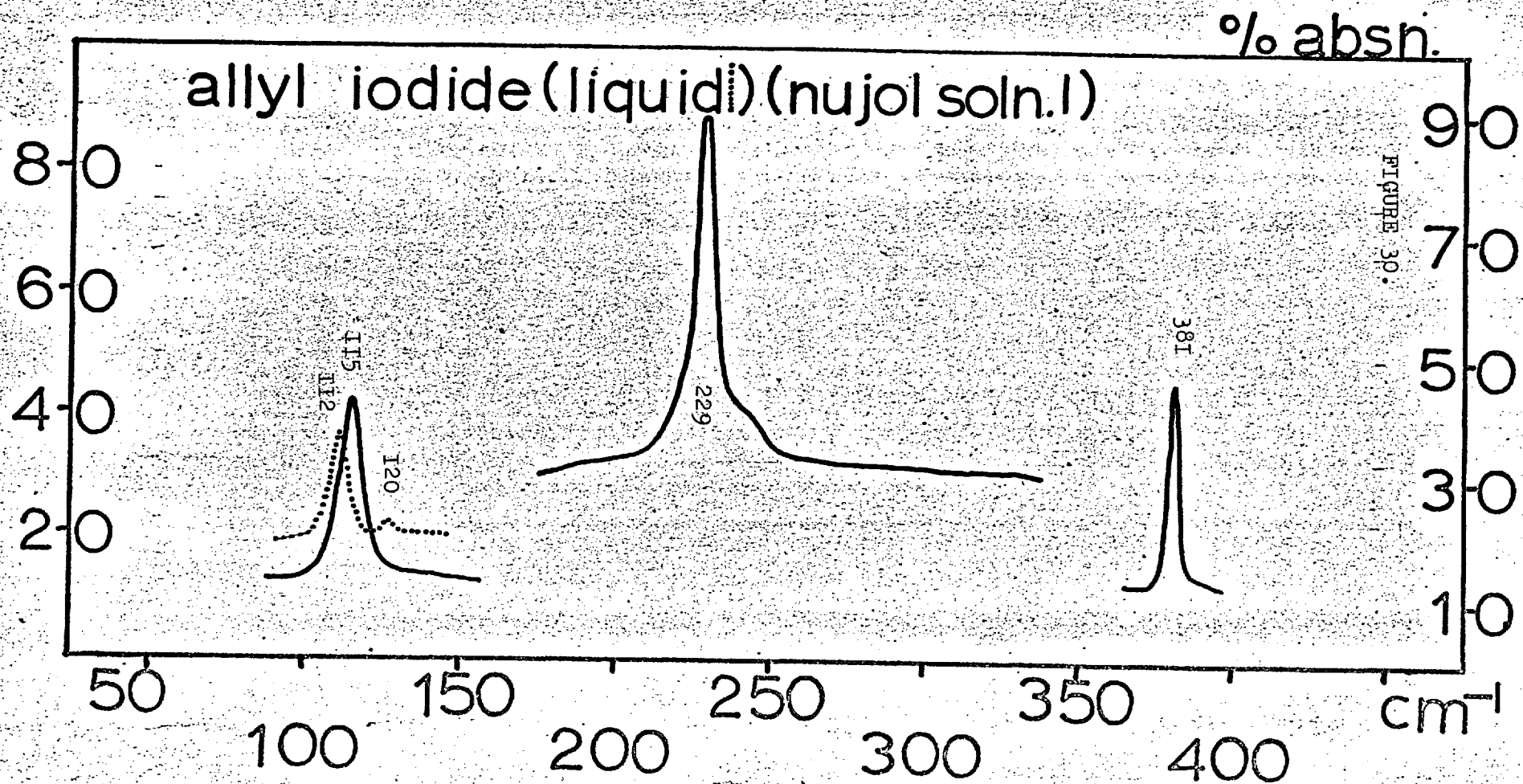


FIGURE 30.

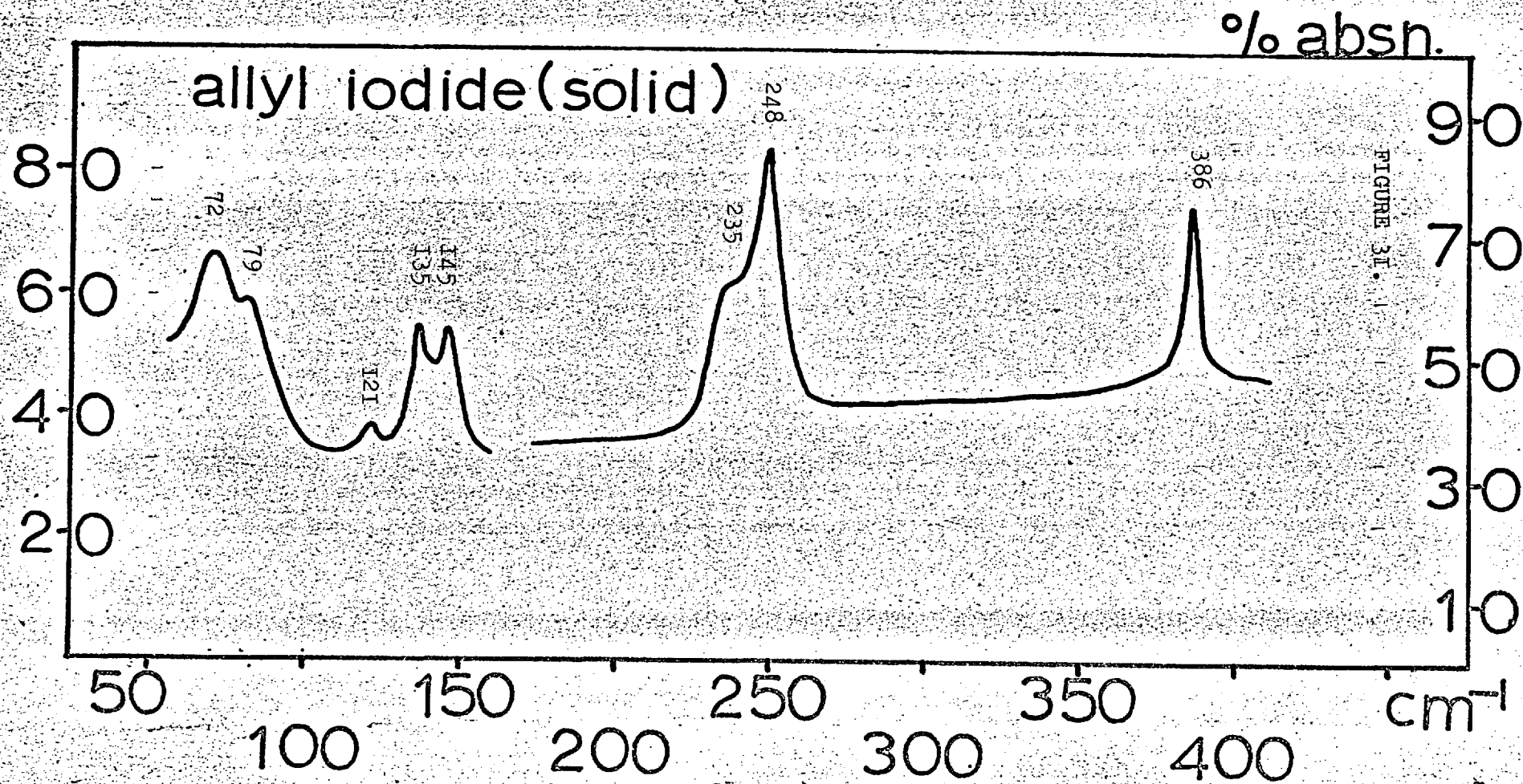


FIGURE 31.

n-PROPYL FLUORIDE --- GAS $\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$.

3 cms. gas pressure in 70 cm. path length cell.

Molecular sieve desiccant.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
2020	270-210	ILiF	464/2	Second order.
2021	"	"	"	"
2014	"	"	Wet sample.	
2034	"	"	Vac BG.	
2016	370-230	2NaF	321, 307, 294	(P, Q, R)
2017	"	"	276, 262	(P, R)
2015	"	"	Wet sample.	
2032	"	"	Vac BG.	
2018	260-170	2NaCl	222, 213, 197, 183	213=0-I (Q)
2019	230-170	"	222, 213, 197, 183	"
2013	260-170	"	Wet sample.	
2033	"	"	Vac BG.	
2026	200-120	2KCl	148, 139, 129	(P, Q, R)
2027	"	"	" " "	Repeat of 2026.
2012	"	"	Wet sample.	
2029	"	"	Vac BG.	
2030	"	"	Vac BG.	
2024	150-100	2KBr	146, 139, 130	2026 better.
2025	"	"	" " "	
2011	"	"	Wet sample.	
2028	"	"	Vac BG.	
2022	150-80	KBr/XQ	148, 139, 127	(P, Q, R)
2023	"	"	110, 97?, 84?	?=weak.
2010	"	"	Wet sample.	
2031	"	"	Vac BG.	

n-PROPYL CHLORIDE in a CCl₄ MATRIX.

Cryostat used. 1% or 2% molar solution as indicated.

RUN No.	FREQUENCY RANGE (cm ⁻¹)	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm ⁻¹)	COMMENTS.
I286	I90-I30	2KCl	clear.	1%
I287	"	"	Vac BG.	
I284	I50-I05	2KBr	I35, I21	1%
I285	"	"	Vac BG.	
I282	I90-90	KRS5/XQ	I56, I27, II5, I09, 97	1% I27=real.
I283	"	"	Vac BG.	
I461	200-I20	2KCl	clear.	pure CCl ₄ .
I462	"	"	Vac BG.	
I459	I50-I00	2KBr	clear.	pure CCl ₄ .
I460	"	"	Vac BG.	
I463	I80-80	KRS5/XQ	I54, II5, II0, 98	pure CCl ₄ .
I464	"	"	Vac BG.	
I465	370-230	INaF	(3I6vs) 250	pure CCl ₄ .
I466	"	"	Vac BG.	
I467	270-I75	2NaCl	250 (2I8)	pure CCl ₄ .
I468	"	"	Vac BG.	
I454	370-230	INaF	365, 3I6, 298, 247?	2% ?=doubtful.
I455	"	"	Vac BG.	
I456	270-I75	2NaCl	247?, 234?, 2I9	2% ?=doubtful.
I457	"	"	Vac BG.	
I452	I90-90	KRS5/XQ	I56, I27, I2I, II0	2% I27, I2I=real.
I453	"	"	Vac BG.	Both forms trapped.
I450	I90-I25	2KCl	I53	2% not real.
I449	I50-I05	2KBr	Vac BG.	
I447	"	"	confusing.	2%
I448	"	"	"	2%

n-PROPYL CHLORIDE --- GAS $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$.

70 cm. path length cell.

22 cms. gas pressure and molecular sieve desiccant used
except where stated otherwise.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
I027	370-230	2NaF	328 247	P_2O_5 desiccant
I028	"	"	Vac BG.	decomposed the
I029	300-190	INaCl	247, 228, 207, 187	halide giving
I030	"	"	Vac BG.	HCl.
I024	190-90	IKBr	146, 125, 104	"
I026	190-80	KRS5/XQ	104 83	"
I025	"	"	not plotted.	"
I045	370-230	2NaF	284 248, 237	CaSO_4 desiccant.
I046	"	"	Vac BG.	"
I047	"	INaF	not plotted.	"
I041	300-190	INaCl	280, 248, 237, 211, 217sh	"
I042	"	"	Vac BG.	"
I043	150-100	2KBr	134, 122 140sh	"
I044	"	"	Vac BG.	
I048	190-80	KRS5/XQ	142, 120 101	unreliable.
I049	"	"	Vac BG.	
2557	160-100	2KBr	121, 132 139sh	14cms. pressure.
2558	"	"	" " "	"
2559	"	"	" " "	7cms. pressure.
2560	"	"	" " "	2cms. pressure.
2561	"	"	Vac BG.	

n-PROPYL CHLORIDE --- LIQUID $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$.

RUN	FREQUENCY	RESTSTRAHLEN	BANDS OBSERVED.	COMMENTS.
No.	RANGE (cm^{-1})	FILTERS.	(cm^{-1})	
780b	450-340	ILiF	426 367	
780c	"	"	"	repeat of 780b.
780a	"	"	BG.	
514	370-230	2NaF	detector cone out of position.	
512	"	"	294 248	
511	"	"	BG.	
517	290-190	INaCl	285 248 213	edge of reststrahlen.
515	"	"	BG.	
516	"	"	sample evaporating.	
522	160-90	IKBr	136 124 108?	?=doubtful.
521	160-105	"	sample evaporating.	
520	160-90	"	BG.	
519	"	IKCl	141 124 107?	?=doubtful.
518	"	"	BG.	
525	150-80	KRS5/CsI	136 127 109?	?=doubtful.
523	150-60	"	BG.	
526	"	"	BG.	
2427	450-340	ILiF	425 363	
2426	"	"	BG.	
2428	370-230	2NaF	363 293 247	
2424	"	"	BG.	
2429	250-170	2NaCl	250 231? 215	?=doubtful.
2425	"	"	BG.	
2433	160-100	2KBr	139 127	
2430	"	"	BG.	
2432	160-95	IKBr	148? 140 127	?=doubtful.
2431	"	"	BG.	
2434	150-70	KRS5/XQ	141 122	
2435	"	"	BG.	
2350	150-100	2KBr	139 128	
2351	"	"	BG.	
2418	"	"	139 126	repeat of 2350.
2417	"	"	BG.	
2546	150-90	KBr/XQ cell	140 126	
2547	"	"	cyclohexane BG.	
2548	"	"	140 126	
2551	"	"	cyclohexane BG.	
2555	370-230	2NaF	291 247	dilute nujol soln.
2556	"	"	nujol BG.	

n-PROPYL CHLORIDE --- SOLID $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
553	360-230	2NaF	250	not frozen.
55I	"	"	296 248	not frozen.
550	"	"	BG.	
89I	360-220	"	unreliable.	
890	"	"	BG.	
895	300-200	INaCl	246	
894	"	"	BG.	
889	430-340	ILiF	367	
888	"	"	BG.	
893	180-100	IKCl		not frozen.
892	"	"	BG.	
885	300-200	INaCl		not frozen.
884	"	"	BG.	
887	160-110	IKCl		not frozen.
886	"	"	BG.	
2454	375-225	2NaF	362 25I 237?	also weak absns.
2448	"	"	362 25I	at 337, 327??
2449	375-280	"	363	
245I	"	"	BG.	
2453	240-165	2NaCl	240 209w	edge of reststrahlen.
2452	"	"	BG.	
2458	200-120	2KCl	147	
2457	150-105	2KBr	150 126w	edge of reststrahlen.
2456	"	"	150 126w	repeat of 2457.
2455	150-90	IKBr	150 122 107? ?=doubtful.	
2459	120-60	KRS5/XQ	109 93 83	
2460	"	"	BG.	

n-PROPYL BROMIDE --- GAS $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$.

7cms. gas pressure in 70cm. path length cell.

Molecular sieve desiccant.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
I872	245-I80	2NaCl	220, 208 I97, I92	best run.
I873	"	"	222, 209 I97, I92	Repeats of I872
I874	"	"	218, 207 I97, I92	at various
I875	"	"	218, 207 I97, I92	stages of
I876	"	"	218, 207 I97, I92	drying.
I870	"	"	Vac BG.	
I87I	"	"	Vac BG.	
I866	I55-I00	2KBr	I27, II7	
I868	"	"	I27, II5	better run.
I867	"	"	Vac BG.	
I869	"	"	Vac BG.	

n-PROPYL IODIDE --- GAS $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$.

3cms. gas pressure in 70cm. path length cell.

Molecular sieve desiccant.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
I860	240-I70	2NaCl	203, I93	doublet.
I86I	"	"	Vac BG.	
I863	I50-I00	2KBr	I40, I27, II6, I07?	?=doubtful.
I862	"	"	I40, I28, II5	
I864	"	"	Vac BG.	
I865	"	"	Vac BG.	

n-PROPYL BROMIDE --- LIQUID $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
738	450-350	ILiF	408	
740	"	"	BG.	
730	370-230	2NaF	314 270	
731	"	"	BG.	
732	300-190	INaCl	poor run.	
733	"	"	BG.	
734	"	"	276 224	repeat of 732.
735	260-190	"	224	"
736	300-190	"	BG.	
742	160-105	IKBr	I40? I29 II3	?=doubtful.
745	"	"	BG.	
743	"	"	sample evaporating.	
746	190-100	IKCl	I40? I32 II2	?=doubtful.
751	"	"	BG.	
747	"	"	I48? I32 II6	?=doubtful.
748	"	"	I48? I35 II6	"
727	180-90	2KRS5	Useless----	
726	"	"	higher orders.	
729	"	"	BG.	
883	150-100	IKBr	I31 III	
881	"	"	BG.	
880	"	"	I33 II0	repeat of 883.
878	"	"	BG.	
2436	370-230	2NaF	313 273	better than 730.
2443	"	"	BG.	
2414	150-100	2KBr	I28 II3	unreliable.
2412	"	"	BG.	
2356	"	"	I35 II2	repeat of 2414.
2358	"	"	BG.	
2549	150-90	KBr/XQ cell	confusing.	
2551	"	"	cyclohexane BG.	

n-PROPYL BROMIDE --- SOLID $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$.

RUN No.	FREQUENCY RANGE(cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
897	440-340	ILiF	clear.	
896	"	"	BG.	
901	370-230	2NaF	3I2 273vw	glass formed?
900	"	"	BG.	
899	300-190	INaCl	224	
898	"	"	BG.	
904	190-60	2KRS5	I06? 94 66	?=doubtful.
903	"	"	BG.	
902	"	"	BG.	
2440	370-230	2NaF	3I2 273w 230	edge of reststrahlen.
2436	"	"	3I3 273 230	liquid run.
2443	"	"	BG.	
2439	260-170	2NaCl	225 184	
2437	240-180	"	223	liquid run.
2438	"	"	BG.	
2444	230-160	"	BG.	
2441	150-105	2KBr	I30 II3	glass formed.
2446	"	"	BG.	
2442	120-70	KRS5/XQ	III 96	
2445	"	"	BG.	

n-PROPYL IODIDE ---- LIQUID $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
767	450-350	ILiF	396	
766	"	"	BG.	
770	370-230	2NaF	290 264	
769	"	"	288 268	poor run.
768	"	"	BG.	
772	310-230	INaCl	290 266	repeat of 773.
773	"	"		poor run.
77I	"	"	BG.	
I536	300-185	"	286 262 200	
I535	"	"	BG.	
I859	220-180	2NaCl	203	
I858	"	"	BG.	
765	300-190	INaCl	290 263 232w 196	poor run.
764	"	"	BG.	
763	180-90	IKCl	I3I	confusing.
762	"	"	BG.	
76I	"	IKBr	I32 II7	
760	"	"	BG.	
759	"	"	BG.	
779	150-90	2KRS5	useless.	
774	"	"	BG.	
775	"	"	useless.	
778	"	"	BG.	
2410	150-105	2KBr	I33	then a fault.
2408	"	"		poor and unreliable.
2407	"	"	BG.	
2550	150-90	KBr/XQ cell	I33 I2I	
255I	"	"	cyclohexane BG.	

n-PROPYL IODIDE ——— SOLID $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
993	440-350	ILiF	396	not frozen.
992	"	"	BG.	
99I	370-230	2NaF	288 260	not frozen.
990	"	"	BG.	
989	"	"	BG.	
9I2	"	"	288	
9II	"	"	BG.	
9I4	280-180	INaCl	203	
9I3	"	"	BG.	Both forms present? better than 9I4.
9I8	I90-60	2KRS5	I47 82 66	
9I7	"	"	BG.	
2465	370-230	2NaF	288 262vw	
246I	"	"	BG.	
2464	260-I70	2NaCl	205 I90w	
2462	"	"	" "	
2466	I50-I05	2KBr	I46	
2467	I20-70	KRS5/XO	I04? 80	
2463	"	"	BG.	

ALLYL CHLORIDE --- GAS $\text{CH}_2=\text{CH}.\text{CH}_2\text{Cl}.$

70cm. path length cell with polythene windows unless
stated otherwise. Molecular sieve desiccant.

**=PTFE windows. *=6cms. gas pressure.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
I748	370-230	2NaF	316vw, 288, 280 244vw *	(wet).
I747	"	"	" " " "	3cms. (wet).
I749	"	"	Vac BG.	
I744	"	"	unplotted.	
I745	"	"	"	
I746	"	"	"	
I74I	"	"	Vac BG--polythene BG--PTFE BG.	
	I50-I05	2KBr	Water bands present.	
I75I	370-230	2NaF	316vw 288, 280 244vw	Icm. (wet) **
I750	"	"	Vac BG.	**
I742	"	"	316 285 244	I5cms. (wet) **
I743	"	"	Vac BG.	**
I756	I50-90	KBr/XQ	I32, I27, II3, IO4, IOO	*
I757	"	"	Vac BG.	
I754	"	"	I3I, I27, II6, IO4, IOO	* PTFE windows.
I755	"	"	Vac BG.	
I752	"	"	I3I, I27, I20, IO4, IOO	* PTFE windows.
I753	"	"	Vac BG.	
I767	440-360	ILiF	404 broad	I2cms.
I766	"	"	VacBG.	
I760	370-230	2NaF	316vw 288, 280 244vw	3cms.
I76I	"	"	316vw 288, 280 240vw	*
I762	"	"	Vac BG.	
I764	I50-II0	2KBr	I27, II9	I2cms.
I765	"	"	I27, I20	"
I763	"	"	Vac BG.	
I759	I50-90	KBr/XQ	I29, I20	I2cms.
I758	"	"	Vac BG.	

ALLYL CHLORIDE --- LIQUID or NUJOL SOLN. $\text{CH}_2=\text{CH}.\text{CH}_2\text{Cl}.$
 N=nujol solution. L=liquid.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
I719	440-360	ILiF	410	N
I718	"	"	BG.	
I715	370-230	2NaF	288 244vw	N v.thick.
I714	"	"	BG.	
I717	"	INaF	288	N thick.
I716	"	"	BG.	
I740	240-175	2NaCl	clear	N
I739	"	"	BG.	
I738	190-120	2KCl	poor run.	N
I737	"	"	BG.	
I736	150-110	2KBr	wet.	N
I734	"	"	BG.	
I733	150-90	CsI/XQ	I22	N unreliable.
I732	"	"	BG.	
I729	"	KRS5/XQ	confusing.	N unreliable.
I728	"	"	BG.	
I726	120-60	2CsI	96	N 286/3
I727	"	"	BG.	
I723	150-90	KBr/XQ	I36 II8 II3 99	N confusing and
I725	"	"	I36 I24 II3 99	N unreliable.
I724	"	"	BG.	
I722	"	"	BG.	
2490	450-360	ILiF	406	L N_2 cooled.
2486	"	"	BG.	
2488	370-230	2NaF	292	L N_2 cooled.
2487	"	"	BG.	
2489	240-175	2NaCl	clear.	L N_2 cooled.
2485	"	"	BG.	
2494	190-150	2KCl	clear.	L N_2 cooled.
2491	"	"	BG.	
2493	150-100	2KBr	I30? I20	L ?=doubtful.
2492	"	"	BG.	
2495	140-95	KBr/XQ	II9	L repeat of I725.
2498	"	"	BG.	
2496	100-60	KRS5/XQ	General absorption.	L confusing.
2497	"	"	BG.	
2552	150-90	KBr/XQ cell	I20	L
2553	"	"	cyclohexane BG.	

ALLYL CHLORIDE --- SOLID $\text{CH}_2=\text{CH}.\text{CH}_2\text{Cl}$.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
2528	440-350	ILiF	406	
2527	370-230	2NaF	292 248w	medium.
2533a	"	"	292 248s	thick.
2533b	270-230	"	248s	v.thick.
2529	260-170	2NaCl	inconsistent.	
2532	"	"	"	
2531	"	"	BG.	
2536	190-120	2KCl	I36	thick.
2539	150-105	2KBr		too thin.
2540	"	"	BG.	
2537	140-90	KBr/XQ	General absorption--too thick.	
2538	"	"	unreliable.	
2525	"	"	too thin.	repeat of 2538.
2534	105-60	KRS5/XQ	83 70	thick.
2526	"	"	84 69	thin.
2535	150-90	IKBr	not plotted.	

ALLYL IODIDE --- SOLID $\text{CH}_2=\text{CH}.\text{CH}_2\text{I}$.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
2470	420-330	ILiF	386	
2483	"	"	BG.	
2484	"	"	BG.	
2468	370-225	2NaF	248 235sh	
2481	"	"	BG.	
2469	265-165	2NaCl	248 235sh	
2482	"	"	BG.	
2472	190-120	2KCl	I46 I36	
2480	"	"	BG.	
2471	150-100	2KBr	I44 I35 I2Iw	
2479	"	"	BG.	
2477	"	"	BG.	electronics faulty.
2473	120-90	KBr/XQ	poor run.	
2476	"	"	BG.	
2474	105-60	KRS5/XQ	79 72	
2475	"	"	BG.	

ALLYL BROMIDE --- GAS $\text{CH}_2=\text{CH}.\text{CH}_2\text{Br}.$

70cm. path length cell. Molecular sieve desiccant.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
I932	450-350	2LiF	bad interference.	5cms. pressure.
I933	"	"	"	"
I934	"	"	Vac BG.	
I935	"	"	Vac BG.	
I938	370-230	2NaF	254, 243.5	5cms. pressure.
I939	"	"	254, 242	"
I940	"	"	Vac BG.	
I941	"	"	Vac BG.	
I936	270-180	2NaCl	253, 242	5cms. pressure.
I937	"	"	Vac BG.	
I958	130-60	KRS5/XQ	119 and interference.	12cms. pressure.
I959	"	"	Vac BG.	
I956	150-90	KBr/XQ	interference.	12cms. pressure.
I957	"	"	Vac BG.	
I955	190-120	2KCl	bad interference.	12cms. pressure.
I953	"	"	"	"
I954	"	"	Vac BG.	
I950	150-100	2KBr	bad interference.	12cms. pressure.
I951	"	"	"	"
I952	"	"	Vac BG.	
I964	370-230	2NaF	253, 242	8cms. pressure.
I963	"	"	252, 244	12cms. pressure.
I965	"	"	poor run.	4cms. pressure.
I966	"	"	Vac BG.	
I960	450-350	2LiF	390	12cms. pressure.
I961	"	"	Vac BG.	
I962	"	"	Vac BG.	
I967	270-170	2NaCl	254, 242	12cms. pressure.
I968	"	"	Vac BG.	
I944	200-130	2KCl	clear.	5cms. pressure.
I945	"	"	Vac BG.	

ALLYL BROMIDE (GAS) continued....

RUN No.	FREQUENCY RANGE (cm ⁻¹)	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm ⁻¹)	COMMENTS.
I942	I50-I05	2KBr	I32, I20	5cms. pressure.
I943	"	"	Vac BG.	
I946	I25-85	KBr/XQ	I20	5cms. pressure.
I947	"	"	Vac BG.	
I948	I25-70	KRS5/XQ	II9 and interference.	5cms. pressure.
I949	"	"	Vac BG.	
2344	I90-I25	2KCl	Poor and	7cms. pressure.
2345	"	"	unreliable.	"
2346	"	"	Vac BG.	
234I	I50-I00	2KBr	I33, II9	7cms. pressure.
2342	"	"	I33, I20	"
2343	"	"	Vac BG.	
2339	I25-85	KBr/XQ	II9.5	7cms. pressure.
2340	"	"	Vac BG.	
2337	I30-60	KRS5/XQ	II9.5 and interference.	7cms. pressure.
2338	"	"	Vac BG.	
2365	I90-I30	2KCl	I34	6cms. pressure.
2364	"	"	Vac BG.	
2367a	I50-I05	2KBr	I34, I20	6cms. pressure.
2367b	"	"	I38, I22	poor run.
2366	"	"	Vac BG.	
2369	I20-80	KBr/XQ	confusing.	6cms. pressure.
2368	"	"	Vac BG.	
237I	I25-60	KRS5/XQ	II9 and interference.	6cms. pressure.
2370	"	"	Vac BG.	

ALLYL BROMIDE --- LIQUID or NUJOL SOLN. $\text{CH}_2=\text{CH}.\text{CH}_2\text{Br}.$
 N=nujol solution. L=liquid.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
I973	440-340	2LiF	388	N
I975	"	"	392	N repeat of I973.
I974	"	"	BG.	
I969	370-230	2NaF	25I	N
I970	"	"	BG.	
I971	260-I90	2NaCl	25I, 224w sh, 2I0w	N
I972	"	"	BG.	
I984	I40-90	KRS5/XQ	I20 and absorption below 80 cm^{-1} .	N
I985	"	"	BG.	
I982	I25-85	"	I19 99?	N ?=doubtful.
I983	"	"	BG.	
238I	I90-I20	2KCl	clear.	L
2378	"	"	BG.	
I978	I90-I30	"	clear.	N
I979	"	"	BG.	
2386	I50-I05	2KBr	confusing.	L
2383	"	"	BG.	
I976	"	"	I20	N poor run.
I977	"	"	BG.	
I986	I05-60	2KRS5	84	N 252/3
I988	"	"	BG.	

ALLYL BROMIDE --- SOLID $\text{CH}_2=\text{CH}.\text{CH}_2\text{Br}.$				
RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
2499	430-340	ILiF	396	
2523	"	"	BG.	
25II	300-230	2NaF	266 258sh	
25IO	"	"	266 258sh	repeat of 25II.
2500	370-230	2NaF	266	too thick.
2522	"	"	BG.	
25I2	265-I60	2NaCl	265 227	edge of reststrahlen.
2524	"	"	BG.	
25I3	I80-I60	"	clear.	
25I4	I90-I20	2KCl	I4I	
252I	"	"	BG.	
25I5	I50-I05	2KBr	I4I I24vw	
2520	"	"	BG.	
25I6	I30-85	KBr/XQ	I24vw 98	
25I9	"	"	BG.	
25I7	I05-65	KRS5/XQ	94 78	
25I8	"	"	BG.	

ALLYL IODIDE --- LIQUID or NUJOL SOLN.

 $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{I}$.

N=nujol solution. L=liquid.

RUN No.	FREQUENCY RANGE (cm^{-1})	RESTSTRAHLEN FILTERS.	BANDS OBSERVED. (cm^{-1})	COMMENTS.
2006	450-340	2LiF	38I	N
2007	"	"	BG.	
2004	"	"	interference.	N
2005	"	"	BG.	
2008	205-I75	1LiF	380/2	N second order.
2009	"	"	BG.	
2000	370-230	2NaF	230	N
2001	"	"	BG.	
2002	270-I70	2NaCl	229	N
2003	"	"	BG.	
I995	I90-I20	2KCl	clear.	N
I994	"	"	"	N repeated I995.
I996	"	"	BG.	
I997	I50-I05	2KBr	poor run.	N repeated I998.
I998	"	"	I20? III	N I20 doubtful.
I999	"	"	BG.	
I992	II5-90	KBr/XQ	II2	N edge of reststrahlen.
I993	"	"	BG.	
I987	I00-60	2KRS5	76	N 229/3
I988	"	"	BG.	
I989	I50-75	KRS5/XQ	II2 99?	N ?=doubtful.
I990	"	"	II2	N
I991	"	"	BG.	
2363	I50-95	KBr/XQ	II5	N
2362	"	"	BG.	
2395	I30-65	KRS5/XQ	II5	N
2392	"	"	BG.	
2380	I90-I20	2KCl	clear.	N
2378	"	"	BG.	
2385	I50-I05	2KBr	poor run.	L repeated 2478.
2383	"	"	BG.	
2478	"	"	II2	L
2479	"	"	BG.	

BIBLIOGRAPHY.

1. BENEDICT, CLAASSEN and SHAW
J.Res. Natl. Bur. Stands. 49 91 (1952)
2. RANDALL, DENNISON, GINSBURG and WEBER
Phys. Rev. 52 160 (1937)
3. BLAINE
J.Res.Natl. Bur. Stands. 67C 207 (1963)
4. OETJEN, HAYNIE, WARD, HANSLER, SCHAUWECKLER and BELL
J O. S. A. 42 559 (1952)
5. MIZUSHIMA, MORINO and NAKAMURA
Sci. Pap. Inst.Phys.Chem.Res. Tokyo 37 205 (1940)
6. KOMAKI, ICHISHIMA, KURATANI, MIYAZAWA, SHIMANOUCHI and MIZUSHIMA
Bull.Chem. Soc. Japan 28 330 (1955)
7. MIZUSHIMA, SHIMANOUCHI, MIYAZAWA, ABE and YASUMI
J.Chem. Phys. 19 1477 (1951)
8. BROWN and SHEPPARD
Trans. Far. Soc. 50 1164 (1954)
9. GOUBEAU and PAJENKAMP
Acta.Phys. Austriaca 3 283 (1949)
10. LAMB
Z. Elektrochem. 64 135 (1960)
11. MORINO and KUCHITSU
J.Chem.Phys. 28 175 (1957)
12. SARACHMAN
J.Chem. Phys. 39 469 (1963)
13. HIROTA
J.Chem.Phys. 37 283 (1962)
14. SAGE and KLEMPERER
- unpublished work.
15. GOUBEAU
Chem.Ber. 81 287 (1948)
16. SMITH, SAUNDERS, NIELSON and FERGUSON.
J.Chem. Phys. 20 847 (1952)
17. HODGMAN
Handbook of Chemistry and Physics.Chem.Rubber Pub.Co.Cleveland
18. NAKAMURA
J.Chem.Soc. Japan 60 1010 (1939)
19. KOHLRAUSCH
"Ramanspektren" Becker and Erlor, Leipzig 1943.
20. RADINGER and WITTEK
Z.Phys.Chem. 45B 329 (1940)
21. BADGER and ZUMWALT
J.Chem.Phys. 6 711 (1938)
22. HERZBERG
"Infrared and Raman spectra" Van Nostrand, New York 1945.
23. GERHARD and DENNISON
Phys.Rev. 43 197 (1932)
24. FATELEY and MILLER
Sp.Acta. 17 857 (1961)
25. HERSCHBACH
J.Chem. Phys. 31 91 (1959)
26. STEJSKAL and GUTOWSKY
J.Chem.Phys. 28 388 (1958)

27. BHAGAVANTIAM and VENKATARAYUDU
"Theory of groups and its application to physical problems"
Andhra University Press 1951.
28. GOLDEN and BRIGHT-WILSON Jr.
J.Chem.Phys. 16 669 (1948)
29. HIROTA -unpublished work.
30. MIZUSHIMA
"Structure of molecules and internal rotation" Academic Press 1954.
31. BROWN, SHEPPARD and SIMPSON
Disc.Far.Soc. 9 261 (1950)
32. BROWN, SHEPPARD and SIMPSON
Phil.Trans. Far.Soc. A247 35
33. BROWN and SHEPPARD
Trans.Far.Soc. 48 128 (1952)
34. NAKAGAWA and MIZUSHIMA
J.Chem.Phys. 21 2195 (1953)
35. SILVER and WOOD
Trans.Far.Soc. 59 588 (1962)
36. SUTTON, BOWEN and GILCHRIST
Trans.Far.Soc. 51 1341 (1955)
37. KOHLRAUSCH and STOCKMAIR
Z.Phys.Chem. 29B 292 (1935)
38. BACHER and WAGNER
Z.Phys.Chem. 43B 191 (1939)
39. KAHOVEC and KOHLRAUSCH
Z.Phys.Chem. 46B 165 (1940)
40. THOMPSON and TORKINGTON
Trans.Far.Soc. 42 432 (1946)
41. SHARIPOV and PENTIN
Vest.Mosk.Univ. Ser.2 Khimii. 18 No.4 (1963)
42. HERSCHBACH and KRISHER
J.Chem.Phys. 28 728 (1958)
43. BELLAMY
"Infrared spectra of complex molecules" Methuen 1962
44. HARRIS
Sp.Acta. 20 1129 (1964)
45. BRAND and WILLIAMSON
Disc.Far.Soc. 35 184 (1963)
46. SHEPPARD
J.Chem.Phys. 17 76 (1949)
47. PITZER
J.Res.Natl.Bur.Stands. 38 191 (1947)
48. LORD
J. O. S. A. 43 1079 (1953)
49. SVEROLOV
Dok. Akad. Nauk. SSSR. 106 80 (1956)
50. THOMPSON and TORKINGTON
J.Chem.Soc. 303 (1944)
51. CUNLIFE-JONES
Sp.Acta. 21 245 (1965)
52. LIN and SWALEN
Rev.Mod.Phys. 31 841 (1959)
53. PITZER and GWINN
J.Chem.Phys. 10 428 (1942)
54. HERSCHBACH
"Tables for the internal rotation problem" Dept.of Chem.Harvard 1957

55. POPLÉ
Qu.Rev. 11 273 (1957)
56. LIBBY
J.Chem.Phys. 35 1527 (1961)
57. NISHIKAWA, ITOH and SHIMODA
J.Chem.Phys. 23 1735 (1955)
58. LIDE
J.Chem.Phys. 27 343 (1957)
59. SWALEN
J.Chem.Phys. 23 1739 (1955)
60. LIN, KILB and WILSON
J.Chem.Phys. 26 1695 (1957)
61. KARPLUS and PARR
J.Chem.Phys. 38 1547 (1963)
62. WILSON
Adv.Chem. Phys. 2 367
63. MANN and PLYLER
J.Chem.Phys. 21 1116 (1953)
64. WARD and WARD
J.Mol.Spect. 12 289 (1964)
65. LIDE
J.Chem.Phys. 29 1426 (1958)
66. KISTIAKOWSKY and RICE
J.Chem.Phys. 8 610 (1940)
67. HERSCHBACH
J.Chem.Phys. 25 358 (1956)
68. LIDE
J.Chem.Phys. 30 37 (1959)
69. KASUYA
J.Phys. Soc. Japan 15 1273 (1960)
70. This work.
71. EYRING
J.Amer.Chem.Soc. 54 3191 (1932)
72. MASON and KREEVOY
J.Amer.Chem.Soc. 77 5808 (1955)
73. VAN DRANEN
J.Chem.Phys. 20 1982 (1952)
74. WILSON
Proc.Natl. Acad.Sci. 43 816 (1957)
75. LASSETRE and DEAN
J.Chem.Phys. 17 317 (1949)
76. OOSTERHOFF
Disc.Far.Soc. 10 79 (1951)
77. PAULING
Proc.Natl.Acad.Sci. 44 211 (1958)
78. SMITH
J.Chem.Phys. 17 139 (1949)
79. EYRING
J.Amer.Chem.Soc. 61 1876 (1939)
80. HARRIS and HARRIS
J.Chem.Phys. 31 1450 (1959)
-