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A SPECTROSCOPIC SEARCH FOR
ABSORPTION DUE TO AMMONIA DIMERS
IN THE FAR INFRA RED REGION OF
THE SPECTRUM

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A Spectroscopic Search for Absorption

Due to Ammonia Dimers in the far

Infra Red Region of the Spectrum

ABSTRACT

The experimental work reported in this thesis has involved the use of a fourier transform Michelson interferometer in a spectroscopic search for absorption due to ammonia dimers in the far infra red region of the spectrum.

Two types of gas cell have been used, fixed path length gas cells and a non-resonant spherical cavity. The fixed path length gas cells gave path lengths of 1.2 cm, 3.2 cm, and 16.4 cm. The non-resonant spherical cavity enabled long path lengths ($\sim 2\text{m}$) to be achieved.

The measurements have been made in the temperature range of 184k to 300k and pressure range of 10 torr to 3000 torr.

Spectral absorption features, whose temperature dependencies at constant density of ammonia molecules are consistent with them being associated with ammonia dimers, have been found at frequencies of 50, 70 and 90 cm^{-1} . More supporting evidence come from the binding energies calculated (of the order 3 K CAL/MOLE) from the pressure and temperature dependence of broad band spectral absorption in the frequency region of 20 to 55 cm^{-1} .

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CHAPTER 1

MOTIVES FOR THE RESEARCH PROJECT.

If ammonia dimers are constituents of the atmospheres of the planets Jupiter and Saturn, or any other planets which have ammonia as an atmospheric constituent, then the dimers will play a role in the energy balance of these planets if they absorb electro-magnetic radiation or if they contribute latent heat.

Therefore knowledge of their absorption coefficients will be needed in order to interpret measurements made of the atmospheric absorption on these planets. Also improved knowledge of their properties will add some enlightenment to long standing problems of reconciling line shape models with experimental observations since many such tests have been made with spectra of ammonia.^{16, 17}

The observation of features near 10CM^{-1} and 30CM^{-1} reported in a previous publication¹ by GYMESTAD provided a further incentive for this investigation.

CHAPTER 2

THE AMMONIA MONOMER AND DIMER MOLECULES.

As this investigation is concerned with the far infra-red absorption spectra of ammonia and its Dimer a brief description of their possible geometries and their present day theoretical absorption predictions will be given in this chapter.

2.1. The Ammonia Monomer(NH₃) Geometry and Spectrum

2.1.1 The ammonia molecule is in the form of a shallow tetrahedron about 1 angstrom on a side and 0.4 angstrom high (see fig. 1). The H-N-H angle being 107°.

The moment of inertia, I_A, about the internuclear axis is 4.4×10^{-40} gm cm² and the moments of inertia, I_B, about the axes at right angles to the internuclear axis and passing through the centre of gravity are 2.8×10^{-40} gm cm².

2.1.2 Far Infrared Absorption Spectrum

The NH₃ molecule is a symmetrical top with a permanent electric dipole moment equal to 1.468 debye. The only contributions to absorption by the NH₃ molecule in the spectral region of 0 to 2000 cm⁻¹ (the region of investigation) are from the pure rotation spectrum, inversion splitting of the of the ν_2 fundamental vibrational resonance (see fig. 1), and inversion splitting of the $2\nu_2$ harmonic.

The rotational spectrum is characterized by the moments of inertia of the molecule, the line spacing being given by $2B$ where B , known as the rotational constant is equal to $\frac{h}{8\pi^2 c I_e}$ cm⁻¹.

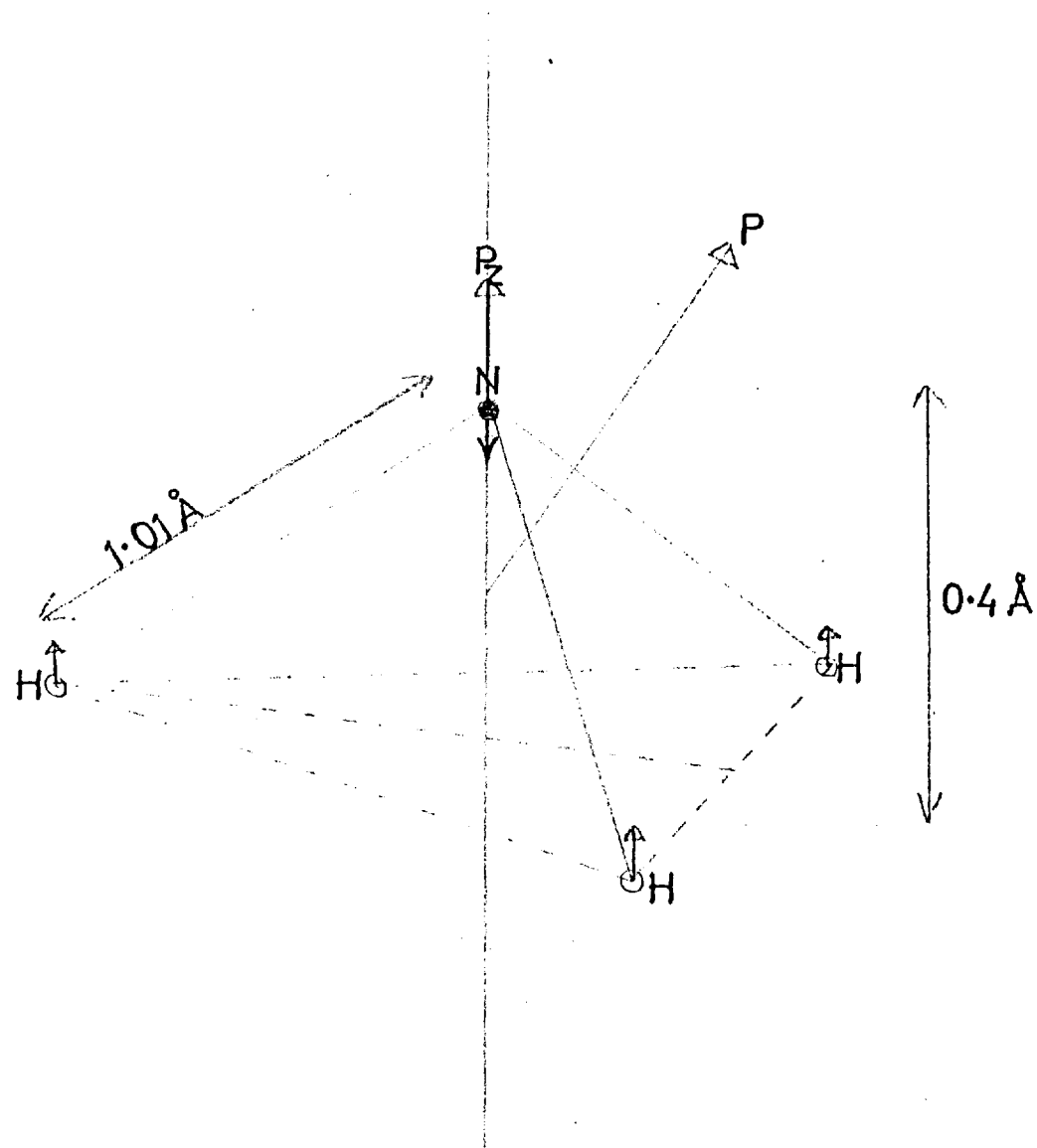


Fig1 The Ammonia Monomer Molecule

The other rotational constant is A equal to $\frac{h}{8\pi^2 I_A} \text{cm}^{-1}$.

The thermal distribution of the rotational levels, in thermal equilibrium, is given by the general formula $N_{J,K} \sim g_{J,K} e^{-\frac{E}{kT}}$ where E, a function of B, is the energy level and $g_{J,K}$ the statistical weight. Hence the pure rotation absorption spectrum has the form shown in figure 2. (See appendix B for a fuller theoretical treatment).

The NH_3 molecule has four fundamental vibrations namely $\nu_1 = 3337 \text{ cm}^{-1}$, $\nu_2 = 950 \text{ cm}^{-1}$, $\nu_3 = 3414 \text{ cm}^{-1}$, and $\nu_4 = 1628 \text{ cm}^{-1}$ (see figure 3). All of these vibrational levels are split into two, this is due to inversion splitting. This splitting is due to the fact that there are two equilibrium positions for the N atom at the two sides of the H_3 plane (see fig. 1). The splittings for the ν_2 mode and the $2\nu_2$ harmonic are 35 and 284 cm^{-1} respectively. (see Appendix B for a fuller theoretical treatment).

Pressure = 1152 Torr
Temperature = 251 K
Path Length = 1.16 cm
Resolution = 1 cm⁻¹

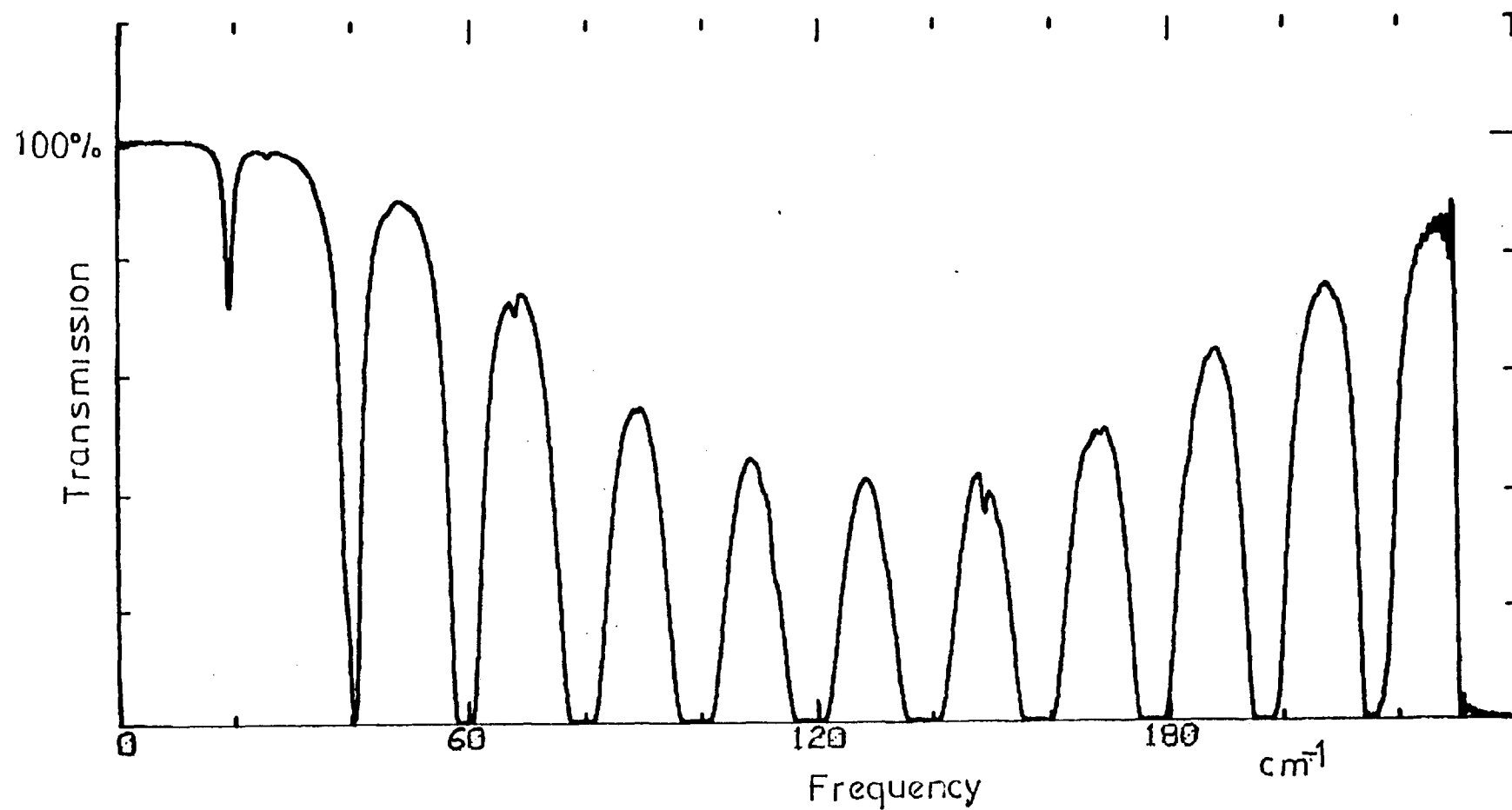


Fig 2 NH₃ Theoretical Transmission Spectrum

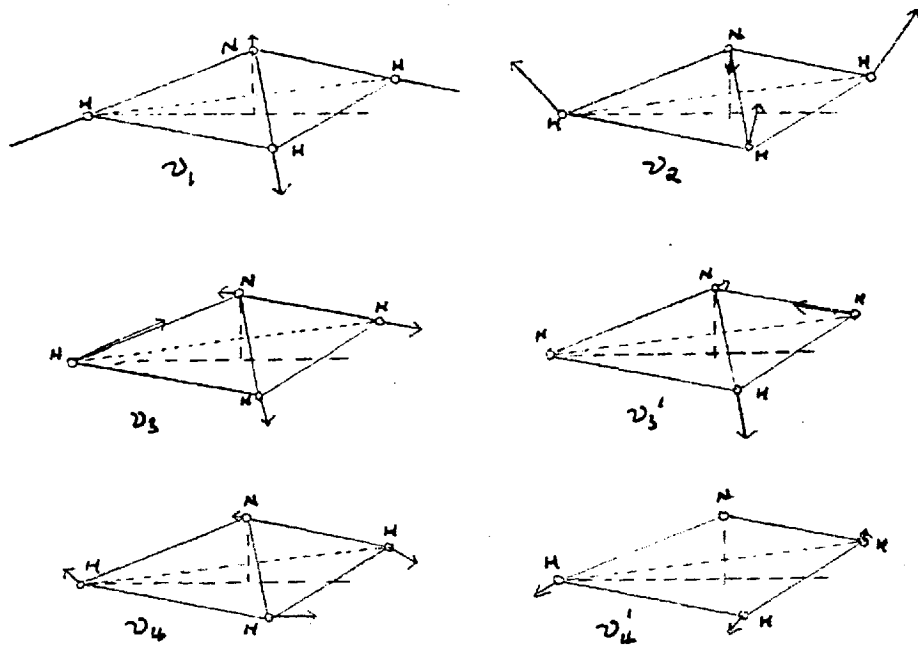


Fig 3 Fundamental Vibrations of the
 NH_3 Molecule

2.1.3

COMPARISON OF OBSERVED AND THEORETICALLY PREDICTED SPECTRA.

At low NH_3 monomer pressures the predicted rotational absorption spectrum is in agreement with the observed transmission spectra (see figure 26a).

At high NH_3 monomer pressures, near saturation, the observed spectra have less absorption beyond 140 CM^{-1} than that predicted by theory (see fig. 5). The excess absorption (anomalous) in the spectral region of 30 to 110 CM^{-1} can be explained in terms of absorption due to the NH_3 dimer (see chapters 5 and 6).

The theoretical prediction in the spectral region of 0 to 15 CM^{-1} is complicated by the presence of the ground state inversion absorption band whose half width is of the same order as its centre frequency. The predicted absorption in this spectral region is greater than that observed if one uses the Van Vleck and Weisskopf line shape (see appendix B) but is negligible if one uses the kinetic line shape (see appendix B).

Pressure = 1152 Torr
Temperature = 251 K
Path Length = 1.16 cm
Resolution = 1 cm^{-1}

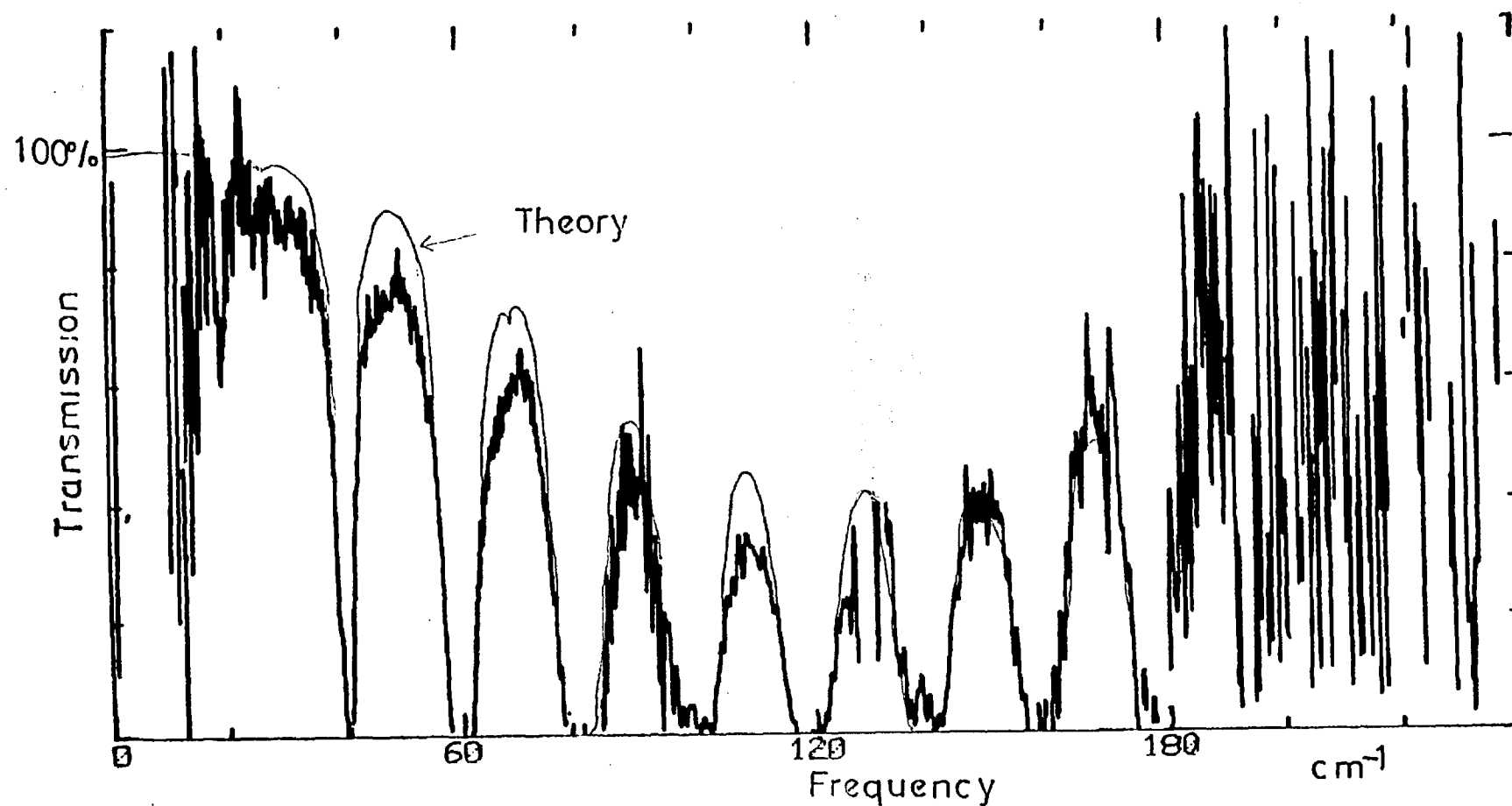


Fig 5 NH_3 Transmission Spectrum (cf Fig 2)

2.2 The AMMONIA DIMER $(\text{NH}_3)_2$

As the postulated binding mechanism for the ammonia dimer is the hydrogen bond a brief description of it, and its importance will be given here.

The hydrogen bond is a bond between a hydrogen atom bound to an atom in a given molecule and a similar atom in another molecule. In the case of the ammonia dimer there is a bond between a poorly screened hydrogen atom and the nitrogen atom from another molecule.

The bond energy, i.e. the energy of the reaction $\text{NH}_3 + \text{NH}_3 \Rightarrow (\text{NH}_3)_2$

of the hydrogen bond lies in most cases in the range 2 to 10 Kcals/mole. Because of this small bond energy and the small activation energy involved in its formation and rupture, the hydrogen bond is especially suited to play a part in reactions occurring at normal temperatures. For instance the structures of many organic crystals and inorganic crystalline hydrates are determined by the hydrogen bond. It has also been recognised that hydrogen bonds restrain protein molecules to their native configurations. Because all of the physical and chemical properties of water are determined or influenced by hydrogen bonding, this interaction pervades Physics and Chemistry simply because all living things evolved from and exist in an aqueous environment.

2.2.1 THE AMMONIA DIMER GEOMETRY.

The spectroscopic observations reported in this thesis have been made in the submillimetre region. One of the reasons for this choice involved a prediction about the structure of the dimers. The dimer is assumed to have a single hydrogen bond such that the N-H-N bonds are co-linear and have a total length of 3.4 Å (see fig. 6). Also the symmetry of the NH_3 was assumed to lie along the N-N axis. (Unpublished work by R.A. BOHLANDER).

2.2.2 Far Infrared Absorption Spectrum

Because the exact structure of the dimer is not known it is not possible to make detailed calculations of energy levels and transitions. But having made a prediction of a possible structure, and therefore the moments of inertia and dipole moment, it is possible to derive a smoothed absorption coefficient.

In this approach (unpublished work by R.A. BOHLANDER) ammonia dimers are considered to be represented by a superposition of dipolar dumbbells (SDD model) where there is one dumbbell for each principal axis of a predicted structure. Each dumbbell has the moment of inertia I of the modelled molecule about its axis of rotation and that component of the dipole moment which rotates about that axis. Rotations about only one axis at a time are considered for which line strengths and positions are calculated. Smoothed absorption coefficients are gotten from these absorption lines (Fig 7).

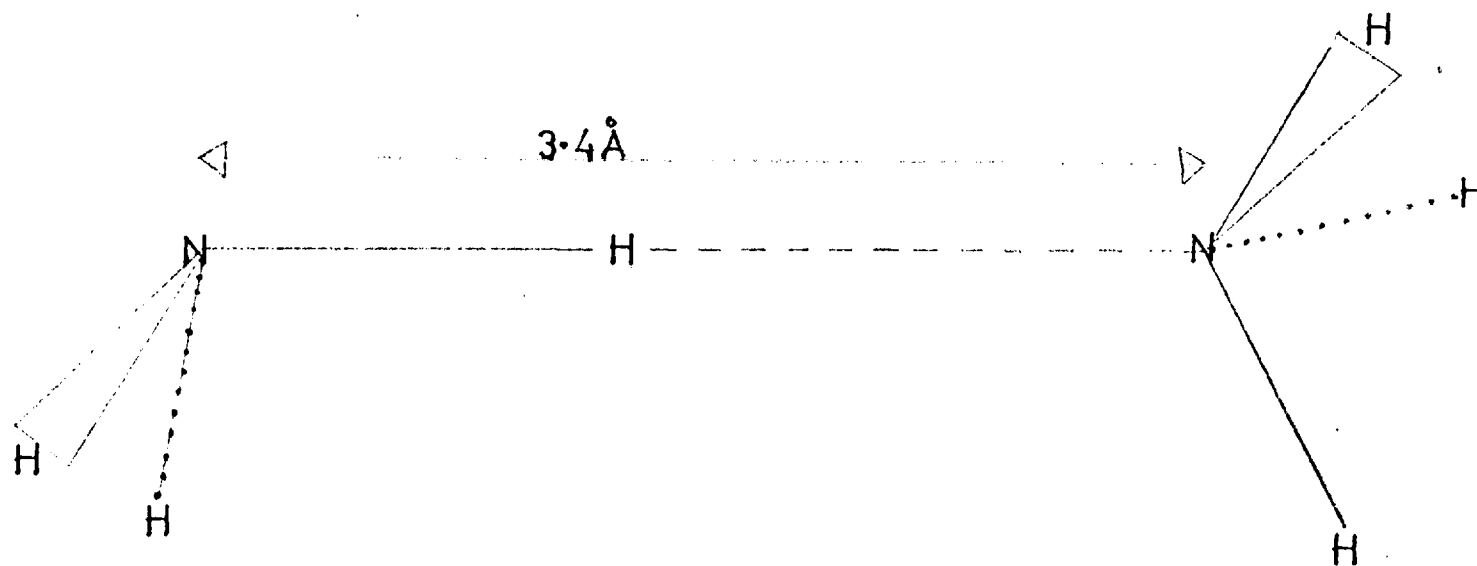
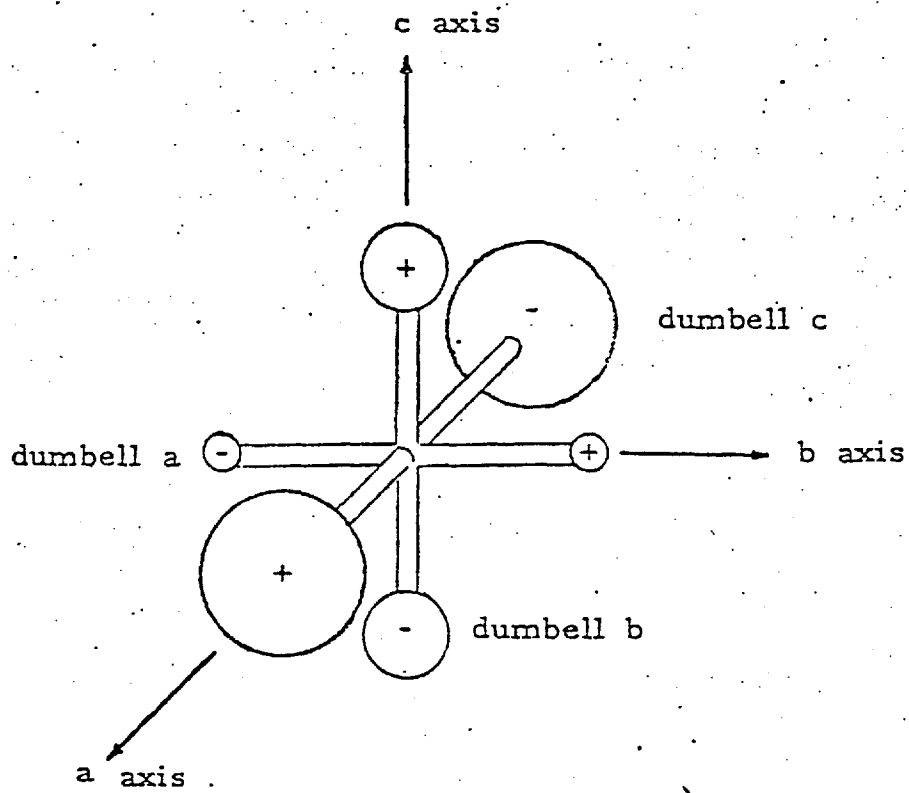


Fig 6 The Ammonia Dimer Molecule



SUPERPOSED DIPOLAR DUMBELLS

Fig 7

The line spacings are $2A$, $2B$ and $2C$ where $A = \frac{h}{8\pi^2 c \overline{I}_A}$
 $B = \frac{h}{8\pi^2 c \overline{I}_B}$ and $C = \frac{h}{8\pi^2 c \overline{I}_C}$ (see fig. 7)
 and correspond to axis a , b , and c .

Using this approach the absorption coefficient shown in the diagram (fig. 8) was obtained. It shows that, assuming the structure prediction to be accurate, the dimeric absorption peaks at about 60 CM^{-1} and falls off at about 110 CM^{-1} .

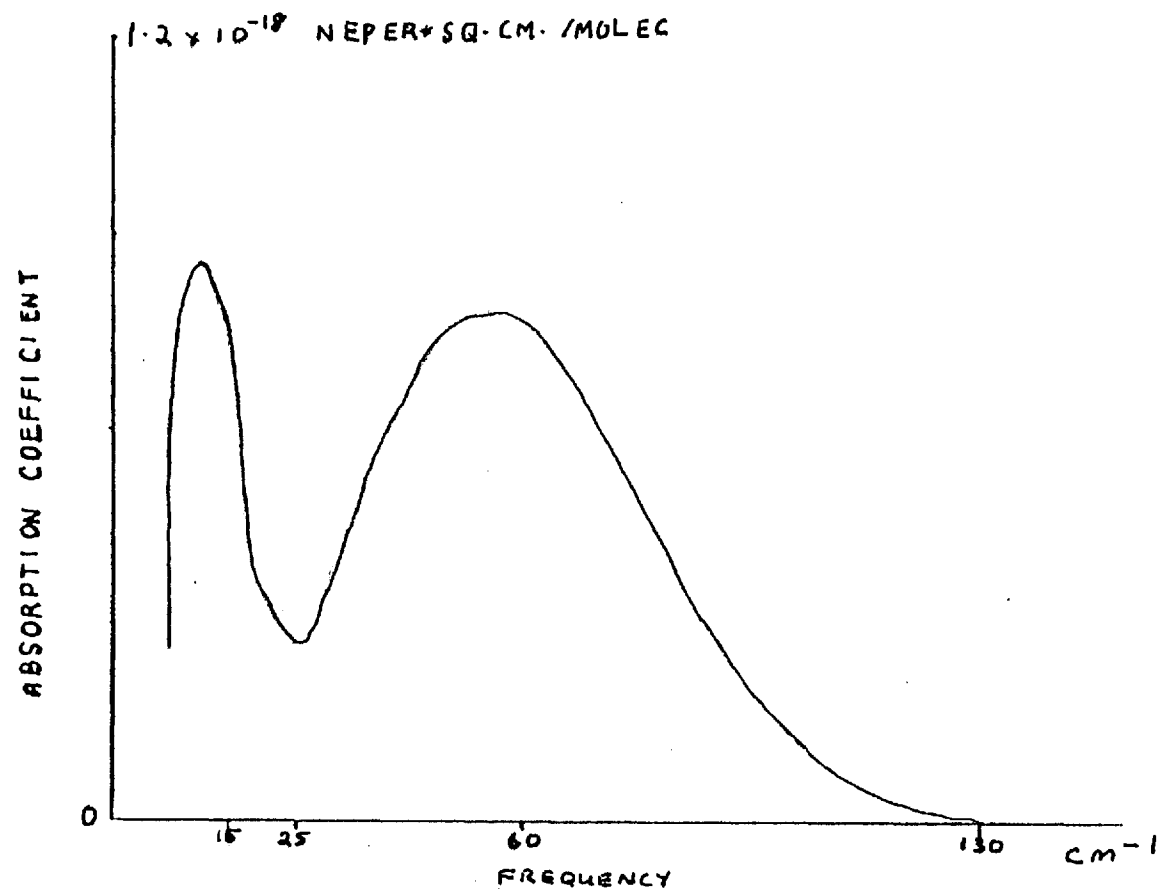


Fig 8 $(\text{NH}_3)_2$ Absorption Coefficient Obtained
from the SDD Model

Previous Work on Ammonia Dimers

3.1 Thermodynamic Measurements

Measurements of the compressibilities of organic vapours² have shown that under certain conditions the second virial coefficient may be used as a quantitative criterion of the degree of dimerisation of the vapour, the second virial coefficient being dependent on the molecular weight of the vapour. Appreciable dimerization was found only to occur with strongly polar substances where the energy of attraction between molecules due to dipole interaction or to hydrogen bonding exceeds KT . It was shown that the second virial coefficients of vapours which do not undergo association may be calculated from the critical data by the BERTHELOT equation for temperatures between $.5 T_c$ and $1.2 T_c$:-

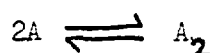
$$Pv = n (RT + Bp) \quad \dots 1$$

$$B = \frac{9}{129} \frac{RT_c}{P_c} \left(1 - \frac{6 T_c^2}{T^2} \right) \dots 2$$

where B is the second virial coefficient, R is the gas constant, P is pressure, T is temperature, and the subscript c stands for critical data.

Vapours which do associate give values of the second virial coefficient higher than those calculated by the Berthelot equation (see reference 2). The effect of dimerization on a vapour can be treated as follows :-

Consider one mole of a gas, A of which a small fraction α is associated to A_2



If the total pressure is P, then

$$K_p = \frac{P_A^2}{P_{A_2}} = \frac{2P(1-\alpha)^2}{(1-\frac{\alpha}{2})} \dots\dots 3 \text{ } K_p \text{ is the}$$

equilibrium constant.

For small values of α , where $1 \gg \alpha$ and terms in α^2 may be neglected.

$$\frac{\alpha}{2} = \frac{P}{K_p} \dots\dots 4$$

The second virial coefficient of a vapour is defined by equation 1.

If B is the second virial coefficient of the monomer A, the equation of state for a mixture of N_1 moles of A with N_2 moles of A_2 may be written (to the first order of small quantities).

$$\frac{PV}{RT} = (N_1 + N_2) + \frac{B N_1 P}{RT} \dots\dots\dots 5$$

$$(N_1 + N_2) = (1 - \frac{\alpha}{2}) + (1 - \frac{P}{K_p}) \dots\dots\dots 6$$

$$\text{and } N_1 = 1$$

$$\text{so } PV = RT + P(B - \frac{RT}{K_p}) \dots\dots\dots 7$$

The vapour thus follows as equation of state

$$PV = RT + B_o P \dots\dots\dots 8$$

where the observed second virial coefficient is

$$B_o = (B - \frac{RT}{K_p}) \dots\dots\dots 9$$

The equilibrium constant K_p can be calculated from equation 9

$$\text{i.e. } K_p = \frac{RT}{B_0 - B} \dots\dots\dots 1 \phi$$

The heat of dimerization was obtained from the slope of the graph of $\text{LOGe } K_p$ against T^{-1} (see reference 2)

- $H = 4400$ cal/mole. The fact that linear plots of $\text{LOGe } K_p$ against T^{-1} were obtained confirms that the process involved is consistent with dimerization in all cases.

This thermodynamic data for ammonia is consistent with the presence of dimers in the vapour phase, but the observations do not allow us to distinguish between a short lived transient species and one with a sufficiently long life time to merit being considered as a distinct molecule, the criterion being whether the dimer can rotate about an axis without dissociating.

3.2 Spectroscopic Measurements.

3.2.1 In a report by J.E.LOWDER,⁶ it has been reported that quantitative gas phase infrared intensity measurements for NH_3 in the 3micron region have been used to determine the energy of hydrogen bonding. In this method a principle of conservation for integrated band intensities of fundamental transitions in the absence of hydrogen bonding and the fact that hydrogen bonding enhances the integrated band intensity for stretching vibrations was used.

First of all Lowder showed by comparing his measurements to measurements obtained at low partial pressures of NH_3 where the contribution due to hydrogen bonded dimers is

unimportant ⁷, that the increased absorption is proportional to p^2 at constant temperature. This relationship is consistent with dimerization as it can be shown that

$$\Delta (\alpha P) = (\alpha_2 - \alpha_1) K_P \frac{(N_0 - 2x)^2}{N_0 - x} P^2 \dots\dots 11$$

where, α is the integrated absorption coefficient, the subscripts 1 and 2 denote properties of the monomer and dimer respectively, N_0 denotes the number of moles of NH_3 present at the total pressure P in the absence of hydrogen bonded molecules, x is the number of moles of $(NH_3)_2$ formed, and $\Delta (\alpha p)$ is the difference between measurements at low partial pressures and measurements at higher partial pressures where the contribution due to hydrogen bonded dimers is important.

Secondly, Lowder determined from the temperature dependence of the integrated absorption coefficients (obtained at constant pressure) a hydrogen bonding energy of 4.5 K cal/mole. This value is agreement with that found from analysis of NH_3 second virial coefficient data (section 3.1)

3.2.2 In a report by GIMMESTAD et al¹, a spectroscopic investigation in the region of 10 to 50 cm^{-1} , using a Michelson interferometer and fourier analysis, of the spectral absorption of the NH_3 DIMER was carried out. The main monomer contribution to absorption in this region is from the first two pure rotational lines. Since these lines are relatively weak it was hoped to maximize dimer absorption in this region. The following method was used to determine an NH_3 dimer binding energy.

At constant temperature the pressure dependence of integrated absorption was plotted (see Ref 1). This plot was fitted with linear and quadratic terms, the quadratic terms was assumed to be due to absorption by dimeric molecules. From the temperature dependence of the quadratic term a binding energy of 3.6 K cal/mole (see REF 1) was determined. This value is in close agreement with those reported in sections 3.1 and 3.2.1. These workers also reported the observations of spectral features attributed to dimeric absorption at 10, 15 and 32 cm^{-1} (see REF 1).

CHAPTER 4.

METHODS AND APPROACH TO THE PROJECT.

While pressure, volume, and temperature (P,V,T) data for ammonia provide evidence for the presence of dimers in the vapour phase, these measurements do not allow us to distinguish between a short lived transient species and one with a long enough life time to be considered a distinct molecular species. If the NH_3 dimer does exist as a distinct molecule then its absorption spectrum(if it has one) would consist of features having widths smaller than their centre frequencies because the molecules are rotating without breaking up.

It was reported in Chapter 2 that the rotation absorption spectrum due to the dimer was expected to peak at about 60 CM^{-1} (on account of its dipole moment and moments of inertia), i.e. in the far infrared(0 to 400 CM^{-1}). The best available tool for spectroscopic absorption measurements in the far infrared is the fourier transform Michelson interferometer(see section 4.1). Therefore this instrument was used. Fortunately the pure rotation spectrum of the monomer was the only significant absorption process in this region(at short path lengths and low temperatures) and the rotational spacing of 20 CM^{-1} provided adequate spectral regions, clear of strong absorption features, in which to make unambiguous spectral measurements.

The initial aim of the project was to repeat and improve on the measurements reported in a previous report, by Gimmetstad et al¹. Their results have been summarized in chapter 3, section 3.2.2.

The approach to the project was basically the same as used by Gimmetstad¹, i.e. using fourier transform spectroscopy with different path length gas cells.

4.1 Brief Introduction to Fourier Transform Spectroscopy.

As all the spectral measurements were made using a Michelson cube interferometer and the spectra were derived by fourier transformation, it will be useful here to give a brief summary of the principles and advantages underlying the use of a Michelson interferometer in far infrared spectroscopy.

One major advantage of fourier transform spectroscopy over dispersion spectroscopy arises because it is not necessary to use narrow slits to obtain high resolution. With the Michelson interferometer the resolution is limited by path difference. Therefore to double the resolution of a given spectrum it is necessary to double the path difference and so to double the measuring time to get the same signal to noise ratio. In contrast to this the entrance and exit slits of a dispersion monochromator must be halved to double the resolution. This in turn reduces the signal intensity by a factor of 4. It will therefore take 16 times as long to obtain a given spectrum with double the resolution and the same signal to noise ratio.

A second advantage is in allowing us to substitute a simple optical instrument for a complicated one at the expense of adding a calculation which can be carried out by use of a digital computer. In fourier spectroscopy a common practice is to record the power incident on the detector as a function of path difference within the interferometer by scanning the path difference in discrete

steps and using amplitude modulation (A.M.). A.M. has several disadvantages in that all of the incident radiation is reflected back to the source for half the duration of the experiment and is effectively wasted. Also unwanted contributions such as stray rays are modulated and so are detected leading to erroneous records. These disadvantages are very significant in the far infrared as the incident radiation is of low power and the signal of interest (the interferogram) is only part of the detected signal. (The interference function).

In order to utilize all the relevant radiation passing through the source aperture and to provide some discrimination in favours of the interferogram at the expense of the unwanted signal to help the signal to noise ratio, A.M. has been replaced by (in the far infrared) phase modulation (P.M.) Other methods have been used by other workers but P.M. has been used in this work.

In P.M. the interference pattern is scanned while a rapid path-difference jitter of only a fraction of a wavelength is superimposed (this produces a signal that is detectable.) The path difference is modulated by a small periodic displacement of one of the interferometer mirrors (the stationary mirror in A.M.).

A comprehensive treatment of P.M. in the far infrared is given in three papers by J. CHAMBERLAIN¹⁰ (see Appendix A for samples of interferograms and their transforms).

4.2 EXPERIMENTAL TECHNIQUE.

The experimental technique is best illustrated by the diagram in figure 9.

The only major change in the apparatus has been in the type of gas cell used. Two types have been used which are fixed path length gas cells, and a non-resonant cavity.⁵

4.2.1 FIXED PATH LENGTH GAS CELLS.

Three fixed path length gas cells were used, having path-lengths of 1.2 CM, 3.2CM, and 16.4 CM. All were made of brass because of its high conductivity.

4.2.2 The NON-RESONANT SPHERICAL CAVITY.

This was a useful absorption cell enabling long path lengths ($\sim 2M$) to be achieved. The importance of the device, apart from the long path length, was that it could be fixed into the existing apparatus and so could be cooled in the same chamber as the fixed path length gas cells.

This device uses multiple specular reflection inside a gold plated spherical cavity acting as an absorption cell. The effective path length i.e. the length of a column of gas which gives the same drop in output power as the cavity, is determined by three parameters which are 1) the absorption loss in the gas, 2) the reflection loss at the cavity walls, and 3) the size of the entrance and exit holes. An increase of any of these quantities reduces the effective absorption path length.

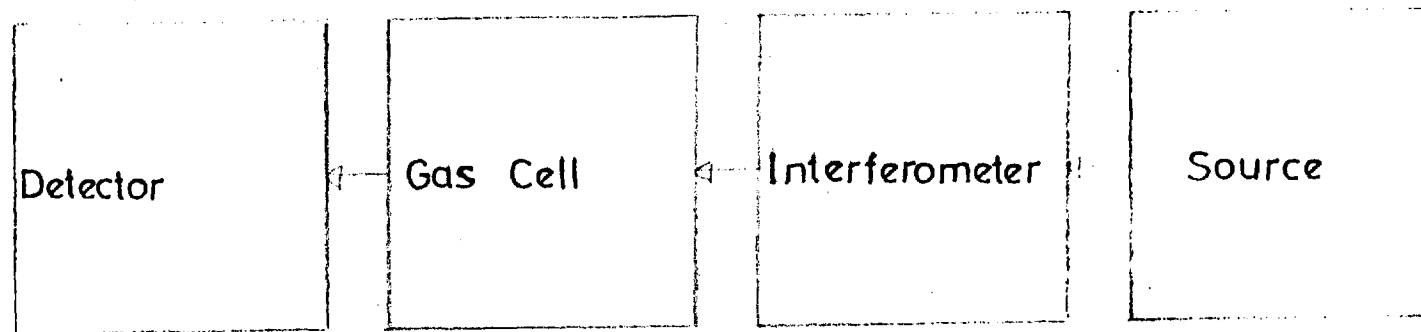


Fig 9 Simple Block Diagram of Apparatus used in the Project

Therefore the path length is effectively longer for a weak absorber than for a strong absorber($(\text{NH}_3)_2$ will have a longer effective path length than NH_3).

4.2.2.1 Theory of Cavity

The quality factor of a cavity is defined by the expression¹⁷

$$Q = 2 \pi \left(\frac{\text{ENERGY STORED}}{\text{ENERGY DISSIPATED PER CYCLE}} \right) \dots\dots\dots 12$$

A quality factor can be defined for each loss mechanism

$$\text{i.e. } \frac{1}{Q_{\text{total}}} = \frac{1}{Q_{\text{vac}}} + \frac{1}{Q_{\text{gas}}} \dots\dots\dots 13$$

where Q_{vac} the quality factor when the cavity is evacuated and Q_{gas} the quality factor when there is gas in the cavity.

A transmission spectrum is the ratio $\frac{Q_{\text{vac}}}{Q_{\text{total}}}$

equation 12 becomes

$$\frac{Q_{\text{vac}}}{Q_{\text{TOTAL}}} = 1 + \frac{Q_{\text{vac}}}{Q_{\text{gas}}} \dots\dots\dots 14$$

Now from reference 5

$$Q_{\text{vac}} \propto 2 \pi \nu \left(\frac{2r}{1 - R} \right)$$

$$\text{and } Q_{\text{gas}} = \frac{2 \pi \nu}{KP}$$

where ν is the frequency (CM^{-1}), r is the radius of the sphere, R is the reflectivity of the walls at normal incidence, K is the absorption coefficient in NEPERS per cm atmosphere, and P is pressure.

$$\therefore \frac{1}{\text{TRANSMISSION}} = 1 + \alpha KP \dots\dots\dots 15$$

$$\text{where } \alpha = \frac{2r}{(1 - R)}$$

The quantity $(1-R)$ is proportional to the square root of the frequency but the prediction⁵ of the constants of proportionality from classical theory is unreliable and must be determined experimentally (see Appendix C).

Chapter 5

Experimental Results

Dimer Absorption Contour and Binding Energies

5.1 Dimer Absorption Contour

The first object was to show that the observed absorption of NH_3 gas could not be explained by what is known about the NH_3 monomer.

The comparison of an observed and predicted transmission spectra is shown in figure 5. It can be seen that there is anomalous absorption in the spectral region of 2θ to $14\theta \text{ cm}^{-1}$. The ratio of these spectra gives the anomalous absorption contour shown in figure 1 θ .

This anomalous absorption up to $1\theta\theta \text{ cm}^{-1}$ is shown to be consistent with it being associated to NH_3 dimers in the following sections.

5.2.1 Apparatus

The apparatus that was used in the initial work in the spectral region of 2θ to $5\theta \text{ cm}^{-1}$ will be called Mark 1 (see Fig. 11).

The interferometer was phase modulated and had a 36 Micron beamsplitter giving a first minimum in the spectrum at $8\theta \text{ cm}^{-1}$. This maximised the signal in the region of interest.

The main part of the optical path was enclosed in a vacuum tank (made of Aluminium) to minimize the effect of atmospheric water absorption and to allow the sample cell to be cooled (see Fig. 11). The gas cell, made of brass (high thermal conductivity) with crystal quartz windows, was fitted onto the bottom of a thin walled stainless steel (low thermal conductivity) container which fitted into the vacuum tank (see Fig.11). The gas cell could be cooled by pouring

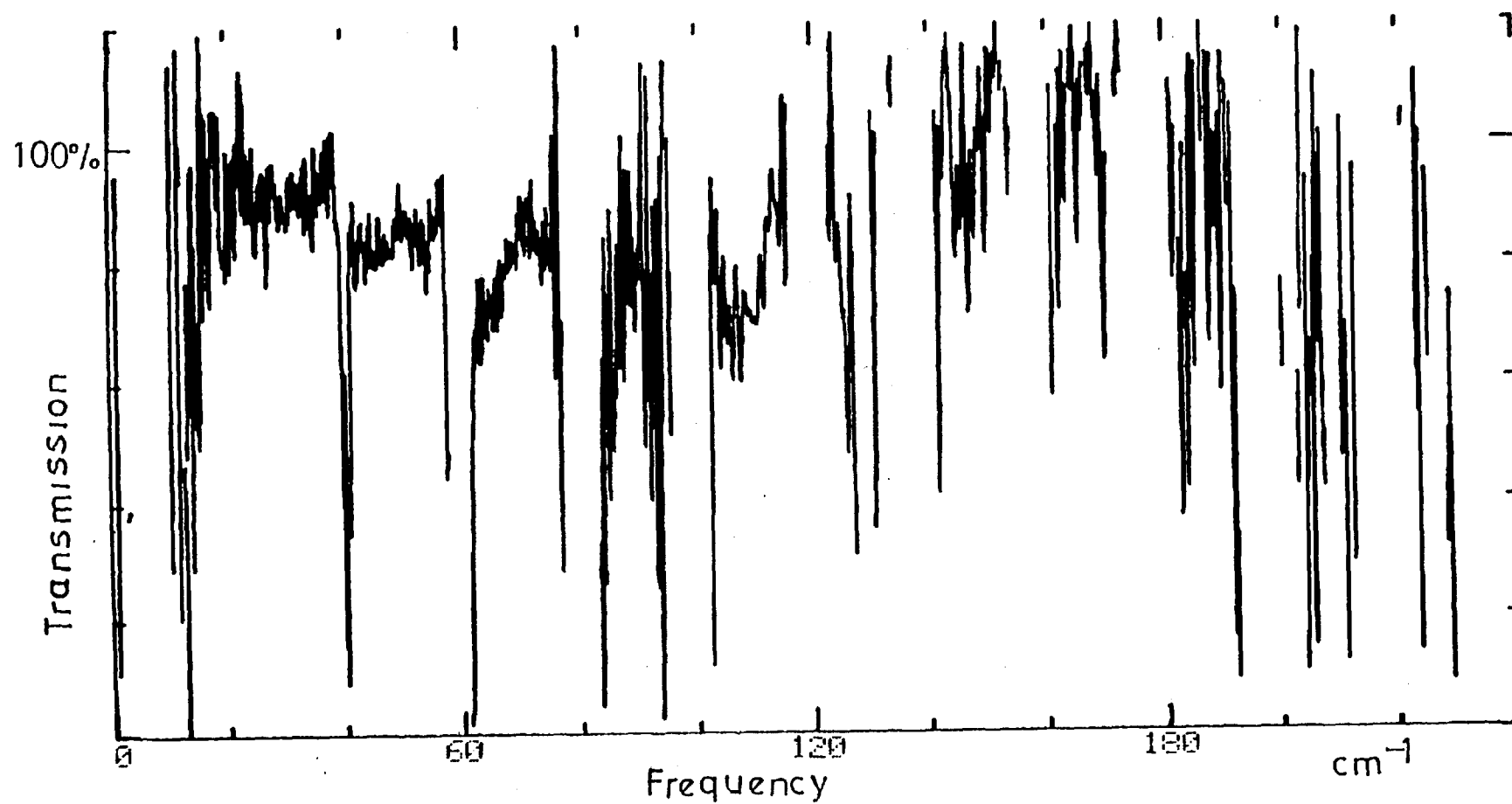


Fig 10 $(\text{NH}_3)_2$ Transmission Spectrum (see fig 5 for conditions)

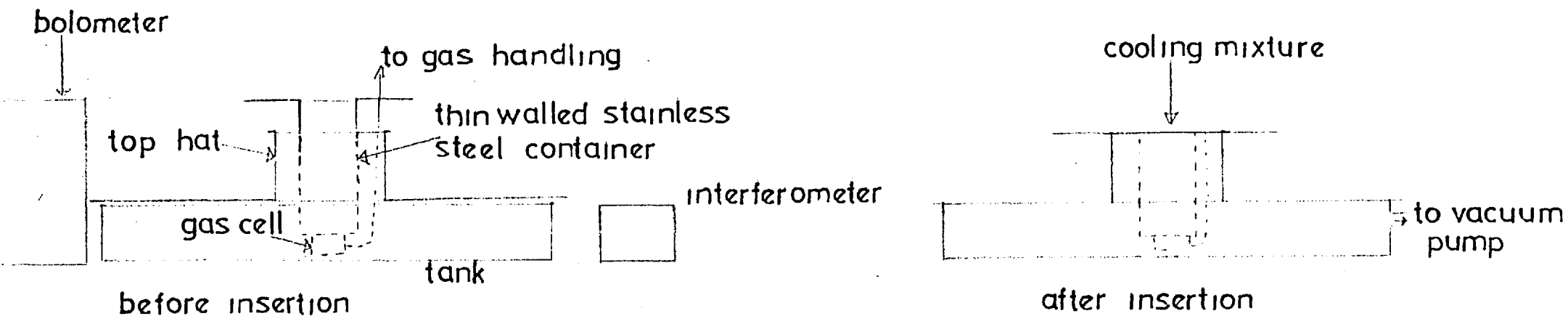
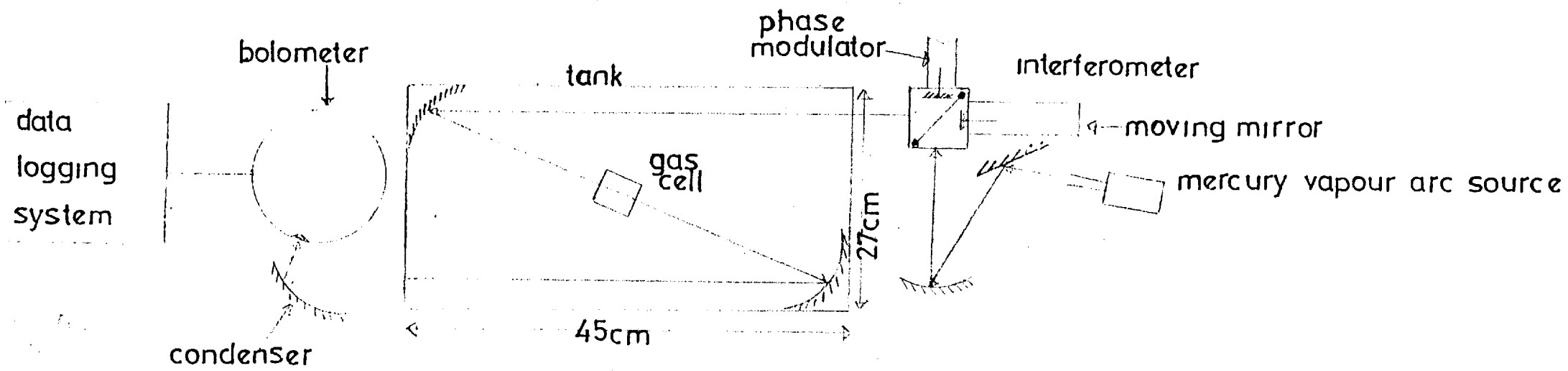


Fig 11 Mark 1

several controlled quantities of liquid nitrogen into the stainless steel container, the temperature being measured by three thermistors stuck onto the absorption cell with epoxy resin.

The source consisted of a high pressure mercury arc lamp contained in a spherical cavity of five inches diameter as described by R. EMERY.¹¹ The purpose of this arrangement was to scramble the radiation emitted by the lamp which normally has a channel spectrum.

The radiation was detected by a helium cooled GERMANIUM bolometer.

5.2.1.1. Vacuum and Gas Handling System

Three pressure gauges were connected to the absorption cell and vacuum tank gas handling system. A PIRANI gauge was used for background pressure measurements, a precision aneroid gauge was used for pressures between $\emptyset$ and 1000 torr, and another aneroid gauge for pressures above 1000 torr. One vacuum pump was used.

5.2.2 Experimental Procedure

Initially the cell was evacuated to a pressure of 70 microns or less, and a "background" interferogram was recorded. Then NH_3 gas was allowed into the cell to the required pressure and a "foreground" interferogram was recorded. Spectra were derived from interferograms by fourier transformation.

Each foreground spectrum was ratioed to its relevant background spectrum giving an observed NH_3 transmission spectrum. The procedure was repeated at various pressures (at constant temperature) constituting a pressure scan.

The observed NH_3 transmission spectra were ratioed to their relevant NH_3 theoretical spectra giving 'Anomalous' transmission spectra i.e.

$$T_{\text{observed}} = T_{\text{theory}} \times T_{\text{anomalous}}$$

$$T_{\text{anomalous}} = \frac{T_{\text{observed}}}{T_{\text{theory}}}$$

where T is transmission. Figures 12 show examples of anomalous transmission spectra obtained during a pressure scan at 259°K

Using a mini-computer calculations of integrated absorption were carried out on the resulting anomalous transmission spectra in spectral regions free from strong absorption due to NH_3 monomer or atmospheric water vapour.

5.2.3 Results

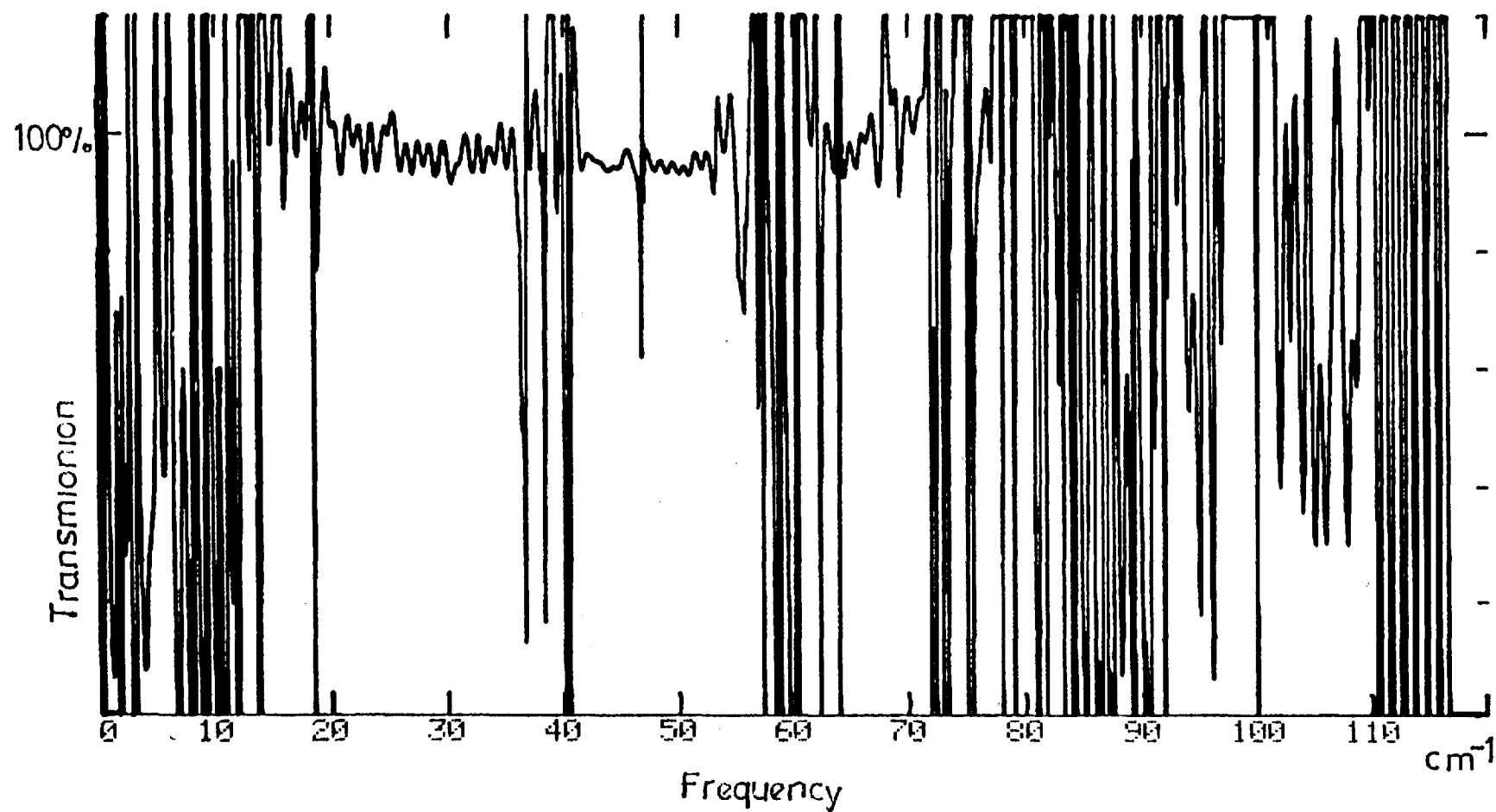
For each pressure scan at constant temperature, the integrated absorption measurements were plotted against pressure (see fig 13).

Since dimer concentration goes as monomer concentration squared the plotted data was fitted by the following quadratic equation.

$$= A \frac{P^2}{T^2} \dots 16$$

As can be seen from the curve (see fig.13) the anomalous absorption does show a quadratic pressure dependence. But this quadratic pressure dependence is not a totally convincing criterion for the anomalous absorption to be associated with NH_3 dimers as it is known that the ordinate of a single absorption frequency at a distance far from line 13 centre varies quadratically with pressure. It was therefore necessary to show that the anomalous absorption had a temperature dependence consistent with dimerization, and which could not be explained in terms of the

225 Torr



Figs 12 Anomalous Transmission Spectra Obtained During
a Pressure Scan at 259K, 3.2 cm Path, 1cm^{-1} Resolution

674 Torr

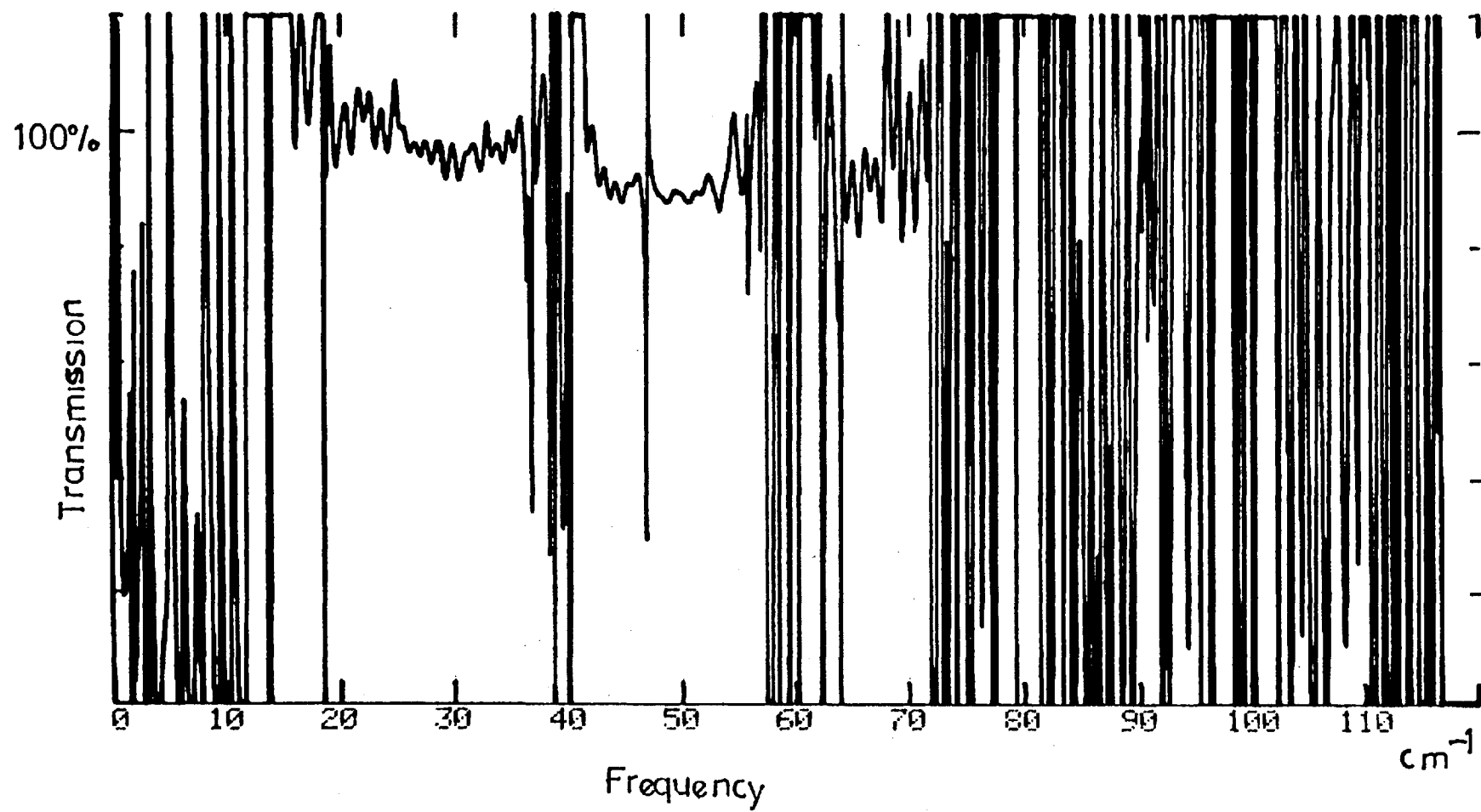


Fig 12

953 Torr

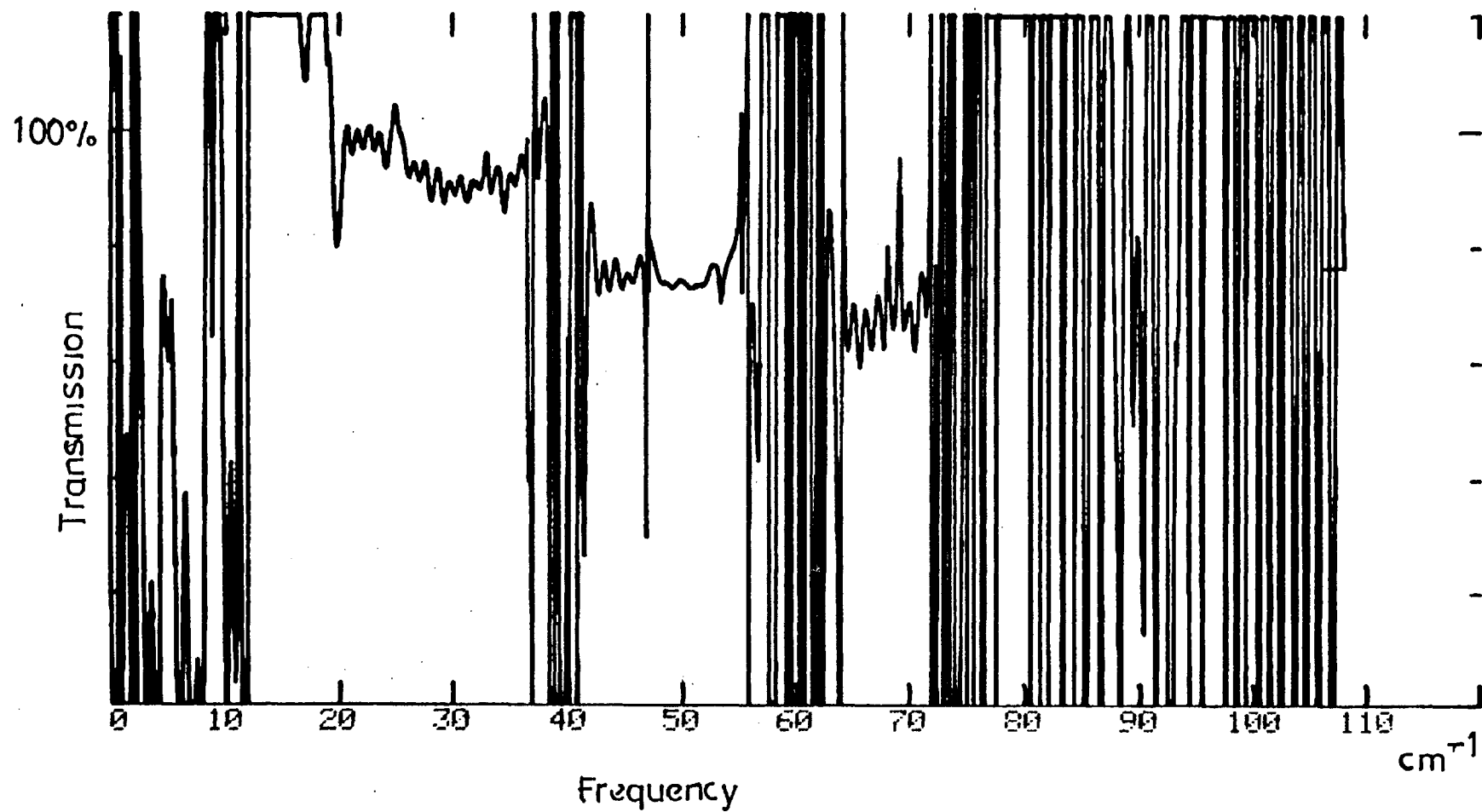


Fig12

1432 Torr

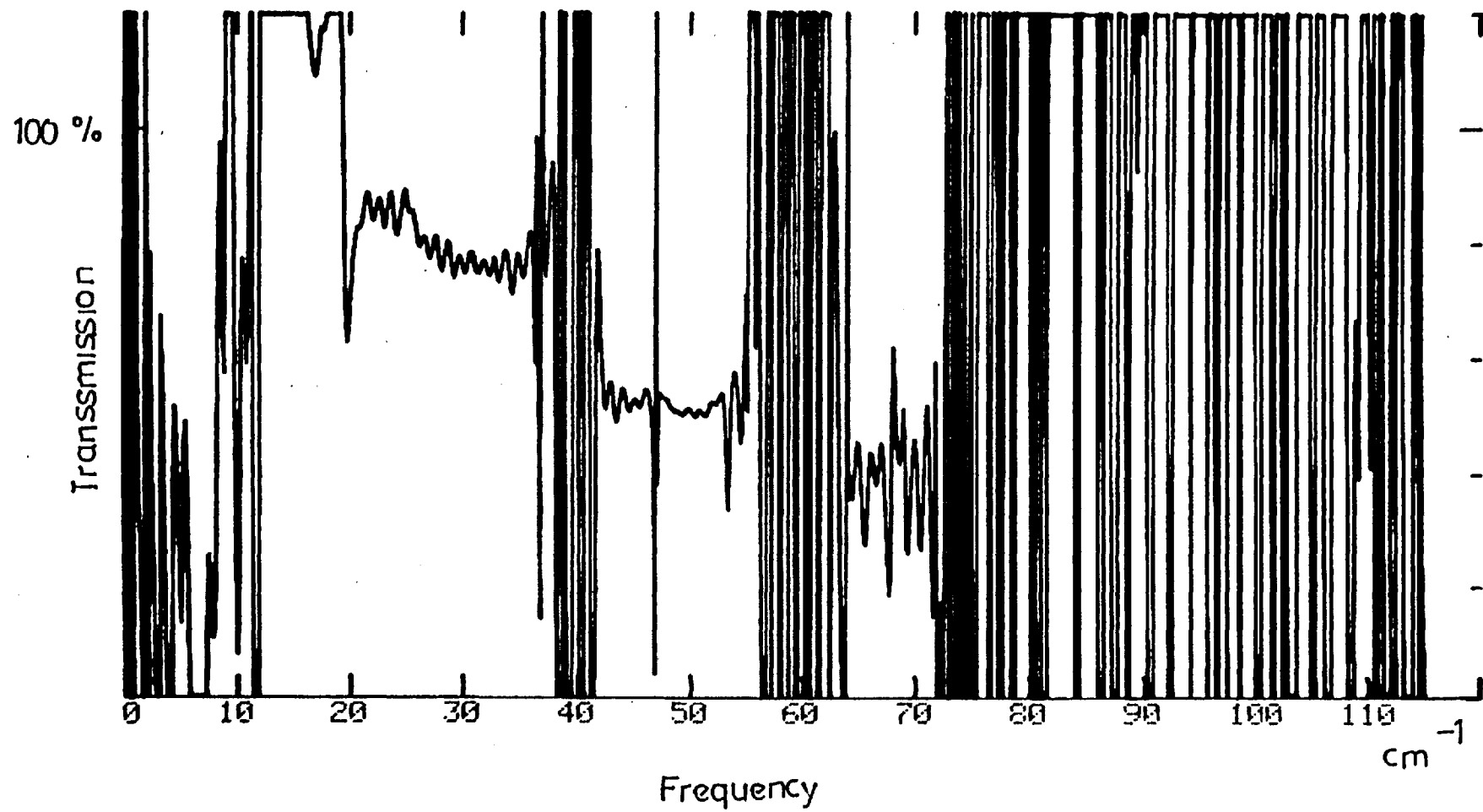
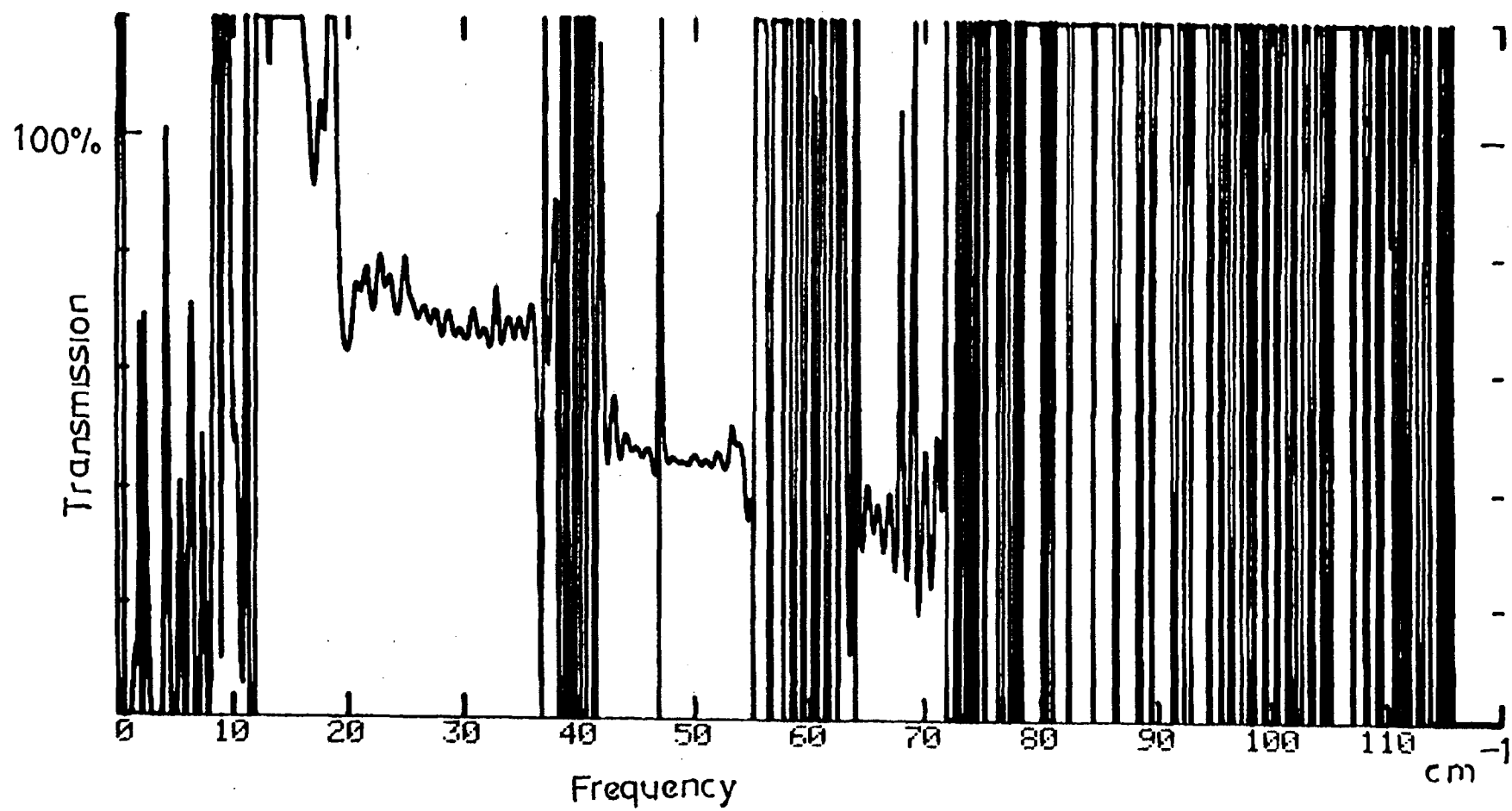


Fig 12

1587 Torr



Frg 12

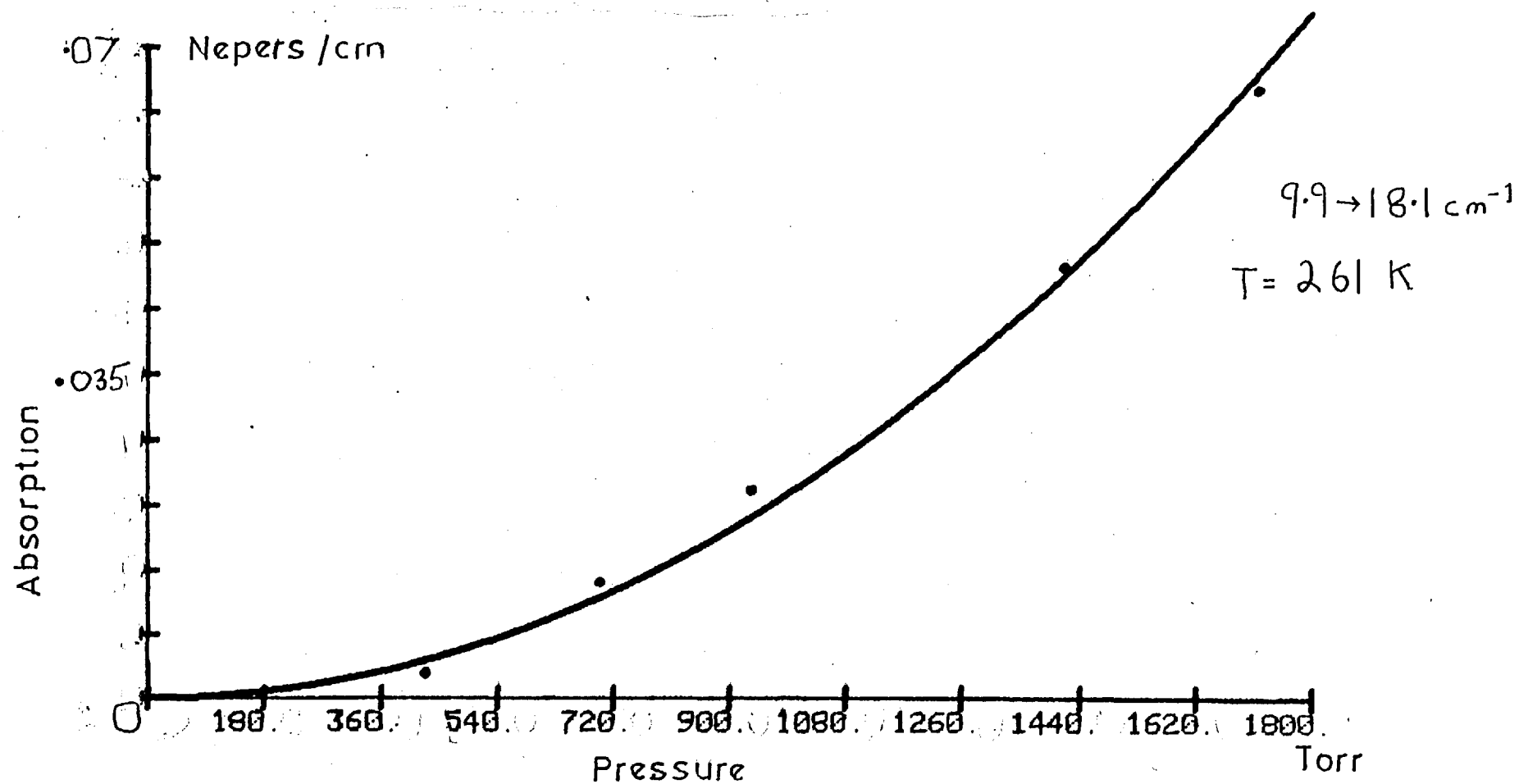


Fig 13a Quadratic Pressure Dependence of
Anomalous Absorption

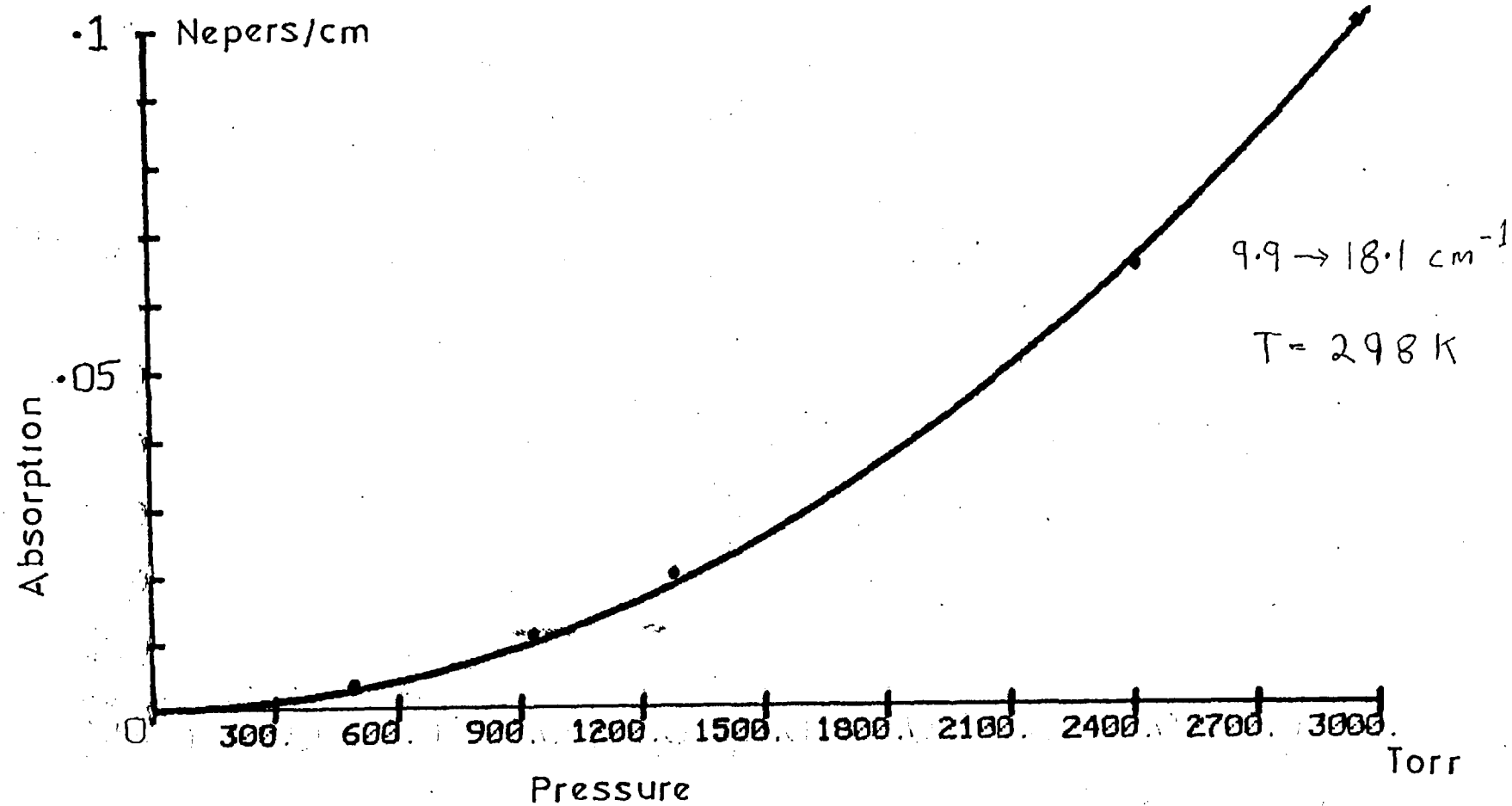


Fig 13b Quadratic Pressure Dependence of
Anomalous Absorption

monomer. This was done in the following way.

The dimer concentration N_2 is given by

$$N_2 = \sigma N_1^2 \exp \left\{ \frac{-E}{KT} \right\} \dots \dots \dots 17$$

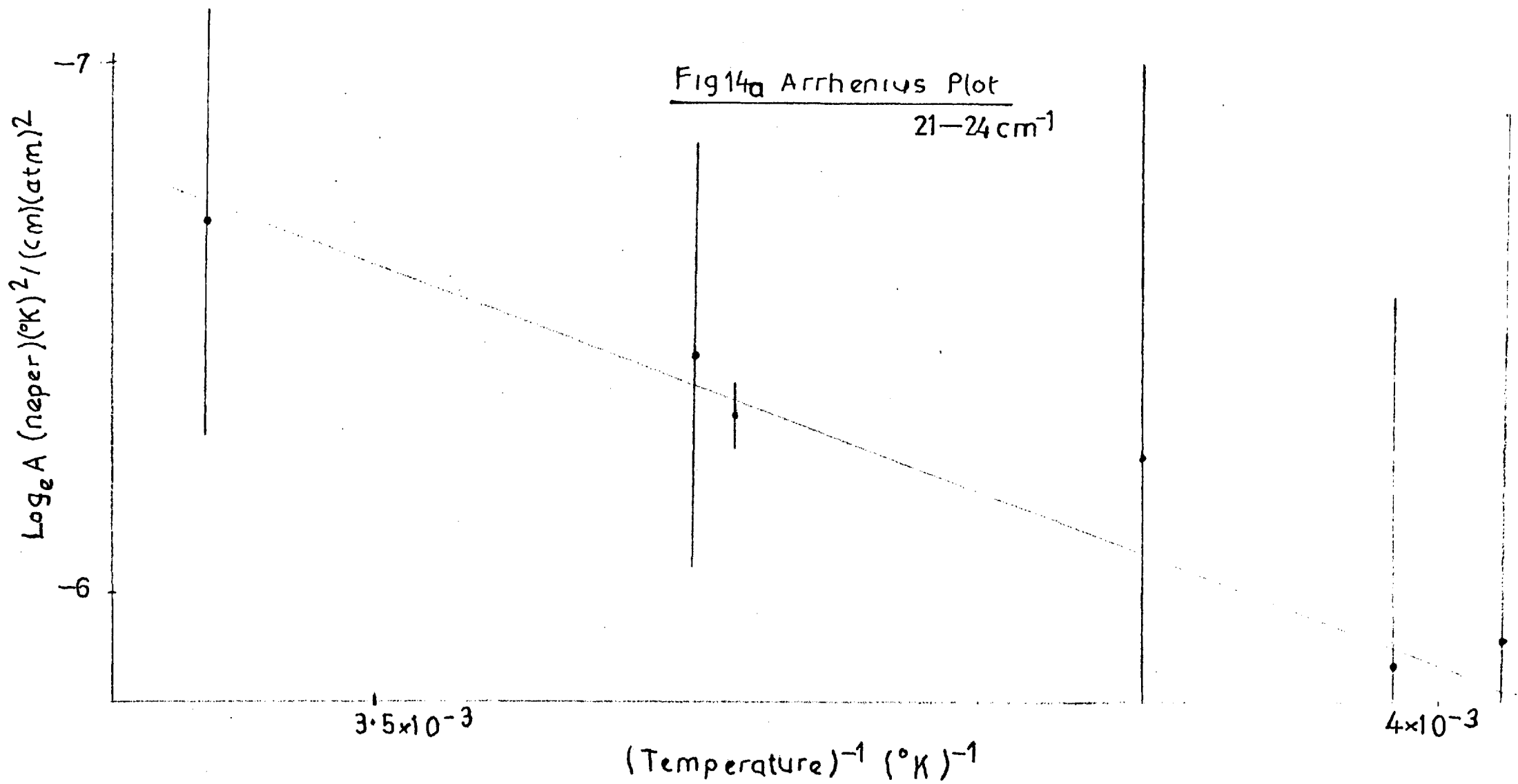
where N_1 is the monomer concentration in molecules/cm³, σ is a constant with units cm³/molecule, and E is the binding energy and is negative so that $(-E)$ is greater than zero.

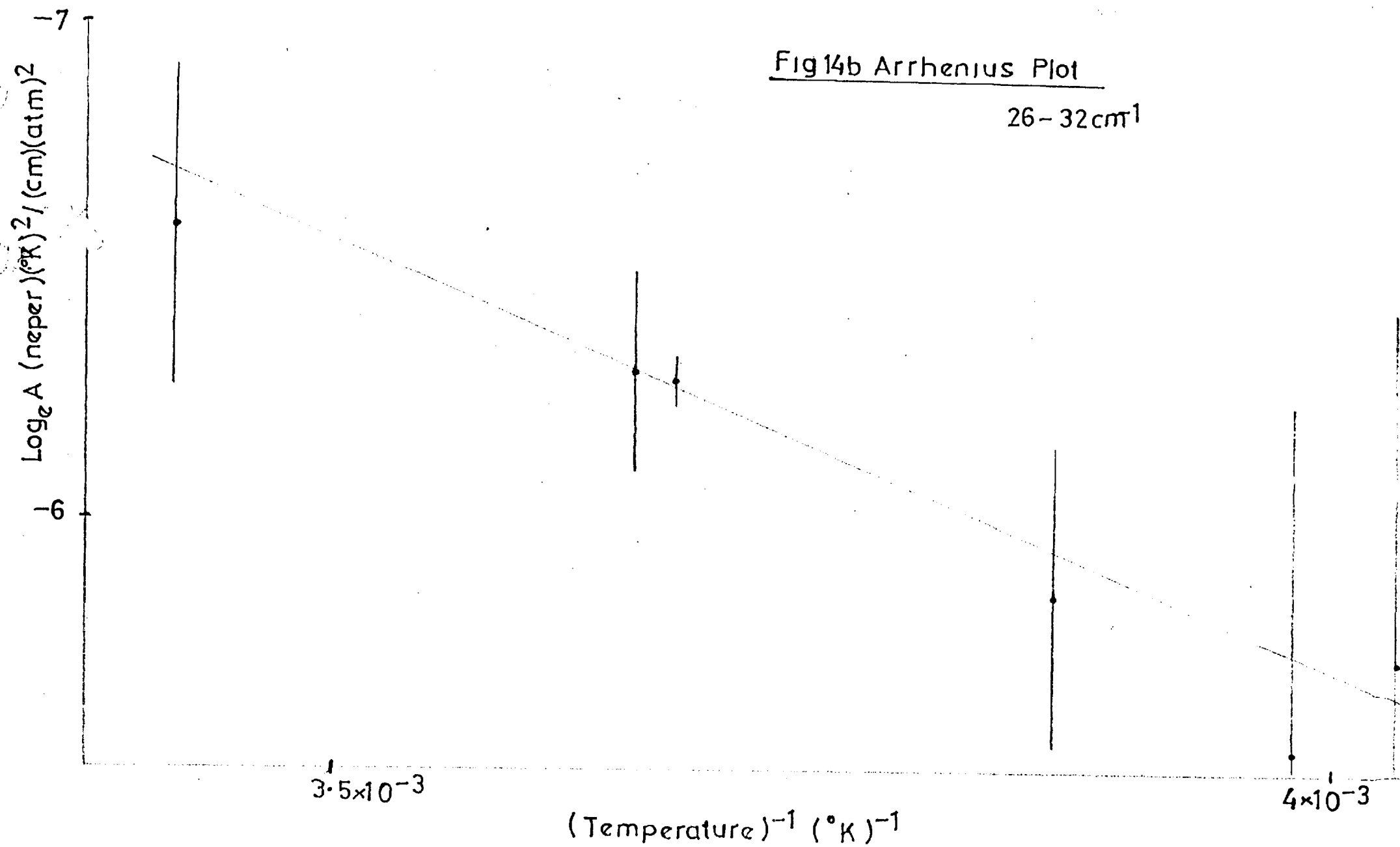
By taking A as a measure of how dimer concentration changes with temperature we get an ARRHENIUS equation

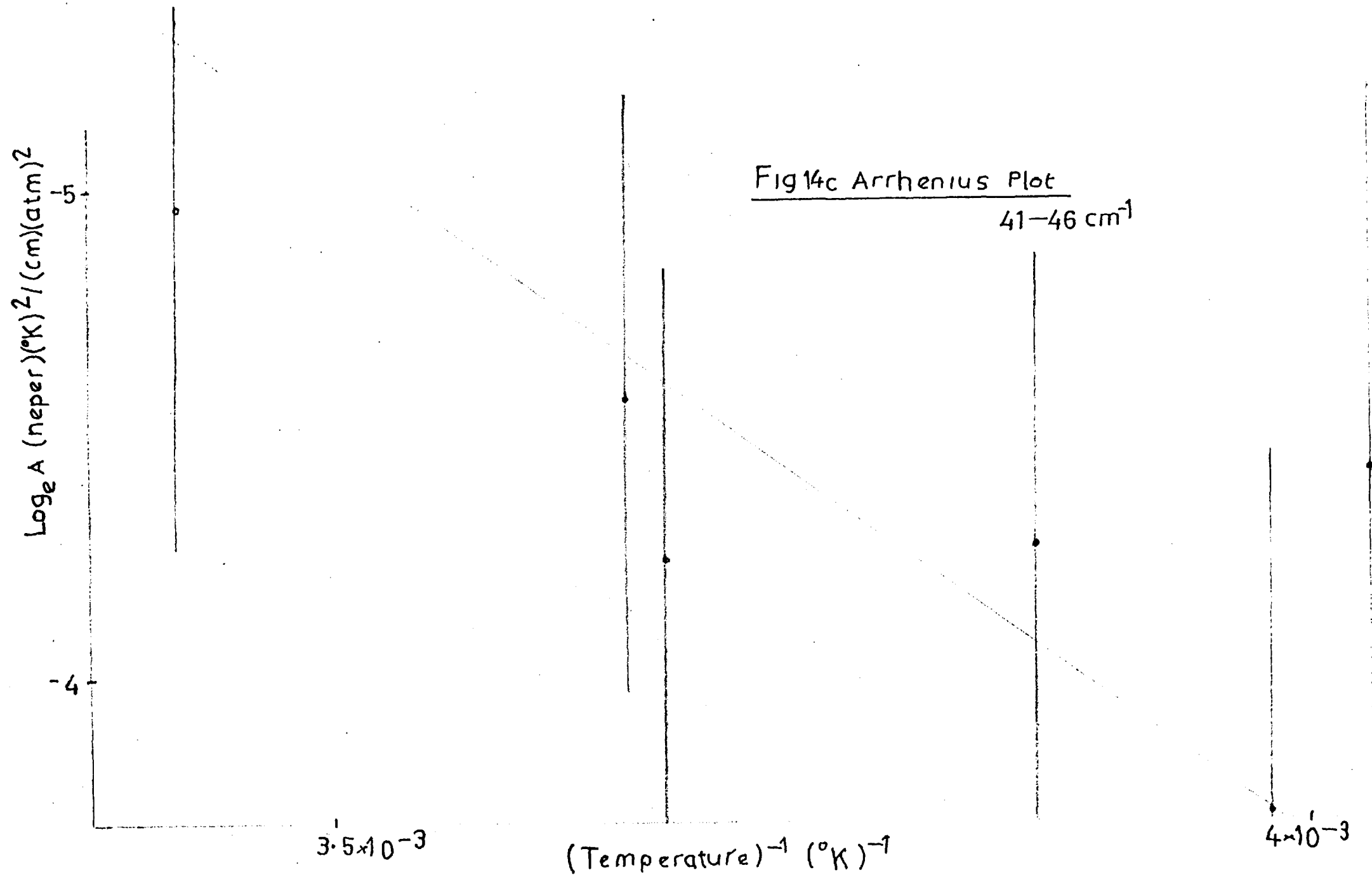
$$E = K \frac{d(\text{LOG} A)}{d(1/T)} \dots \dots \dots 18$$

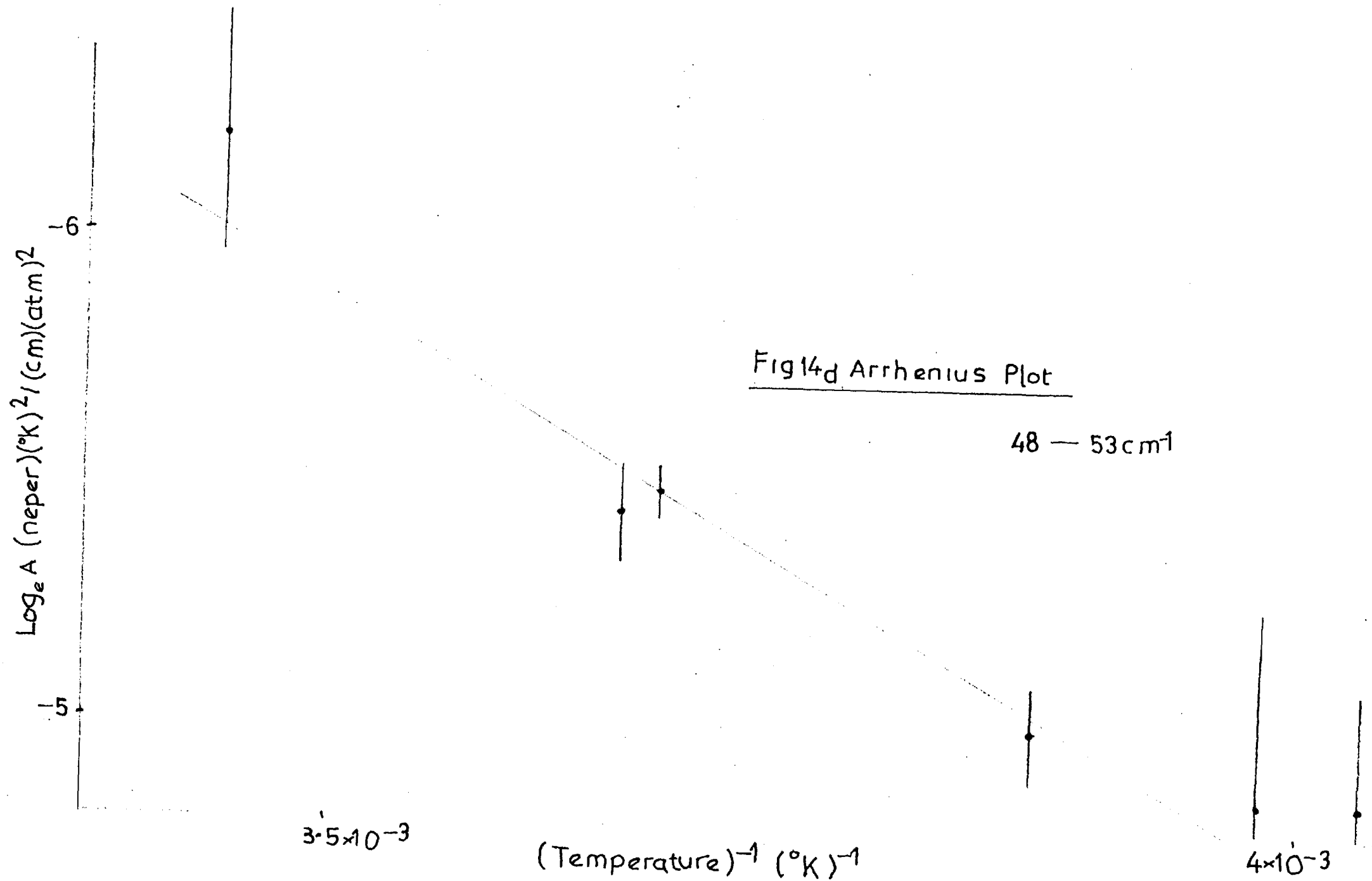
The plots of $\text{LOG} A$ against $1/T$ (see figs 14) shows that the anomalous absorption has an exponential temperature dependence which is consistent with dimerization but cannot be explained in terms of the NH_3 monomer which has only a $T^{5/2}$ temperature dependence (An exponential temperature dependence is far steeper than a $T^{5/2}$ temperature dependence).

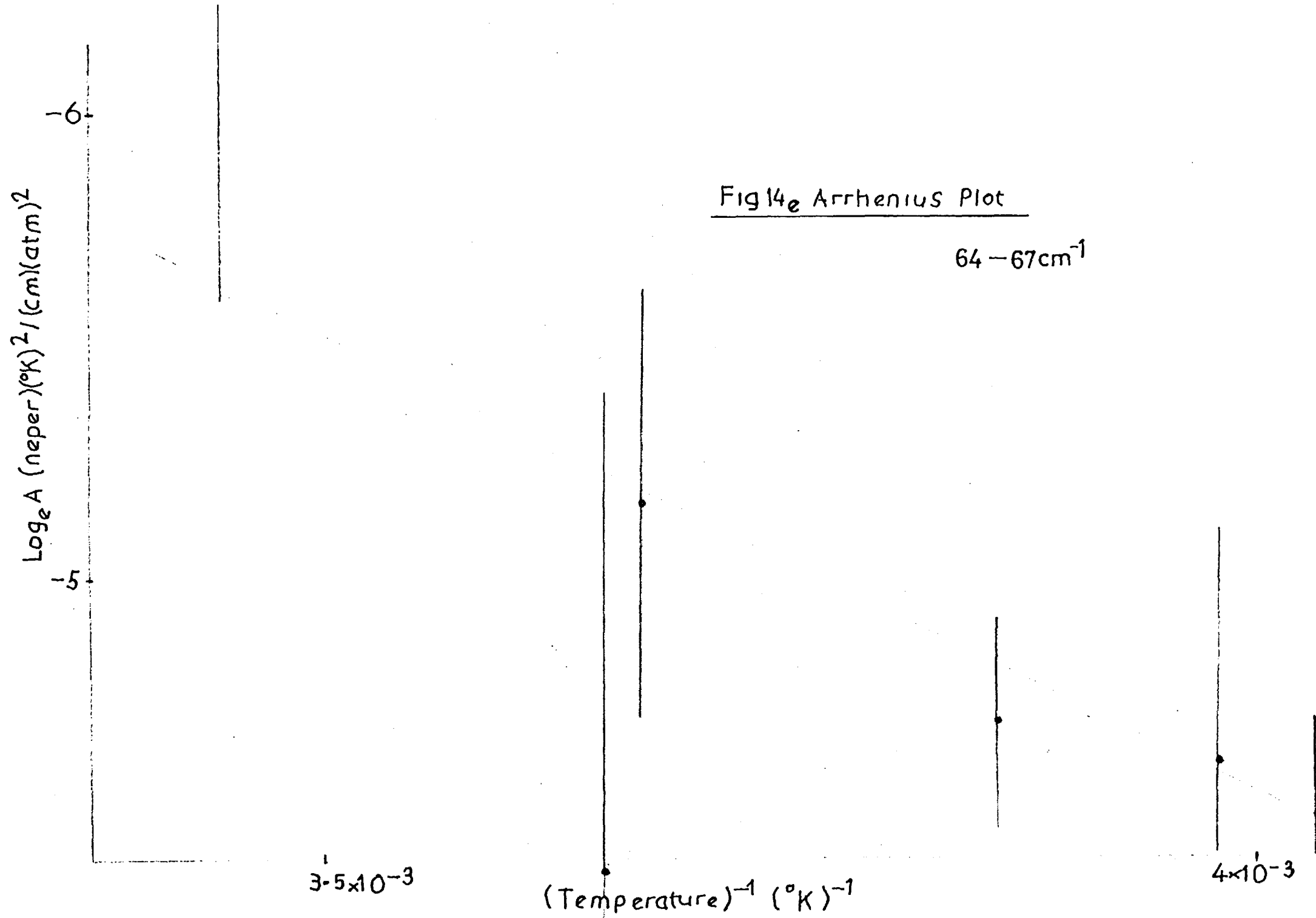
The fact that the anomalous absorption has a quadratic pressure dependence, at constant temperature, and an exponential temperature dependence at constant NH_3 density is consistent with the hypothesis that the anomalous absorption is due to the NH_3 dimer. Also the calculated binding energies are in close agreement with those obtained by other workers.^{1, 3, 6}











Binding Energies Calculated from Anomalous transmission Spectra

<u>Spectral region</u>	<u>E K Cals/mole</u>
21 TO 24 cm ⁻¹	3.3 ± .9
26 TO 32 cm ⁻¹	3.1 ± .9
41 TO 46 cm ⁻¹	2.3 ± .1
48 TO 53 cm ⁻¹	2.7 ± 1
64 TO 67 cm ⁻¹	2.6 ± 1

5.3

It was stated in Chapter 4 that the initial aims of the project were to repeat the measurements of Gimmedstad et al.¹ Having calculated a binding energy in close agreement with that of Gimmedstad it was decided to concentrate on a search for distinct spectral features due to dimeric absorption. For this purpose new apparatus, to be known as Mark 2, with a longer path length (16.45 cm) gas cell was used.

5.3.1 Apparatus

As can be seen from figures 15 the basic lay out and function of the apparatus is essentially the same as that used in Mark 1, i.e. source (scrambler), interferometer, gas cell connected to a dewar ("cold finger") contained in a vacuum tank, bolometer and data logging equipment.

The gas cell was again made from brass and was 16.45 cm long. The two ends of the cell were wedged so as to prevent channel spectra. An aluminium block positioned between the cell and the cold finger provided a temperature gradient between the cell and the cold finger, which made it easier to control the temperature of the cell.

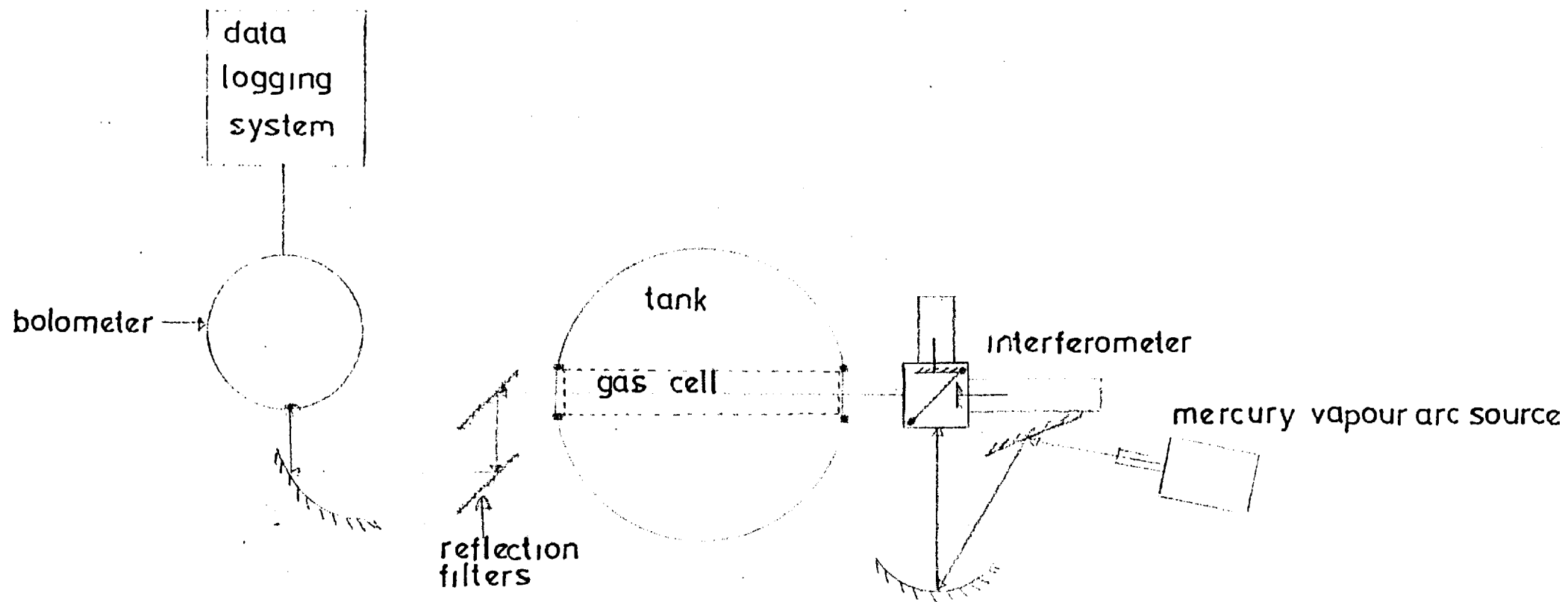


Fig 15a Mark II

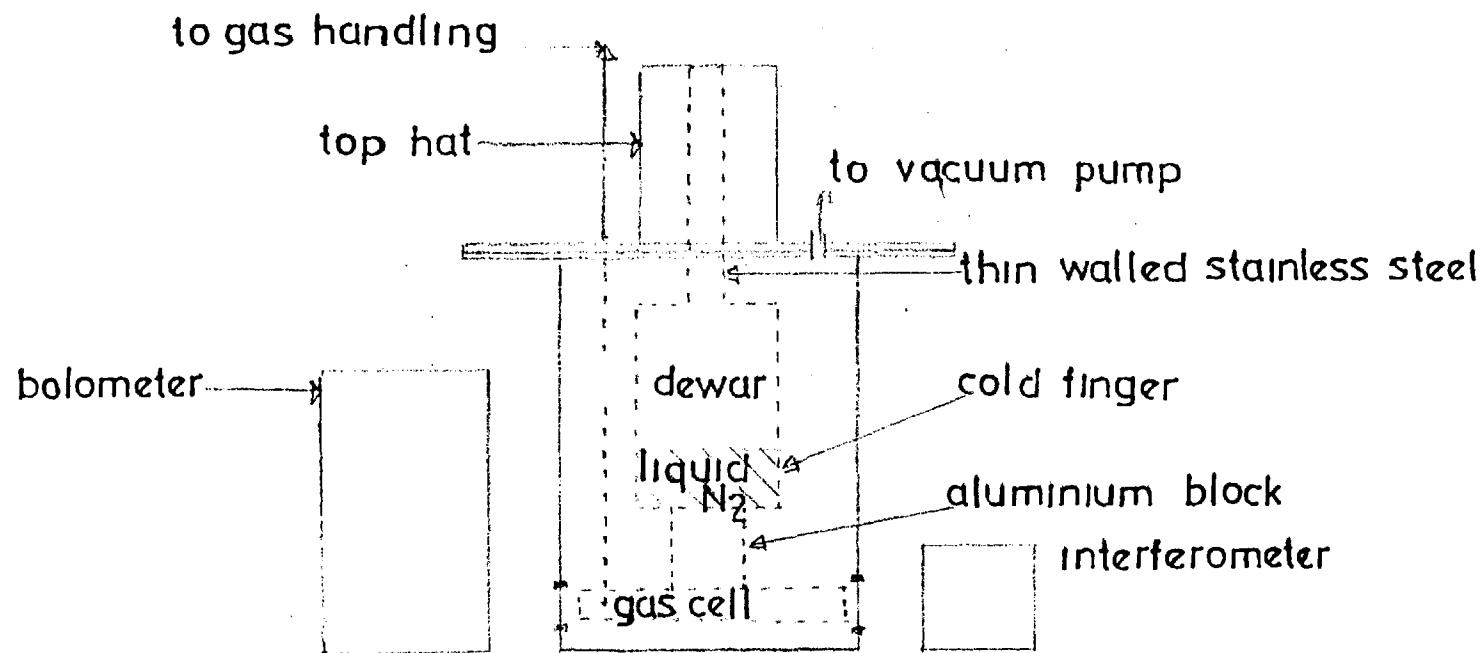


Fig 15b Mark II

The temperature of the gas cell was again measured by attaching, using epoxy resin, three thermistors to different points on the cell. The table in figure 16 shows that the temperature variation across the cell was no greater than 3° K

In order to observe any spectral features (as reported by Gimmetad¹) near 10 cm^{-1} with good signal to noise ratio a 125 micron beamsplitter, which gives a first minimum at about 23 cm^{-1} , was used. The phase modulation was adjusted to give a maximum between 4 and 23 cm^{-1} . A wire mesh filtering system was used to cut down high frequency radiation as the cell was fitted with TEFLON windows instead of crystal quartz windows ($\frac{1}{4}$ " teflon windows were used instead of crystal quartz windows in order to work at higher pressures up to 4000 torr).

The vacuum and gas handling system was similar to that used with Mark 1.

5.3.2. Experimental Procedure

The experimental procedure was nearly the same as that used with Mark 1, i.e. pressure scans at constant temperature, except that this time the observed transmission spectra were not ratioed to their relevant theoretical transmission spectra. The reasons for this were that a) as mentioned in section 2.1.2. there is some confusion over which line shape to use for the ground state inversion line, and b) according to the kinetic line shape there is negligible monomer absorption in the spectral region (0 to 20 cm^{-1}), temperature and pressure range, and path length in which observations were being made. Therefore any absorption in this region was assumed to be due to the NH_3 dimer.

Thermistors	Resistance	Temperature	Temperature used in calculation
1	189 k Ω	237 K	240 K
2	160 k Ω	240 K	
3	147 k Ω	241 K	
1	56 k Ω	260 K	261 K
2	52 k Ω	261 K	
3	49 k Ω	262 K	

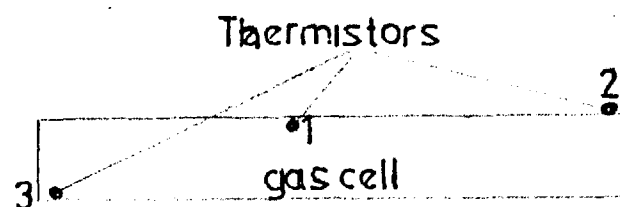


Fig 16

Integrated absorption measurements were calculated in the spectral regions of 4.9 to 9.9 cm^{-1} , 7 to 9.9 cm^{-1} , and 9.9 to 18.1 cm^{-1} . The 7 to 9.9 cm^{-1} region was included so that the binding energy calculated in this region could be compared to 7 cm^{-1} work, carried out at the Appleton Laboratory by LLEWELLYN-JONES, on NH_3 using an untuned cavity.

The results were analysed in the same manner as with Mark 1, i.e. binding energy obtained from the temperature dependence of the quadratic coefficient of the pressure dependence (at constant temperature) of the absorption (see fig. 17).

Binding Energies

<u>Spectral Region</u>	<u>E</u>	<u>K</u>	<u>cals/mole</u>
4.9 to 9.9 cm^{-1}			$2.5 \pm .4$
7 to 9.9 cm^{-1}			$2.3 \pm .3$
9.9 to 18.1 cm^{-1}			$2.3 \pm .1$

5.3.3. Discussion of Results obtained with Mark 1 and Mark 2

The results obtained with Mark 2 are consistent with those obtained by LLEWELLYN-JONES, but the value of the binding energy is less than that obtained with Mark 1 and by other workers^{1 3 6}. A possible reason for this is that there is more absorption in the region of 0 to 20 cm^{-1} than predicted by the theory using a kinetic line shape. A valuable extension of this work would be to determine which line shape would be needed in order to calculate a dimer binding energy consistent with the Mark 1 experiment and with other workers.

Fig17_a Arrhenius Plot

4.9 — 9.9 cm⁻¹

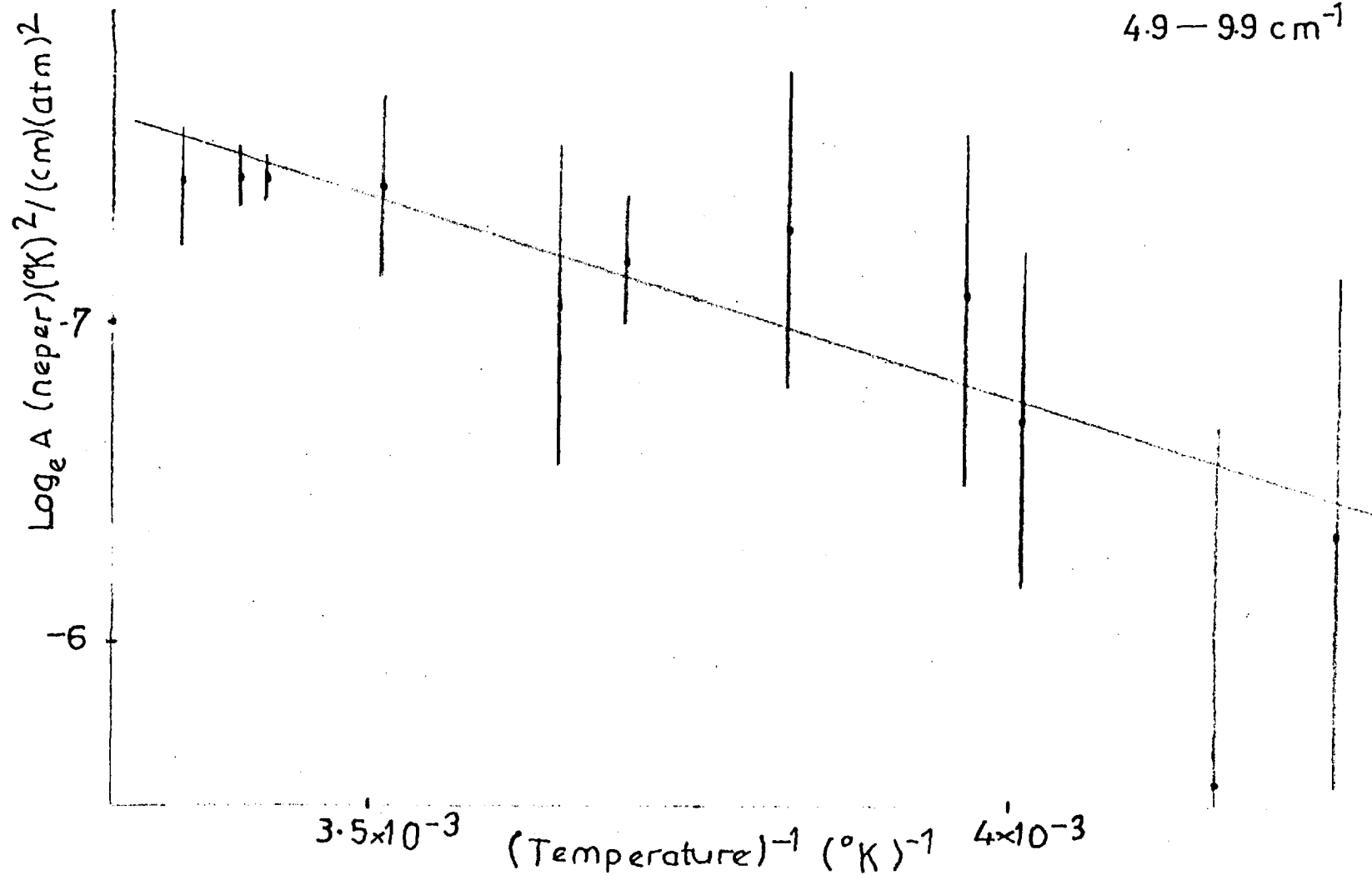


Fig17_b Arrhenius Plot

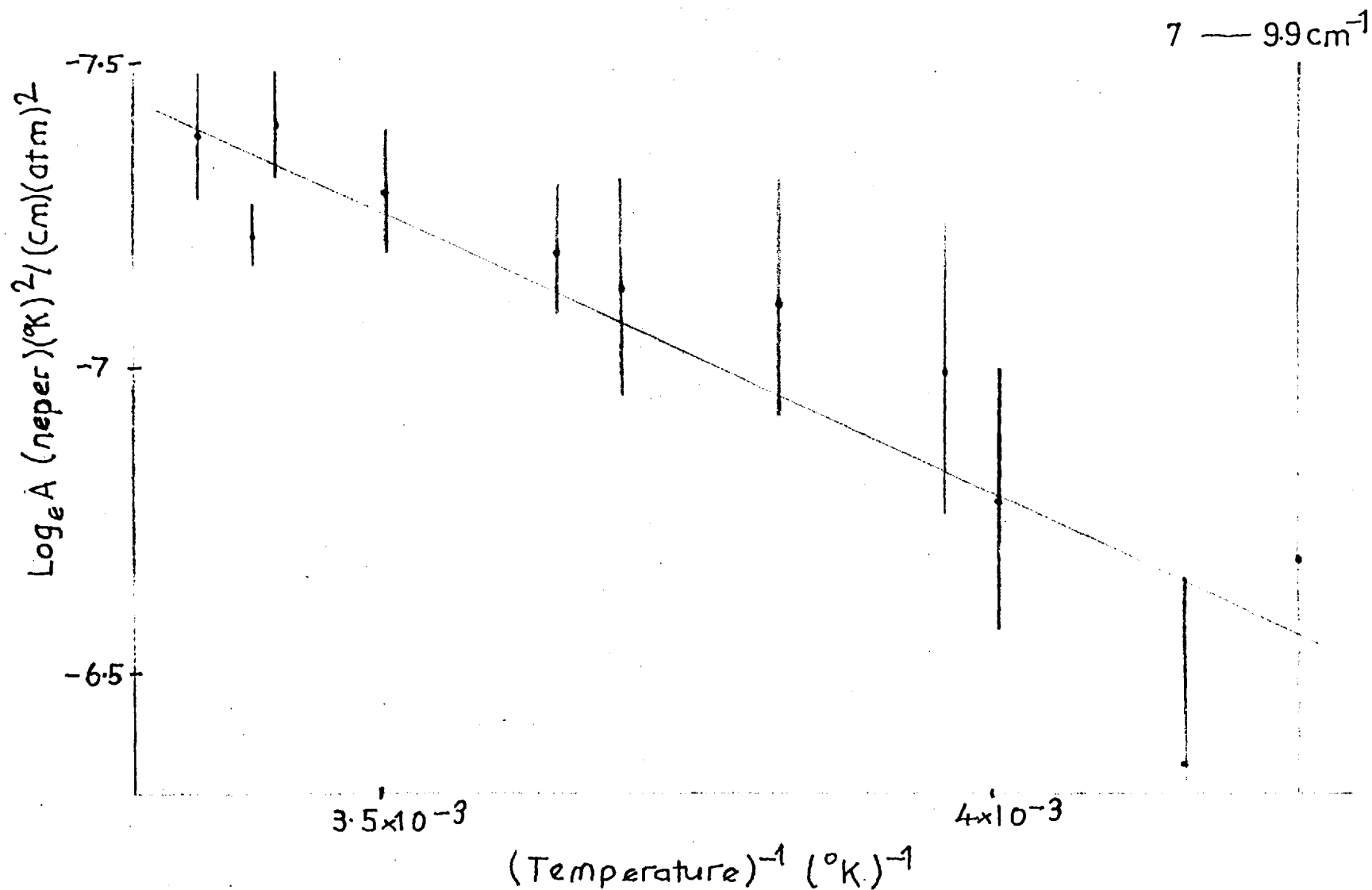
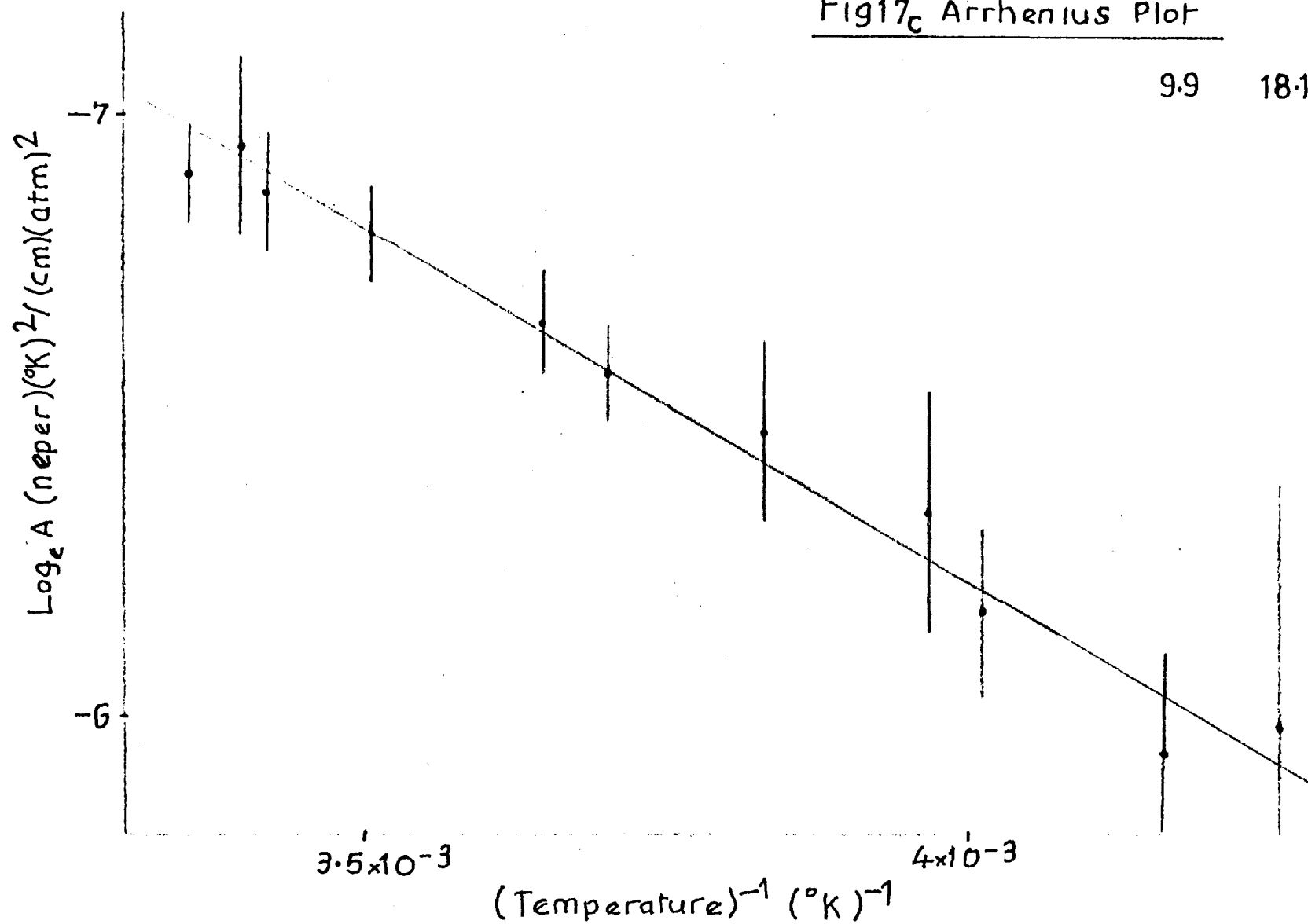


Fig 17_c Arrhenius Plot

9.9 18.1 cm⁻¹



5.4

In section 6.2.3.2. chapter 6 absorption features attributed to the NH_3 dimer (because of their temperature dependence) will be reported. The measurements resulting in the observation of these features were obtained at low temperatures and pressures i.e. 19 ϕ K and 19 torr. Therefore the NH_3 monomer absorption lines were narrow and weak with no absorption between the lines (greater than 99% transmission), and so any measurements made on features in between the lines were completely independent of the NH_3 monomer prediction.

The temperature dependence of these features was found by making observations at different temperatures but at constant density of NH_3 molecules. This dependence was found to be exponential i.e. they could not be explained in terms of NH_3 monomer absorption. (see figs. 18).

Again binding energies were determined from the temperature dependencies of these features.

Binding Energies

<u>Spectral Region</u> <u>(Position of Feature)</u>	<u>E K cals/mole</u>
46 to 51 cm^{-1}	3.5 $\pm$.2
68 to 73 cm^{-1}	3.2 $\pm$.2
9 ϕ to 95 cm^{-1}	3. ϕ $\pm$.3

Fig 18_d Arrhenius Plot

46-51 cm⁻¹

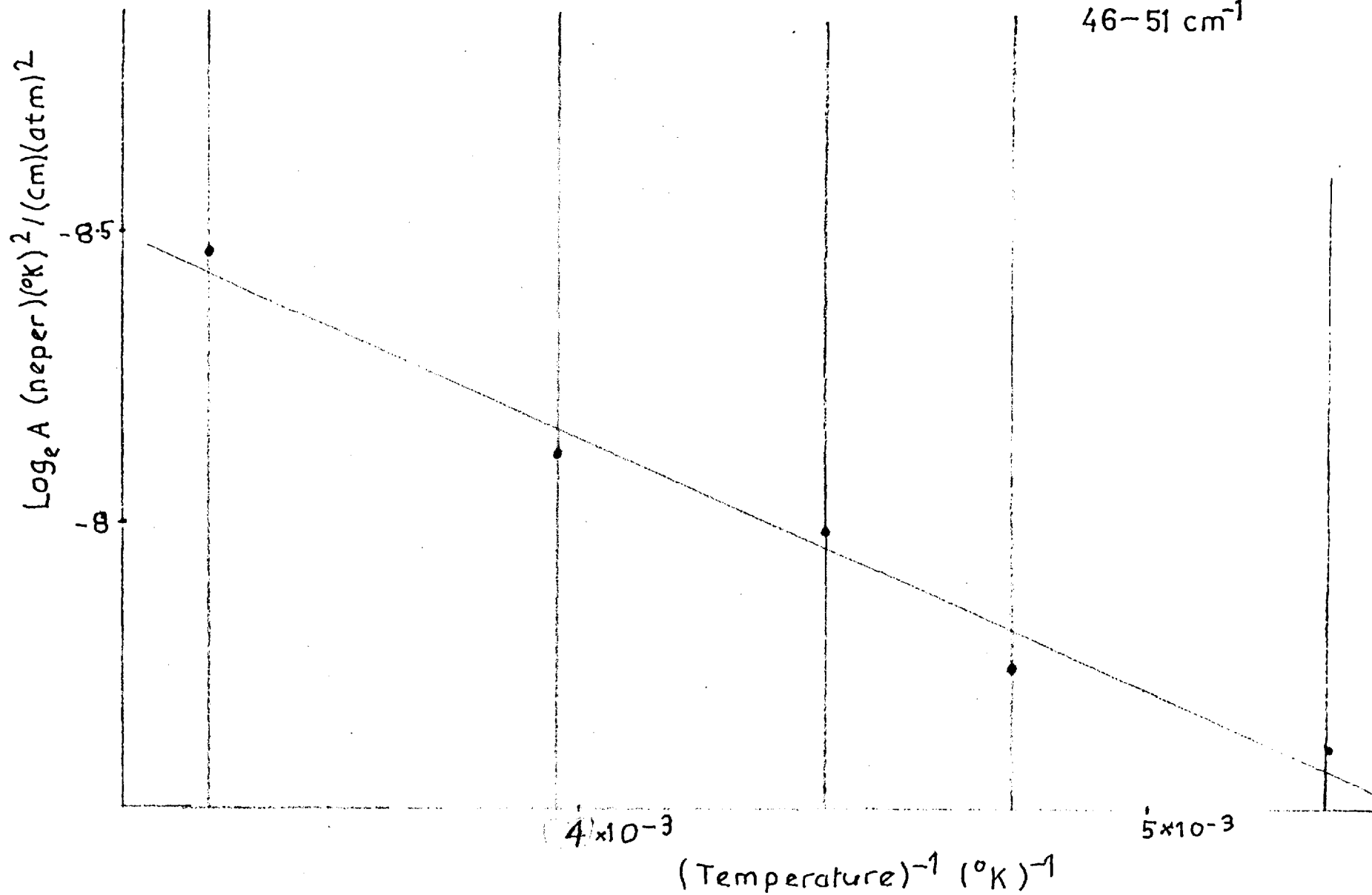
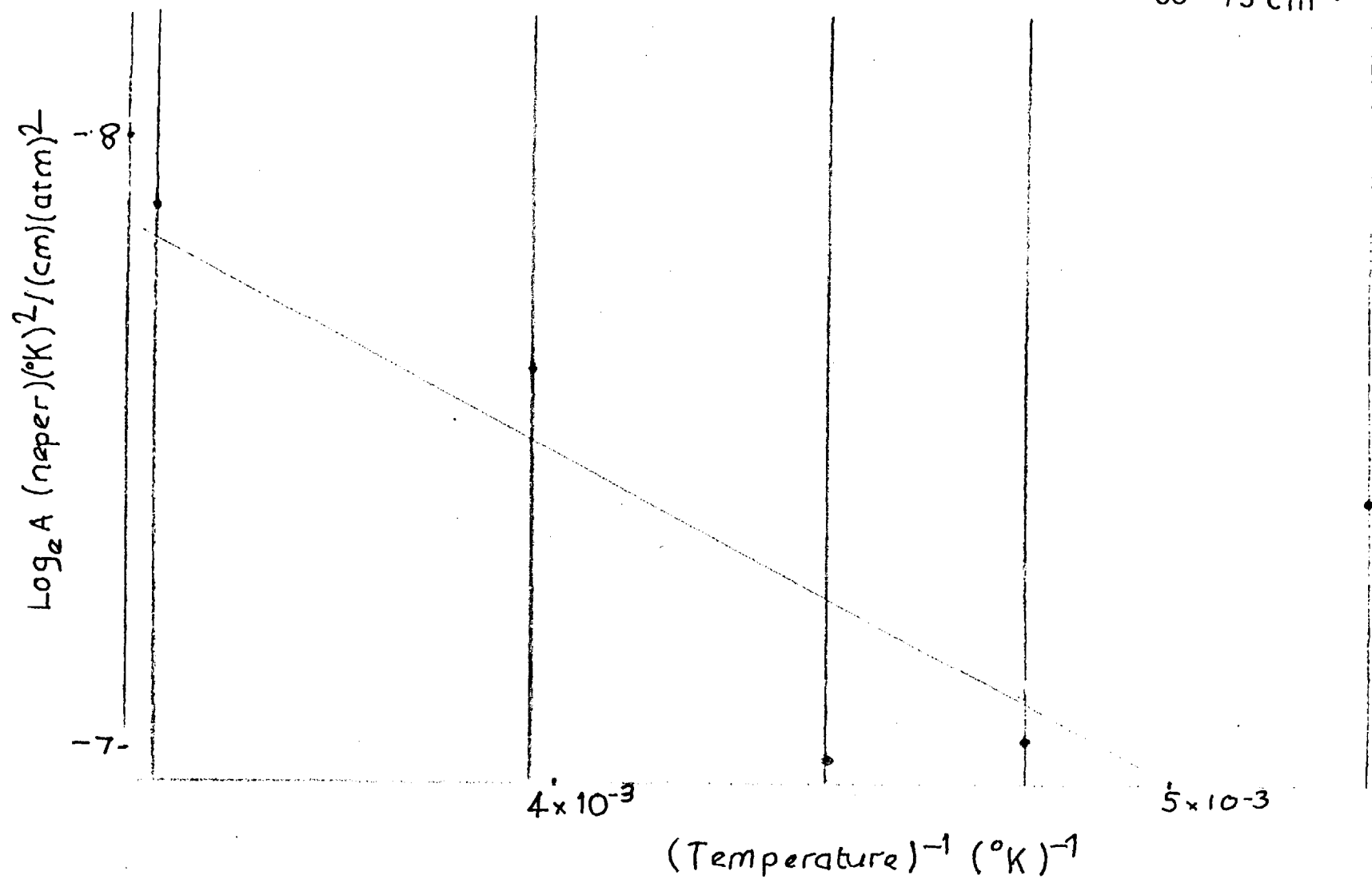
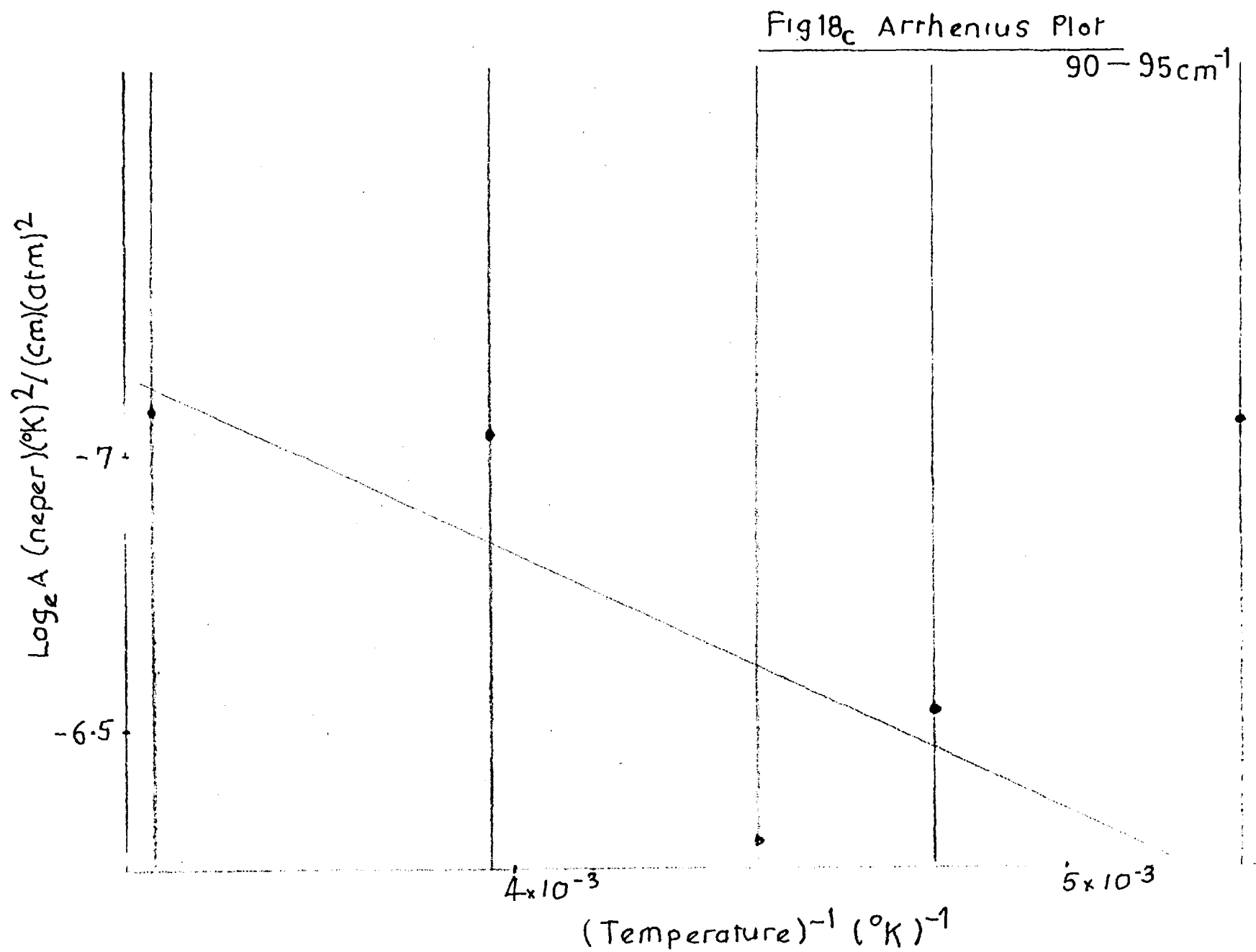


Fig 18_b Arrhenius Plot

68-73 cm⁻¹





It can be seen from the theoretical NH_3 monomer predictions (see chapter 6) that the transmission in the spectral region of 46 to 51 cm^{-1} is 100%, but the transmission becomes less as the frequency increases i.e. about 99% in the region of 68 to 73 cm^{-1} and about 98% from 90 to 95 cm^{-1} . This together with the fact that the signal to noise ratio (in the observed spectra) is a maximum at about 50 cm^{-1} and decreases with increasing frequency is the reason for the variation in binding energies.

The apparent decrease of binding energy with increase of NH_3 monomer absorption, which is ignored in the calculations, is consistent with the low binding energy results obtained in section 5.3, in which the NH_3 monomer absorption was ignored.

CHAPTER 6

Experimental Results

The Search for Spectral Features due to the NH_3 Dimer

6.1 The Search using Mark 1 and Mark 2

The initial search for spectral features involved the use of 3.2 cm (Mark 1) and 16.45 cm (Mark 2) gas cells. Observations were made in the spectral region of 4 to 6 cm^{-1} and were made at different temperatures, ranging from 24 $^\circ\text{K}$ to 300 $^\circ\text{K}$, and at different pressures near to the saturated vapour pressure at the relevant temperatures.

In this initial search no anomalous spectral features were found. As can be seen from figure 19 there is a definite correlation between the apparent spectral features in the transmission spectra and the back ground spectra. These apparent features were caused by variations in the background signal - level which would be quite significant in this low power spectral region.

Observations were also made close to the conditions reported in the paper by Gimmetstad ^I et al except that a longer path length gas cell, and a different geometrical configuration was used in the apparatus. The spectrum shown in figure 20 does not show his reported features.

6.1.1 Summary of initial Search

Even though no distinct spectral features were observed there was still considerable anomalous absorption which through its temperature dependence has been shown to be consistent with dimerization.

If spectral absorption features due to NH_3 dimers do exist then a possible reason why no such features were

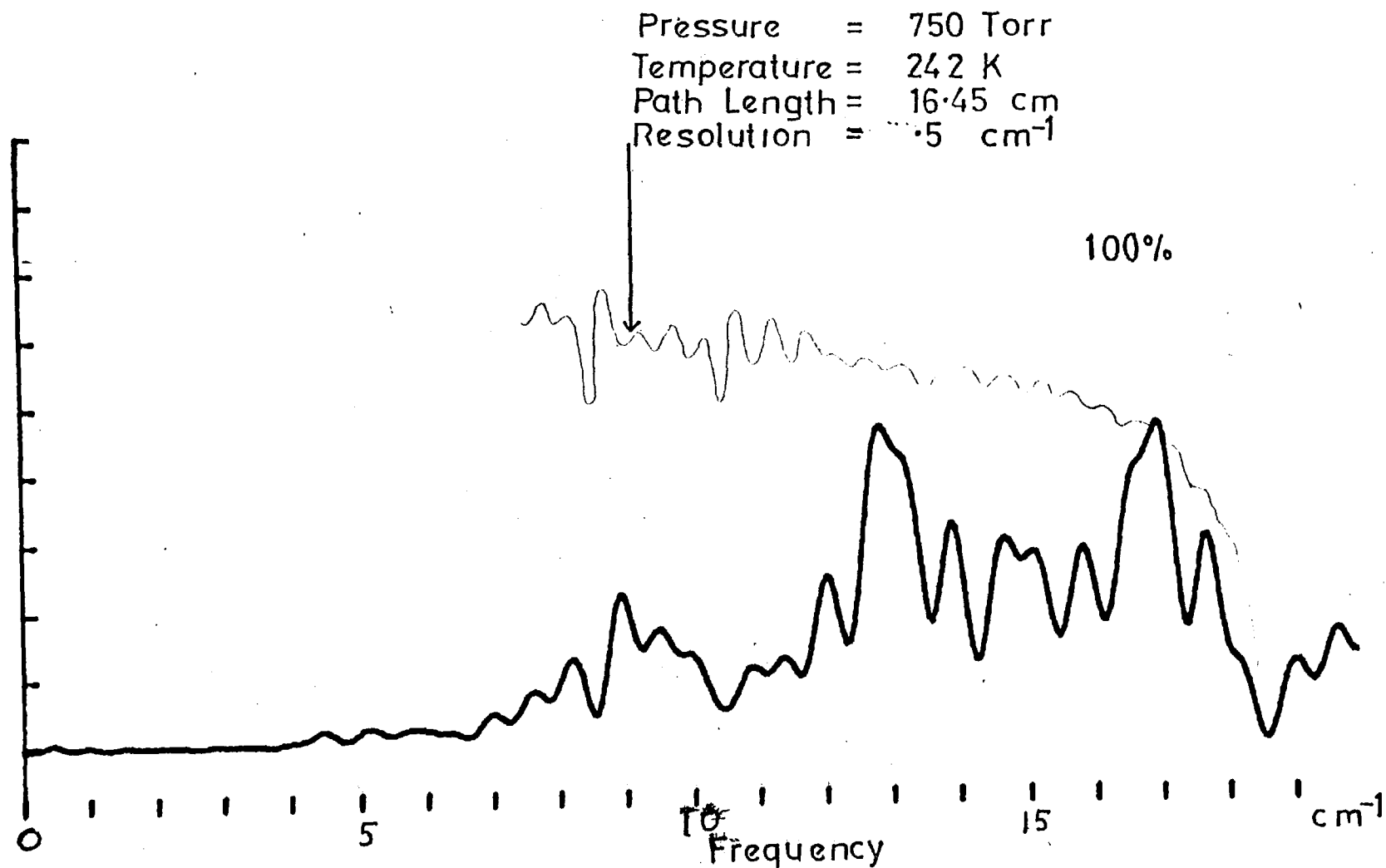


Fig 19 Comparison Between Transmission and Background Spectra

Pressure = 1900 Torr
Temperature = 261 K
Path Length = 16.45 cm
Resolution = 1 cm⁻¹

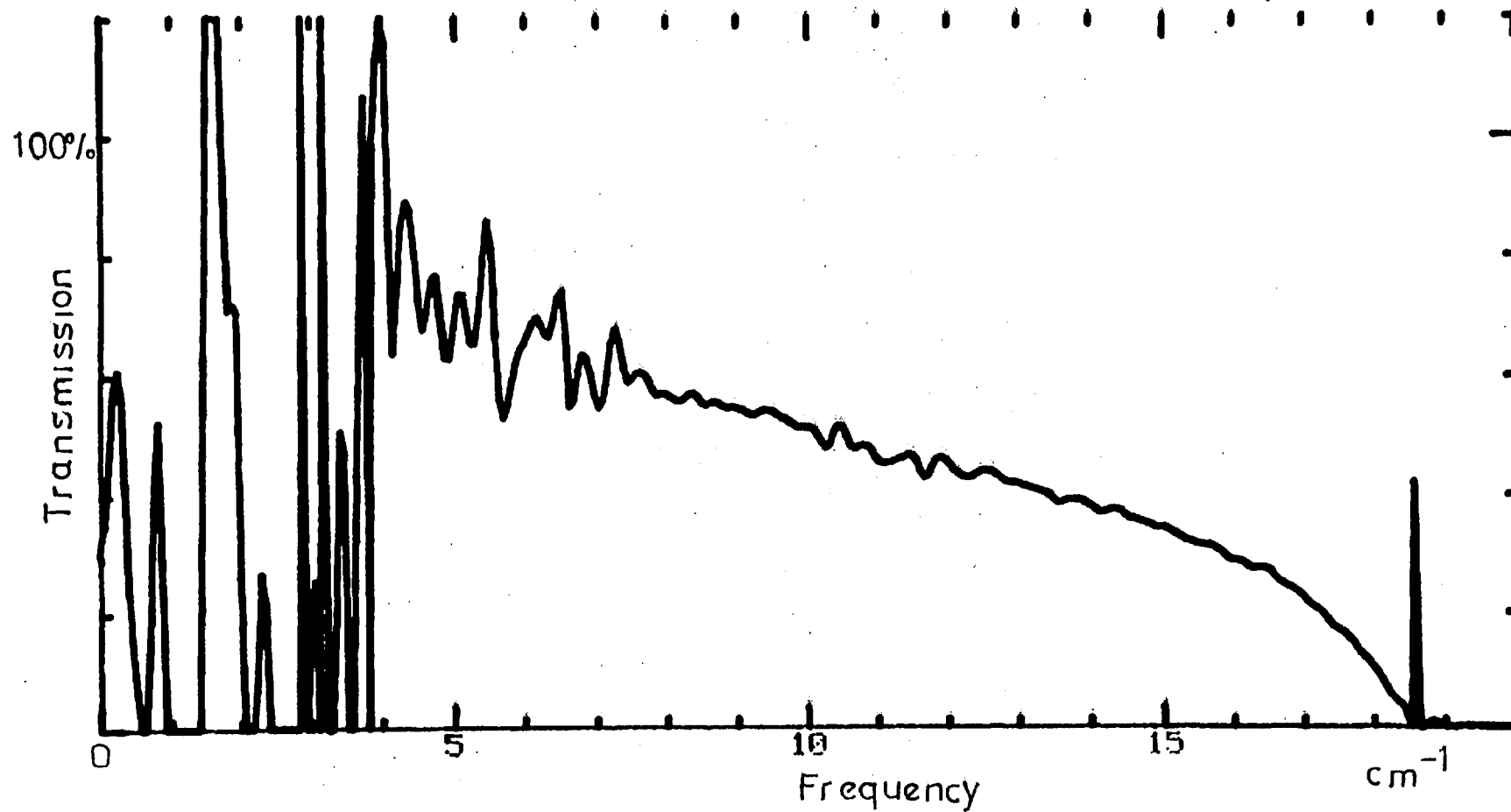


Fig 20 NH₃ Transmission Spectrum

observed was that each individual dimer rotational line was pressure broadened (by the NH_3 monomer), and because of the small dimer rotational spacing, the result was a smoothed spectrum. The observed NH_3 dimer contour is in close agreement with that obtained from the S. D.D.S model (see fig 10).

6.2

Low Temperature Work

In order to observe distinct spectral features due to dimeric absorption it would be necessary to accomplish three experimental aims which were to make observations 1) at low pressure, to reduce pressure broadening of NH_3 dimer lines by NH_3 monomer, and also to reduce the NH_3 monomer contribution between rotation lines to negligible values, 2) at low temperatures to increase the dimer concentration, and finally 3) with a long path length.

An additional incentive to make observations at pressures near 20 torr was some recent unpublished work (Appleton Laboratory) carried out on saturated water vapour at pressures near 20 torr, in which a water dimer binding energy, higher than that previously found, was calculated.

6.2.1

Low Temperature Work carried out with a modified Mark 1 (Mark 1a)

6.2.1.1

Apparatus

Mark 1 was modified so that it was fully pumpable thereby completely removing atmospheric water vapour from the apparatus (see appendix A).

Two different path length gas cells were used with Mark 1a, one having a path length of 1.16 cm and the other 3.2 cm.

The initial cooling of the gas cell was achieved by pouring liquid nitrogen into the stainless steel container and then, when the temperature of the cell was near 200°K a mixture of Acetone and dry ice was poured into the container. This method enabled a temperature of 200°K be achieved.

6.2.1.2

Results

The first measurements were obtained with the 1.16 cm cell, at a pressure of 40 torr and at two different temperatures, room temperature (297°K) and 200°K . Several measurements were made at each temperature and the resulting transmission spectra were averaged together.

The results looked very promising with absorption not predicted by NH_3 monomer theory in the region from 45 to 55 cm^{-1} (see fig 21) and so the cell was replaced with the 3.2 cm cell. Several measurements were made at a pressure of 40 torr and a temperature of 200°K . Again the results looked promising (see fig 22). These results showed that a longer path length cell was needed and also that it would be better to decrease the temperature further in order to reduce the contribution to absorption from ν_2 inversion lines. For this purpose Mark 2 was modified so that it was fully pumpable.

Pressure = 40 Torr
Temperature = 297 K
Path Length = 1.16 cm
Resolution = 1 cm⁻¹

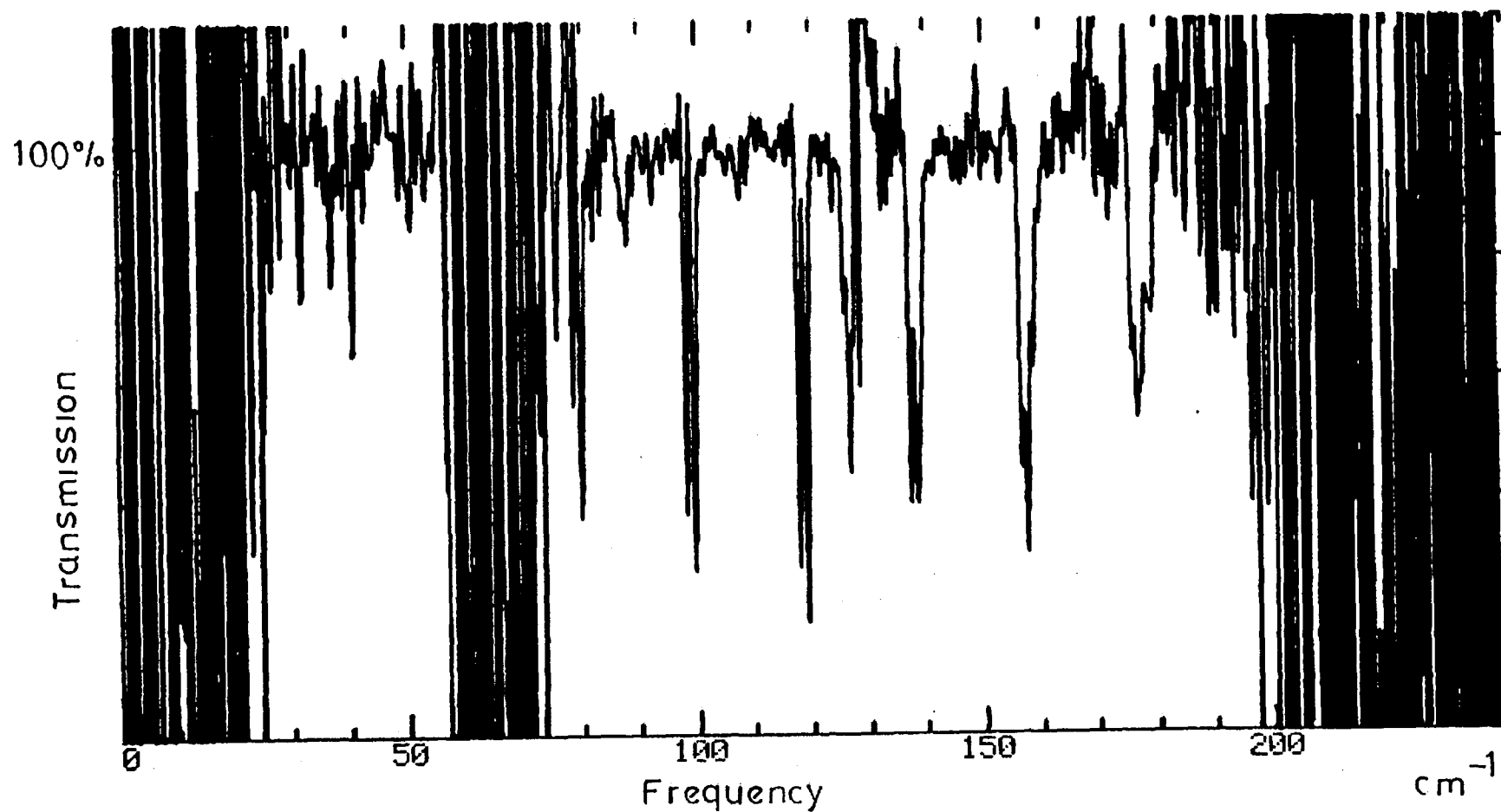


Fig 21a NH₃ Transmission Spectrum

Pressure = 40 Torr
Temperature = 200K
Path Length = 1.16 cm
Resolution = 1 cm⁻¹

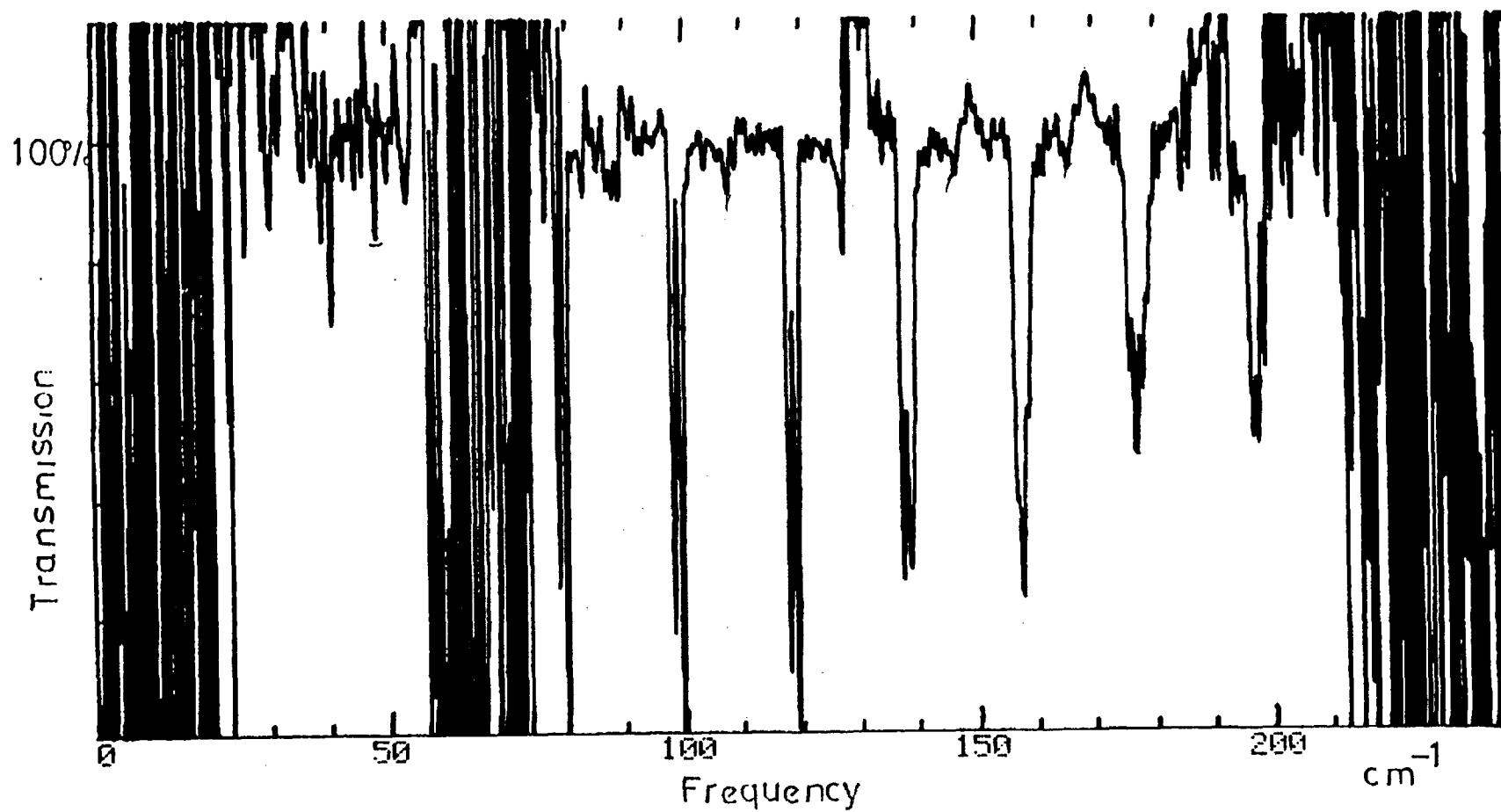


Fig 21b NH₃ Transmission Spectrum

Pressure = 40 Torr
Temperature = 200 K
Path Length = 3.2 cm
Resolution = 1 cm⁻¹

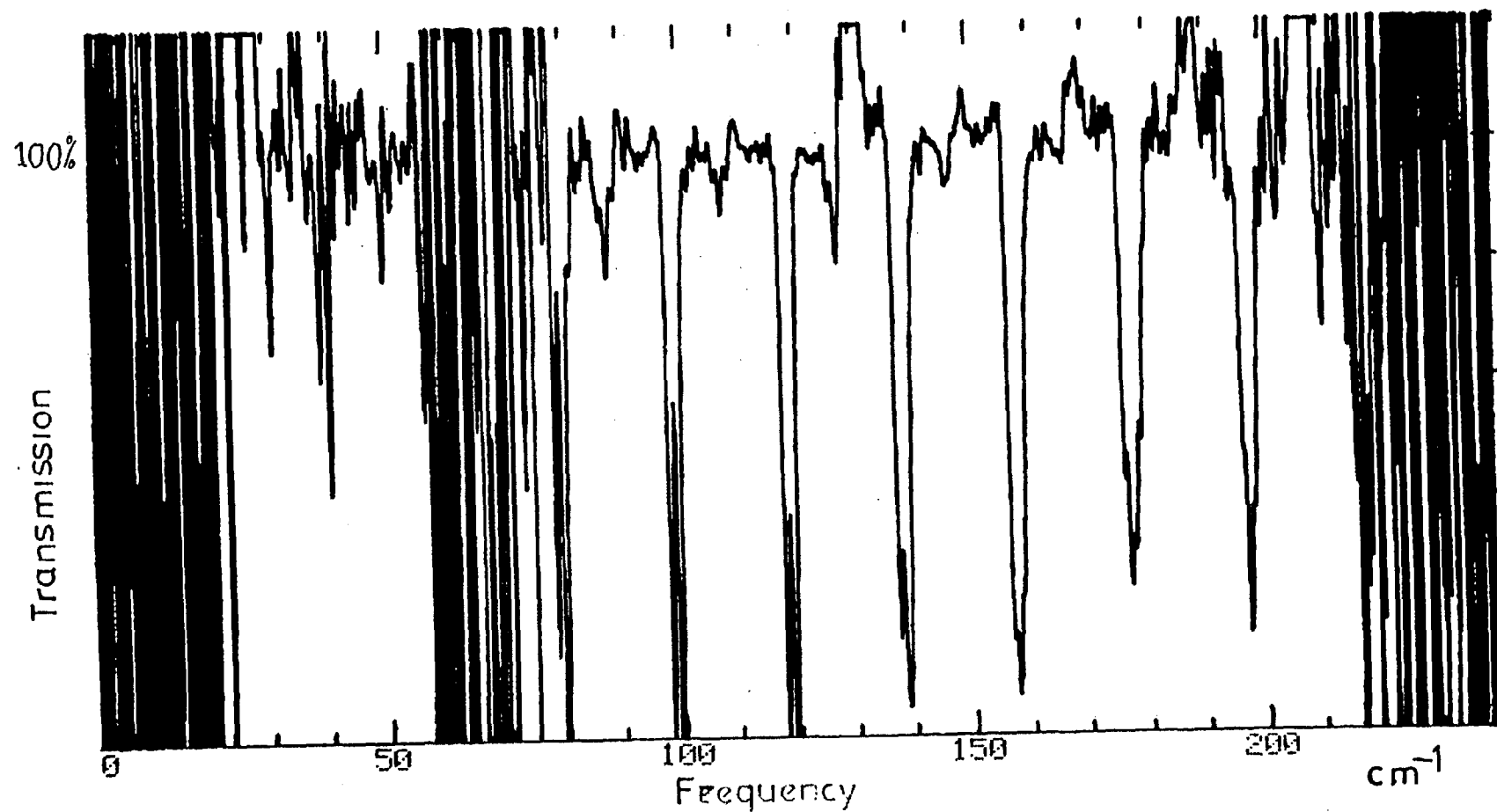


Fig 22 NH₃ Transmission Spectrum

6.2.2

Low Temperature Work Carried out with modified Mark 2 (Mark 2a)

6.2.2.1

Apparatus

Mark 2 was quite easily converted into a fully pumpable system. The interferometer and source arrangement was taken off Mark 1a and fixed onto the vacuum tank. An aluminium flange was designed and built to attach the bolometer to the tank, the flange being permanently fixed onto the bolometer. This proved to be the most difficult operation as even a slight stress on the flange was enough to cause a minute leak into the bolometer with a subsequent increase in the rate of loss of helium.

An improvement in the temperature measurement was achieved by the use of a thermocouple in conjunction with the thermistors. It was fitted to the cell (16.45 cm) by drilling a small hole into the cell's side and then fixing the thermocouple into the hole using epoxy resin. Also a 12 watt electric heater was inserted between the aluminium block and the cell to provide greater control over the cooling at these low temperatures.

6.2.2.2

Results

Three transmission spectra were obtained at a pressure of 19 Torr, a temperature of 195°K , the resolution being 1 cm^{-1} . The average of these three spectra is shown in figure 23. Comparing this transmission spectrum to those obtained with Mark 1a (Section 6.2.1.2) it seemed that there was definite anomalous absorption in the region of 45 to

Pressure = 19 Torr
Temperature = 195 K
Path Length = 16.45 cm
Resolution = 1 cm^{-1}

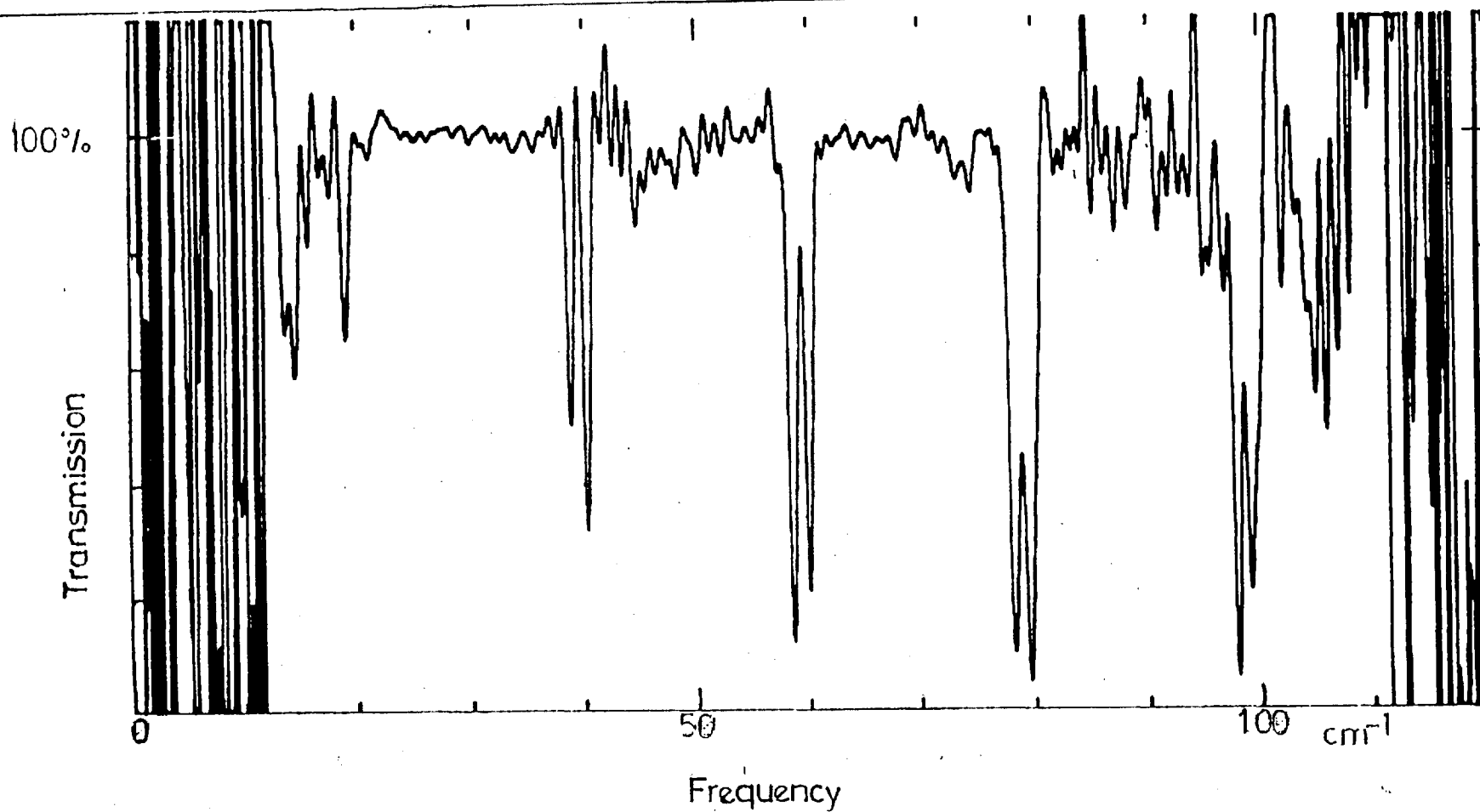


FIG 23 NH_3 Transmission Spectrum

55 cm^{-1} (because of the absence of NH_3 monomer lines in this region) and possible anomalous absorption in the region of 65 to 75 cm^{-1} . The only way to confirm this would be to increase the path length by an order of magnitude.

6.2.3 Low Temperature Work carried out with non-resonant Spherical Cavity MARK 3

6.2.3.1 Apparatus

The only differences between Mark 3 and Mark 2a were that the fixed path length gas cell was replaced by the cavity absorption cell and that two electric heaters were used instead of one.

Again low temperatures were achieved using liquid nitrogen and the cavity temperature was measured using two thermistors and a thermocouple (attached in the same manner as with Mark 2a).

6.2.3.2 Results

The first observations were made at a temperature of 193°K and an NH_3 pressure of 20 torr with a resolution of .3 cm^{-1} . Normally it took 1½ hours to produce one set of background and foreground spectra.

As can be seen from the spectra in figures 24 these first observations were very exciting as there appeared to be definite anomalous spectral features around 50, 70 and 90 cm^{-1} .

More observations were made at the same pressure but at temperatures of 208°K, 257°K and 298°K to give an indication of their temperature dependence (see figs 24).

Pressure = 10 Torr
Temperature = 184 K
Path Length = 130 cm
Resolution = 3 cm^{-1}

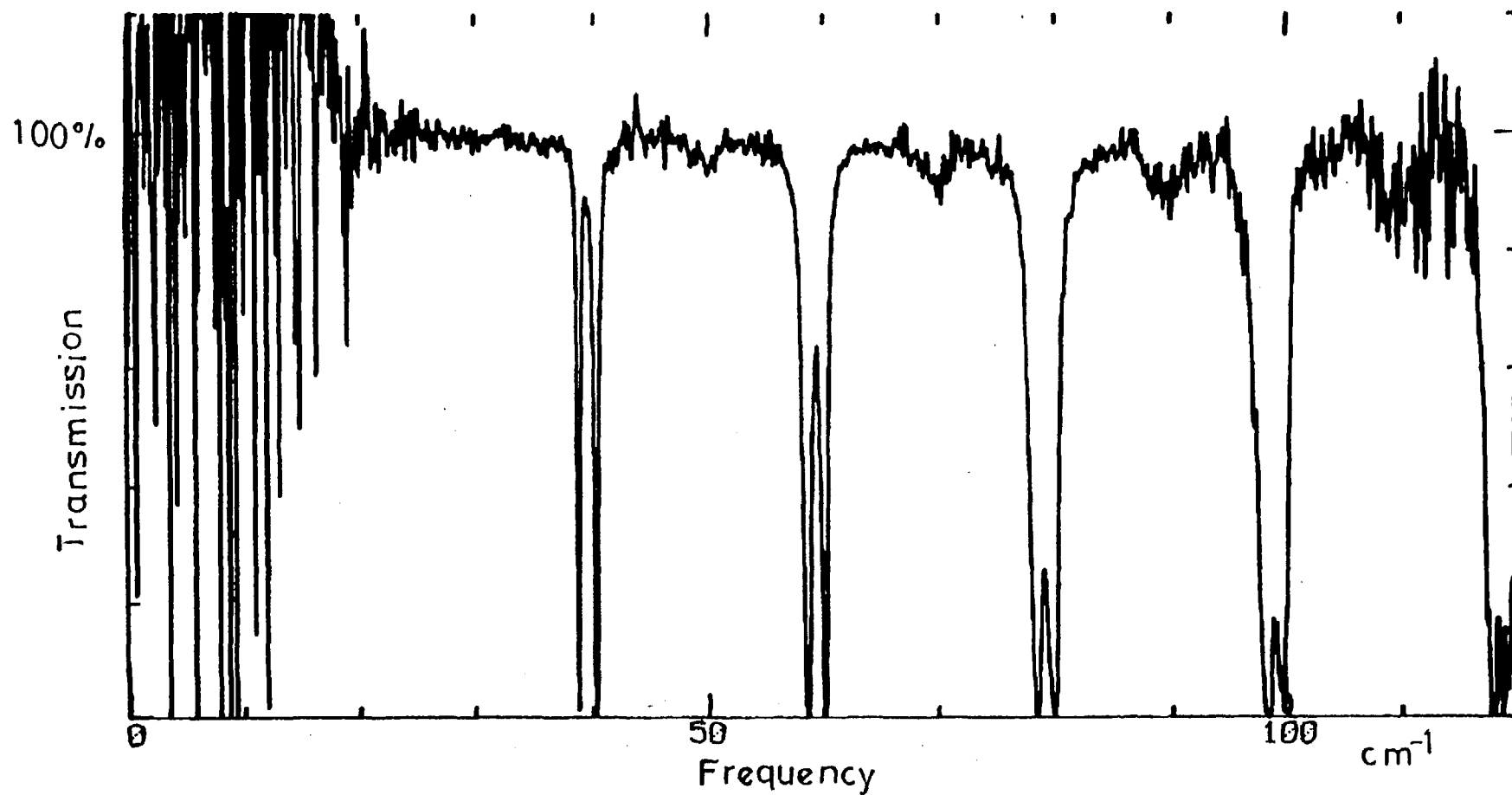


Fig 24a₁ NH₃ Transmission Spectrum

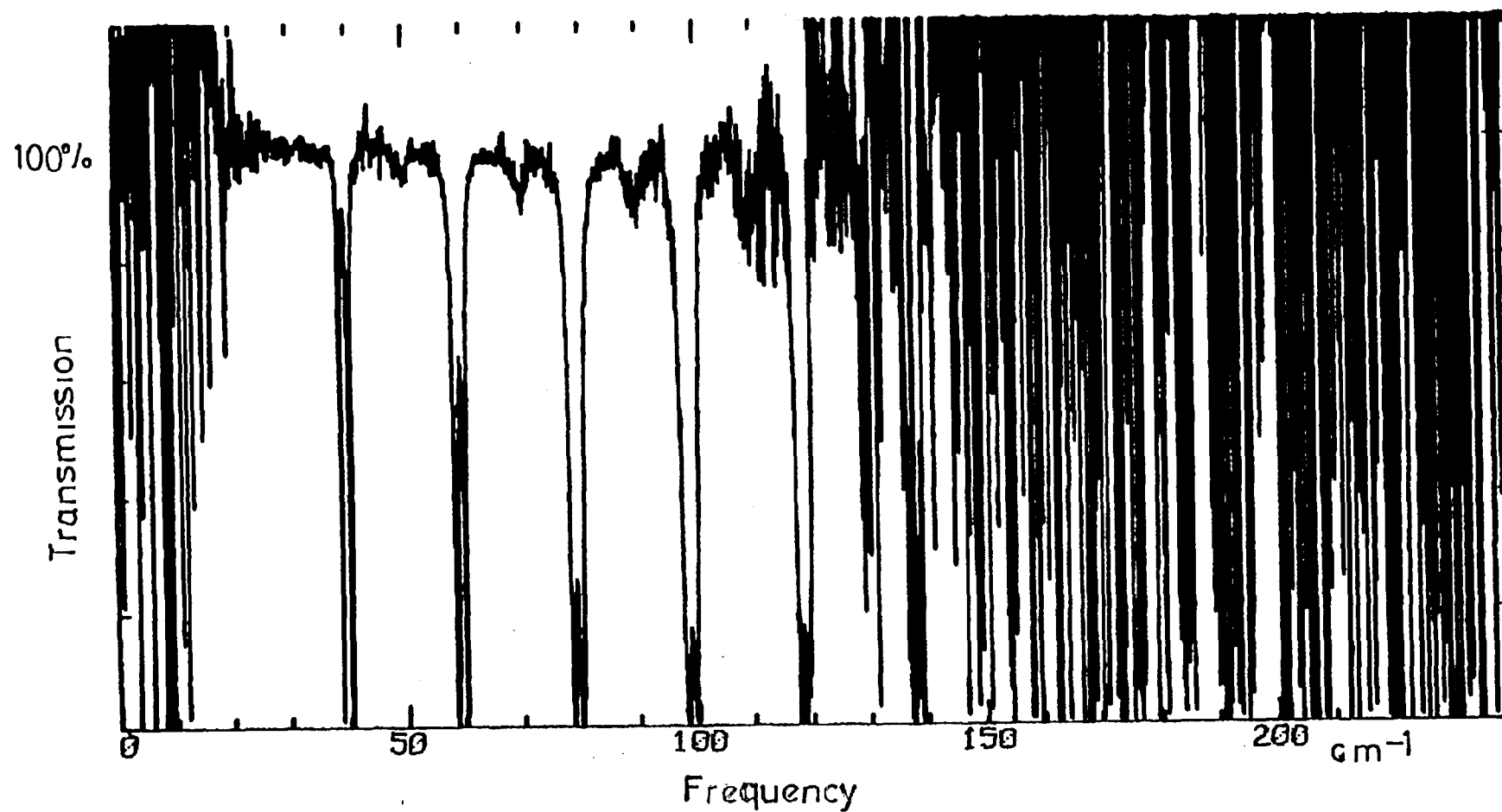


Fig 24a₂ NH₃ Transmission Spectrum(see 24a₁ for expanded horiz scale)

Pressure = 20 Torr
Temperature = 193K
Path Length = 130 cm
Resolution = 3 cm^{-1}

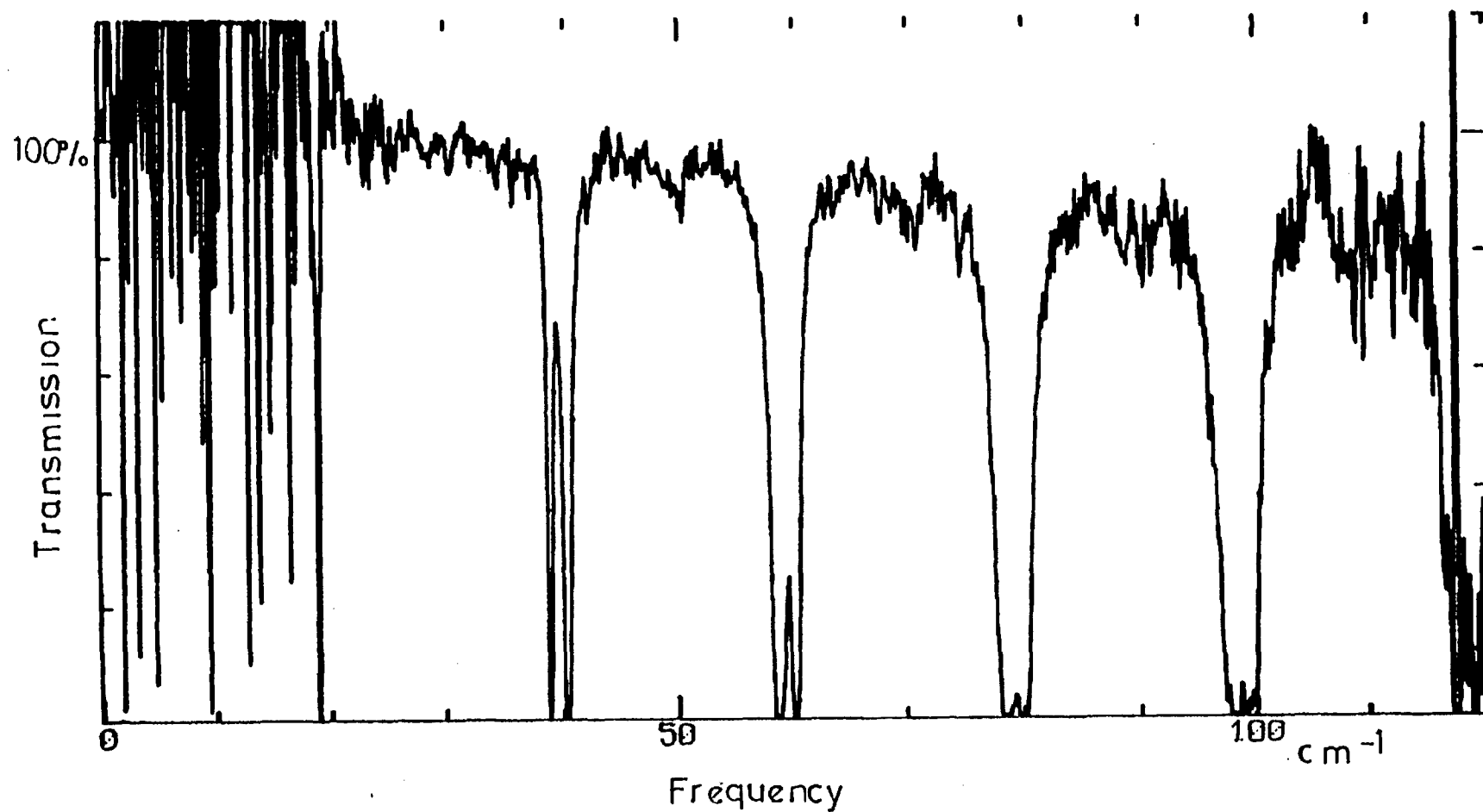


Fig 24b₁ NH₃ Transmission Spectrum

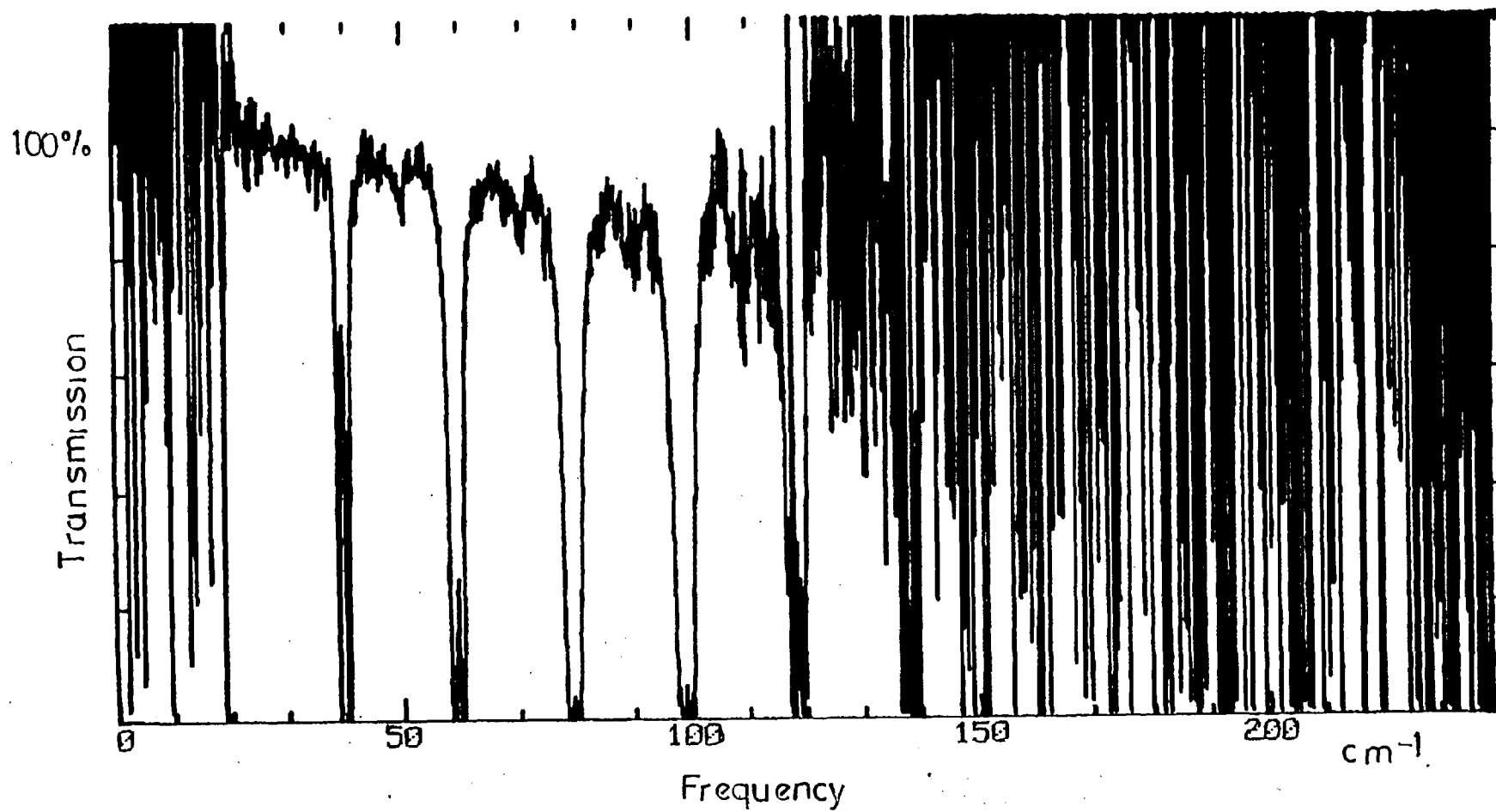


Fig 24b₂ NH₃ Transmission Spectrum (see 24b₁ for expanded horiz scale)

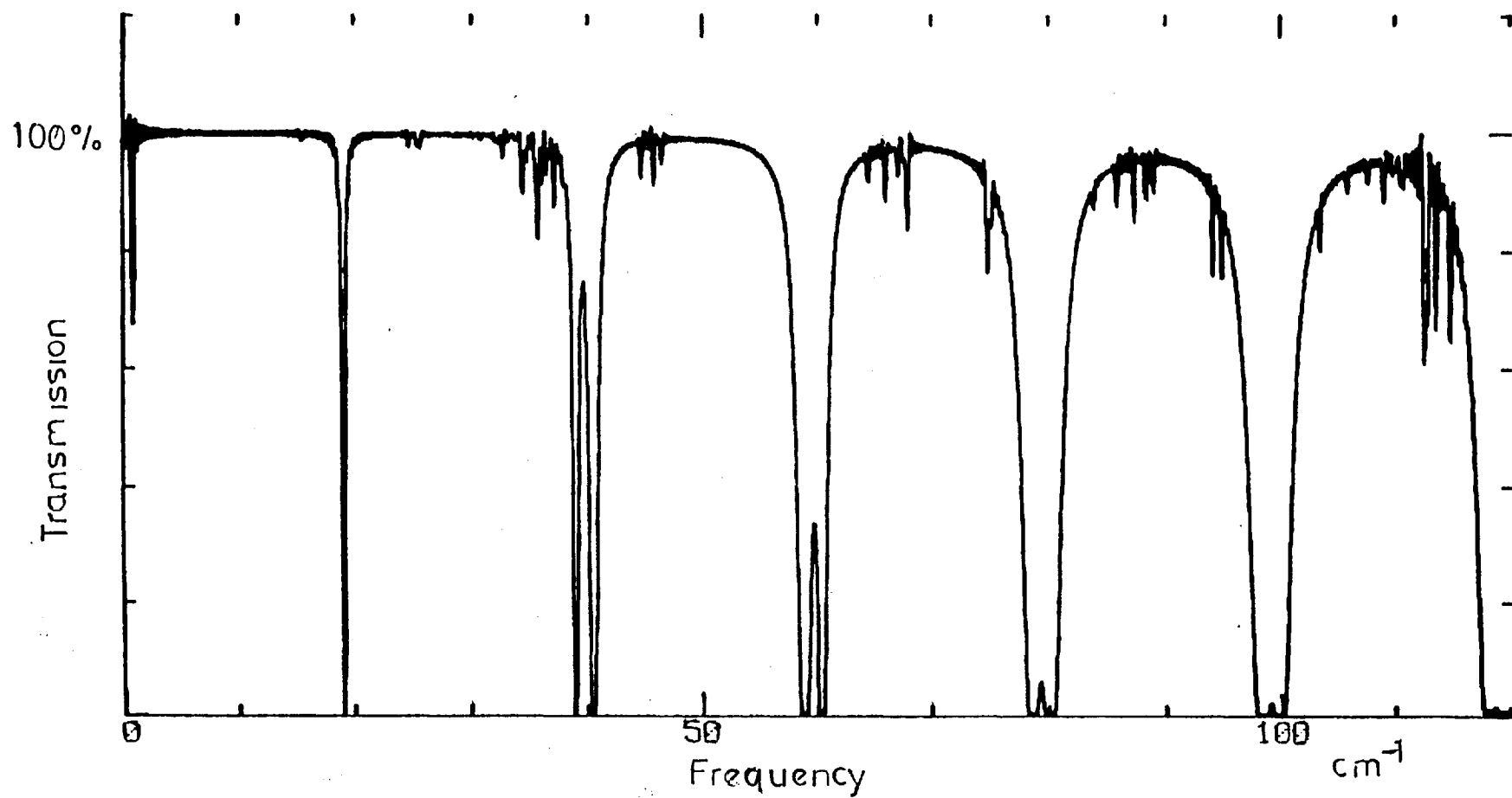


Fig 24b₃ NH₃ Theoretical Transmission Spectrum c.f 24b₁

Pressure = 20 Torr
Temperature = 208. K
Path Length = 130 cm
Resolution = 3 cm^{-1}

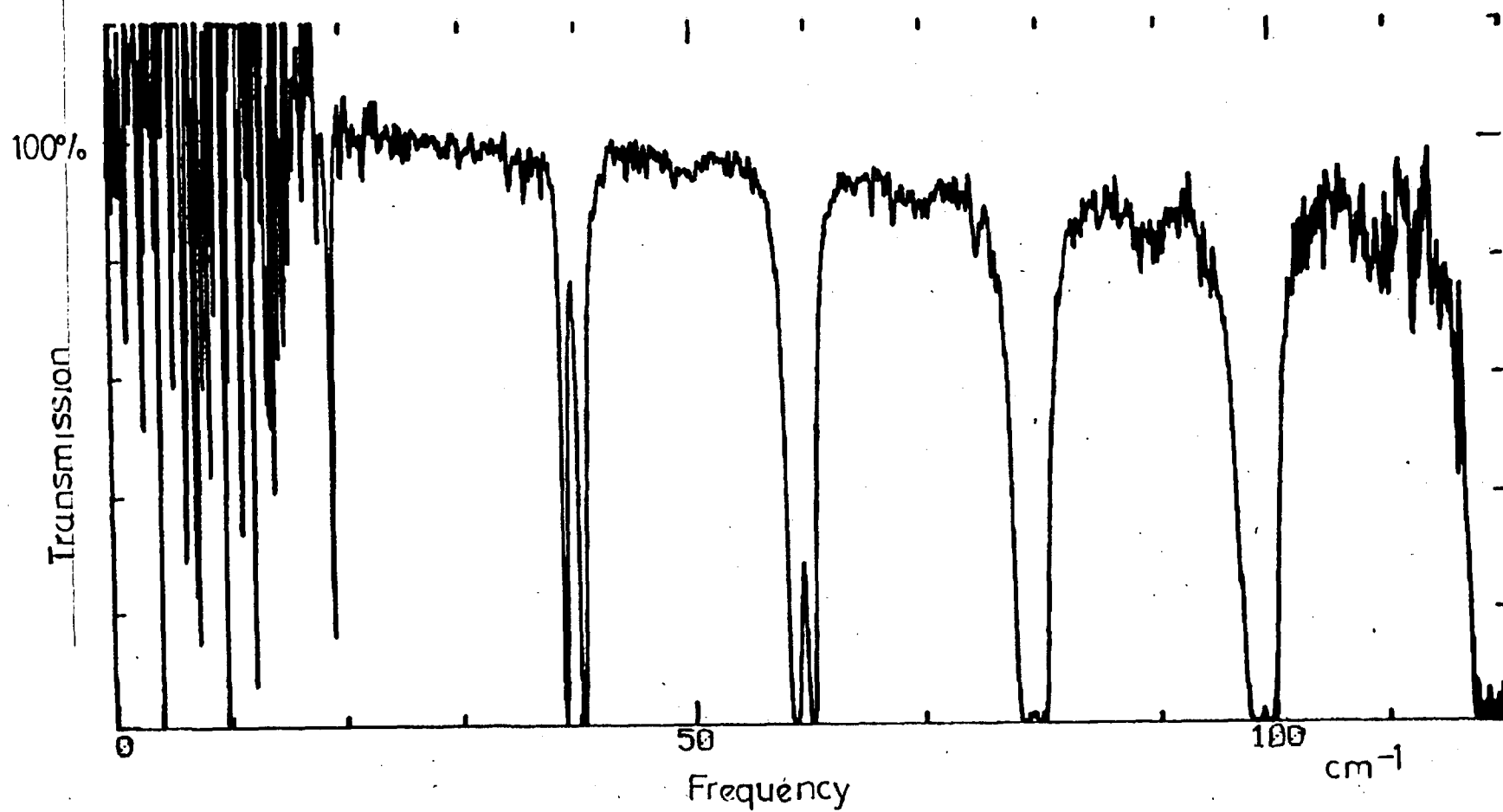


Fig 24c₁ NH_3 Transmission Spectrum

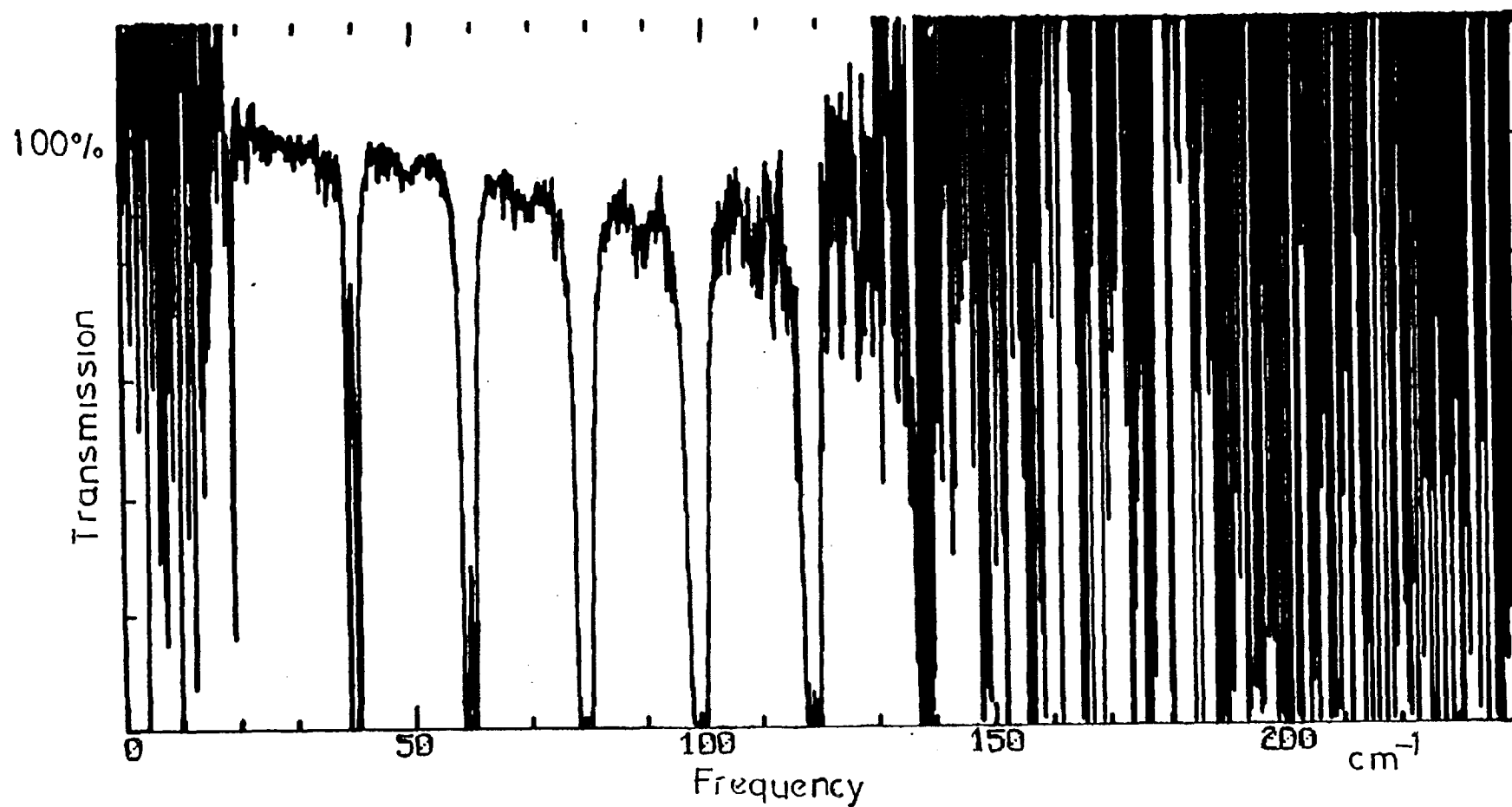


Fig 24c₂ NH₃ Transmission Spectrum (see 24c₁ for expanded horiz scale)

Pressure = 20 Torr
Temperature = 257 K
Path Length = 130 cm
Resolution = 3 cm^{-1}

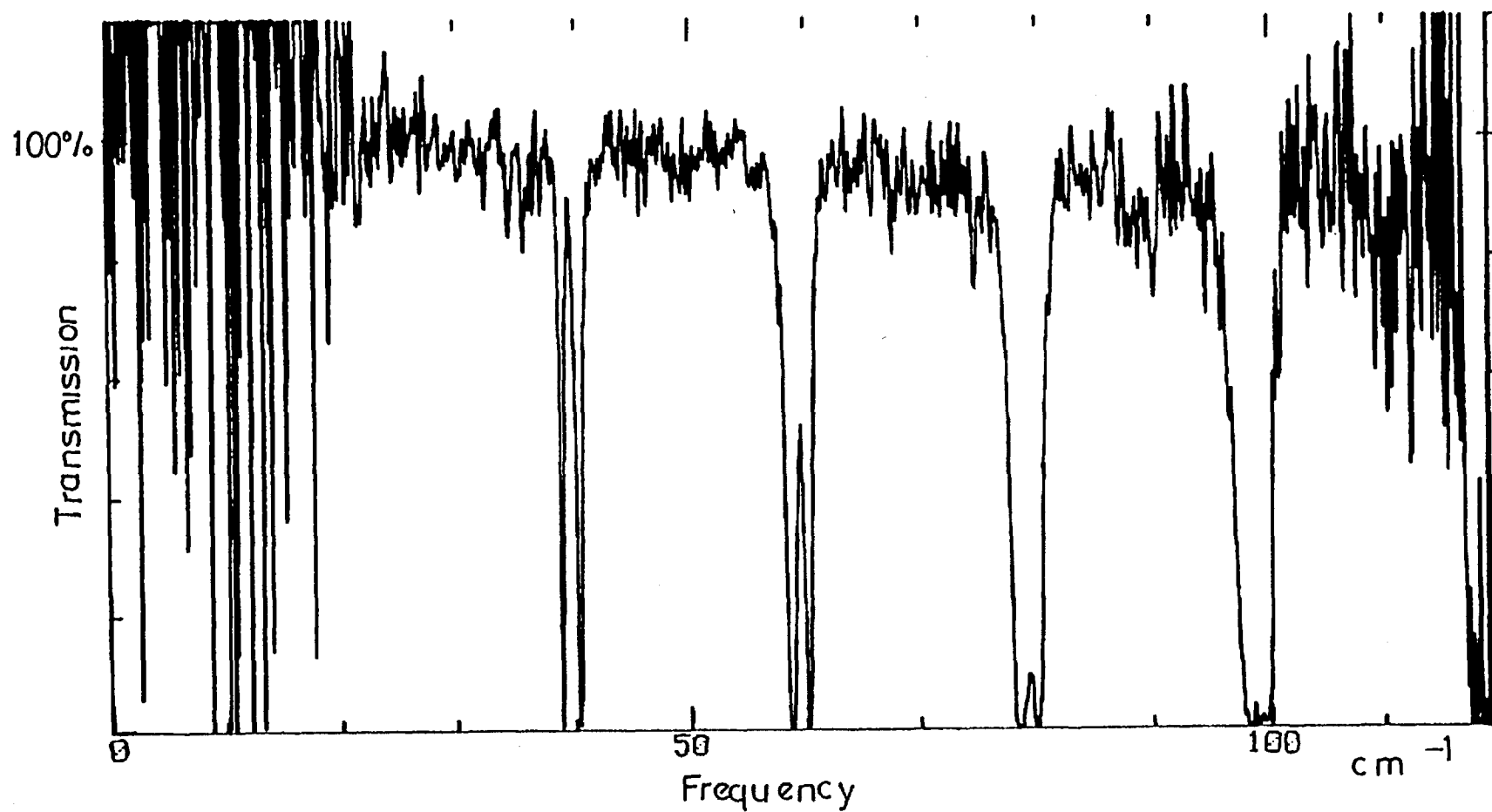


Fig 24d₁ NH_3 Transmission Spectrum

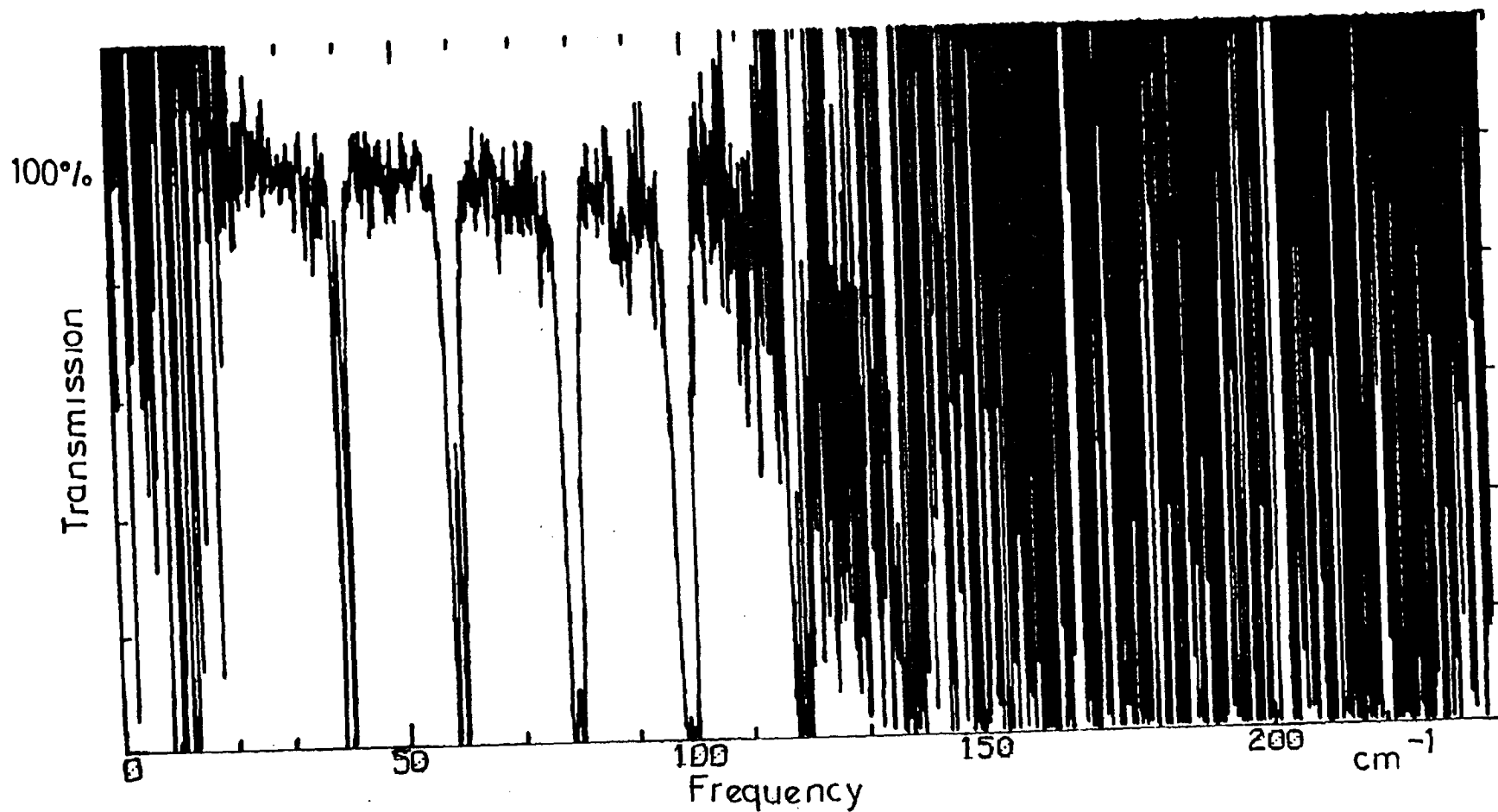


Fig 24d₂ NH_3 Transmission Spectrum (see 24d₁ for expanded horiz scale)

Pressure = 20 Torr
Temperature = 298 K
Path Length = 130 cm
Resolution = 0.3 cm^{-1}

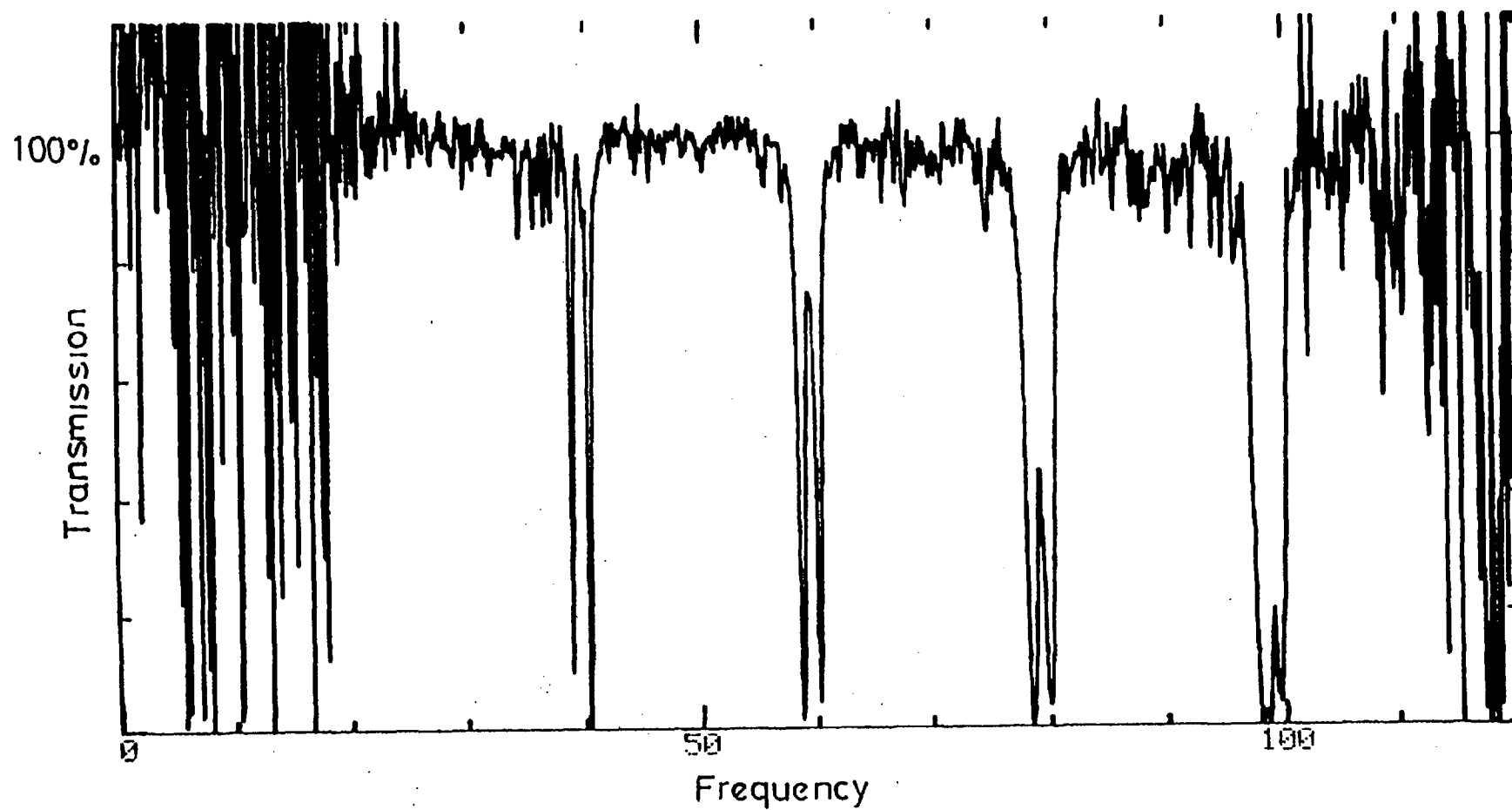


Fig 24e₁ NH_3 Transmission Spectrum

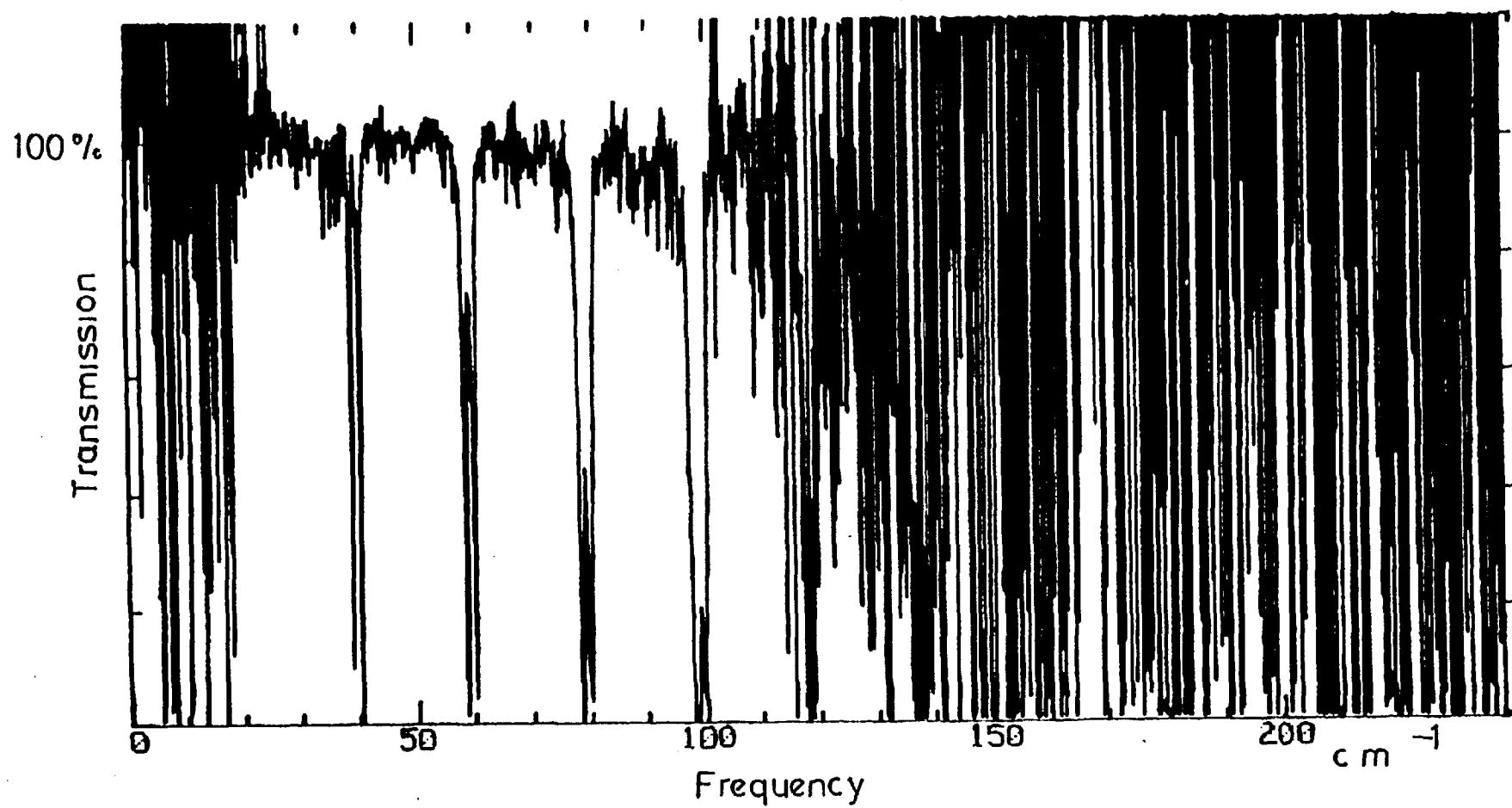


Fig 24e₂ NH_3 Transmission Spectrum (see 24e₁ for expanded horiz scale)

Also some measurements were made at a pressure of 10 torr and a temperature of 184°K. The spectra show that the features disappeared with increasing temperature. It can be seen from the spectra in figures 24 that they are of high quality. This is because each one is the average of several independent transmission spectra. During the time in which the observations at the temperatures 193°K and 208°K were made the bolometer developed a fault and was therefore replaced by a new bolometer which was used through out the rest of the project. This new bolometer allowed measurements to be made out to a frequency of 120 cm⁻¹, whereas the transmission characteristic of the previous bolometer fell off at about 90 cm⁻¹ (the only difference between the two bolometers was that the new bolometer had a different germanium element). This difference was presumed to be characteristic of the element because the internal filtering could not account for this.

6.2.3.3

Observations of Saturated Vapour

Sometimes at the end of a day there wasn't enough time to obtain foreground and background spectra of high resolutions (0.3 cm⁻¹). Therefore additional observations of the saturated vapour at low temperature (+ 193°K) and low resolution (1 cm⁻¹) were made (see figures 25). Again the apparent spectral features can be seen particularly the feature at 50 cm⁻¹.

Pressure = 25 Torr
Temperature = 193 K
Path Length = 130 cm
Resolution = 1 cm^{-1}

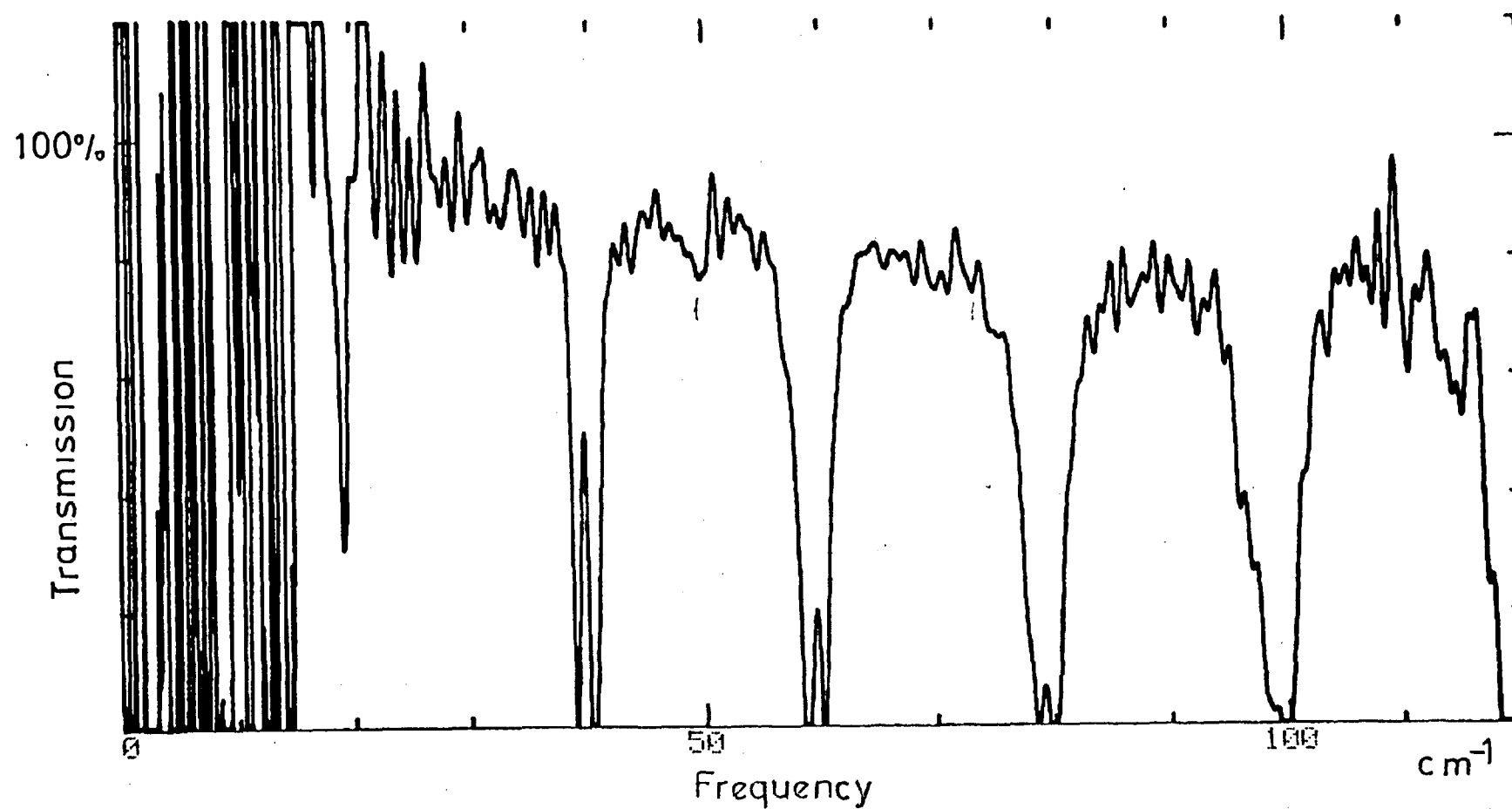


Fig 25 Saturated NH_3 Vapour Transmission Spectrum

6.2.3.4

Observations made at constant density of NH_3 molecules

In order to be confident of attributing these features to absorption by NH_3 dimers it was necessary to show that they had a temperature dependence which would only be explained in terms of the NH_3 dimer. This method has been described in section 5.3, the temperature dependence and the resulting binding energy being consistent with the absorption being of dimeric origin.

Again the spectra (see figs 26) are of high quality, each being the average of several independent transmission spectra.

Even though the evidence, i.e. the spectra obtained from Mark 1a Mark 2a Mark 3 and the calculated binding energies, of the features being of dimeric origin is very convincing, checks had to be made to ensure that the features could not be caused by some other means.

6.3

Possible Sources of Errors

There are three mechanisms which could be thought of as a possible means of causing the absorption features. These are a) A part of the cavity which has a temperature dependence, b) A periodic error in the screw drive of the moving mirror which would cause ghosts and c) a standing wave pattern in the cavity. b) and c) can be ignored as they could not show such a steep temperature dependence.

Dealing with a), analysis of the background spectra obtained with the cavity showed two absorption bands at 45 and 54 cm^{-1} which grew stronger as the temperature was lowered (see figs 27).

Pressure = 18 Torr
Temperature = 188 K
Path Length = 130 cm
Resolution = 0.3 cm^{-1}

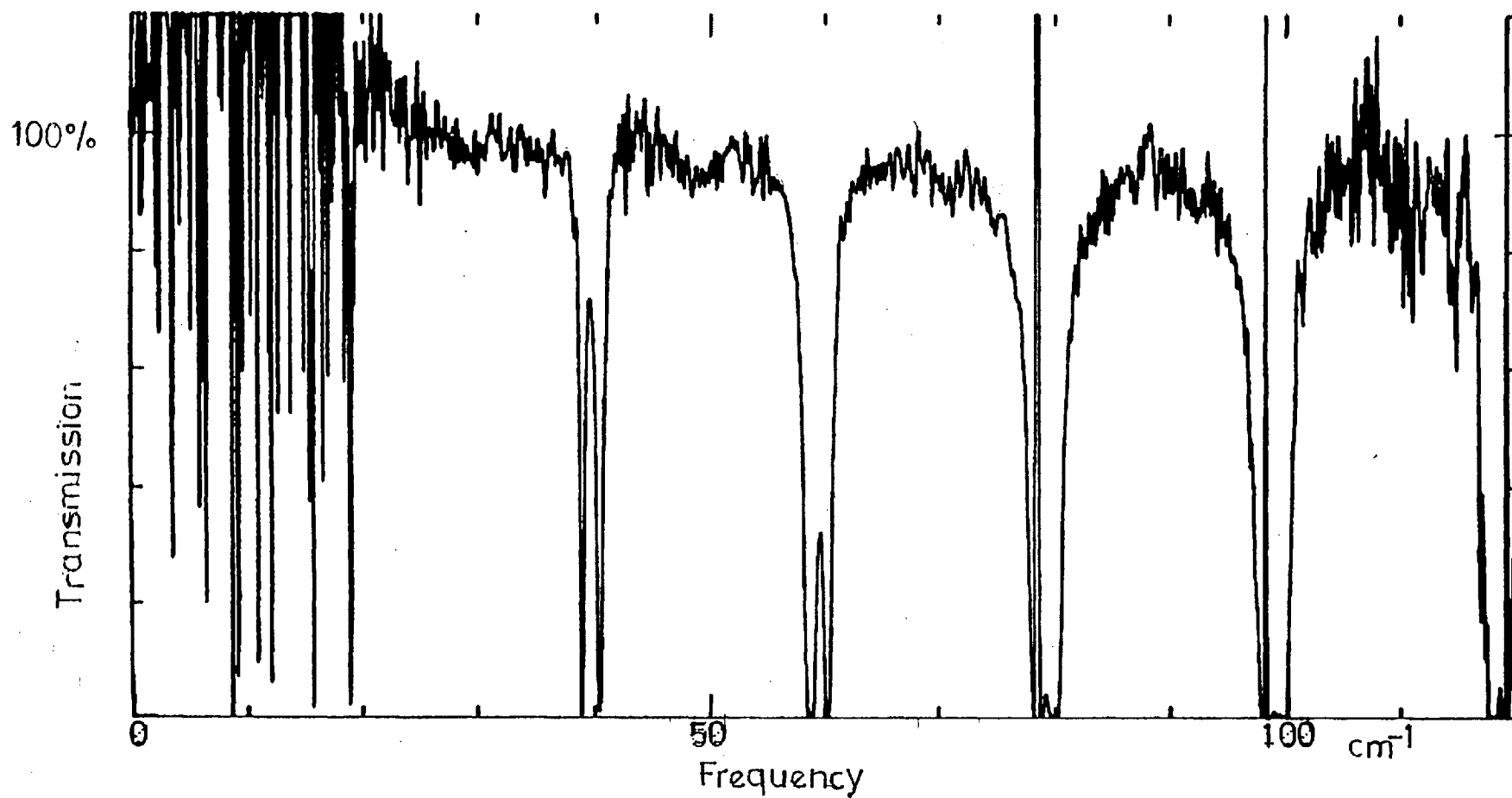


FIG 26a₁ NH_3 Transmission Spectrum

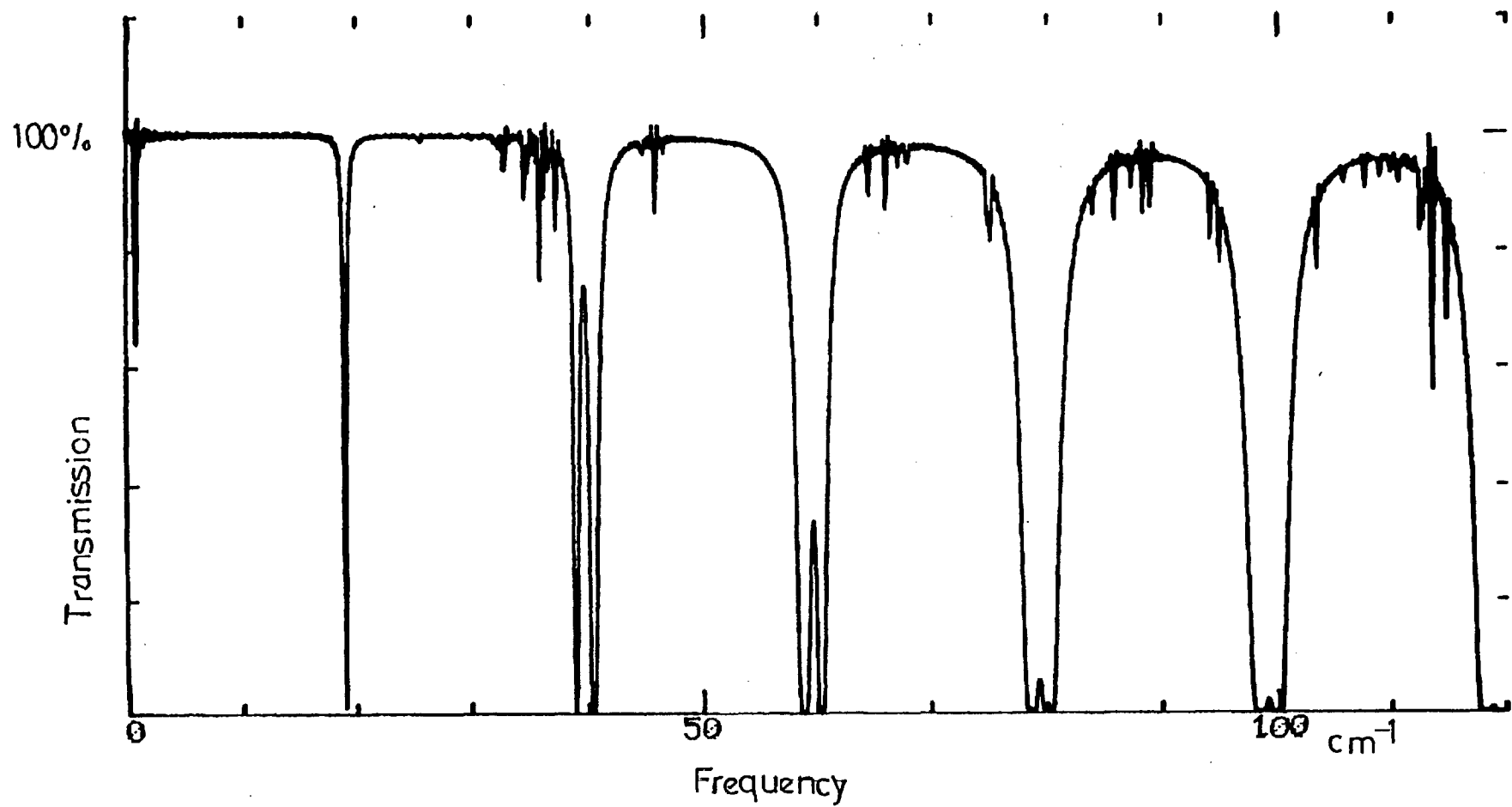


FIG 26a₂ NH₃ Theoretical Transmission Spectrum c.f 26a₁

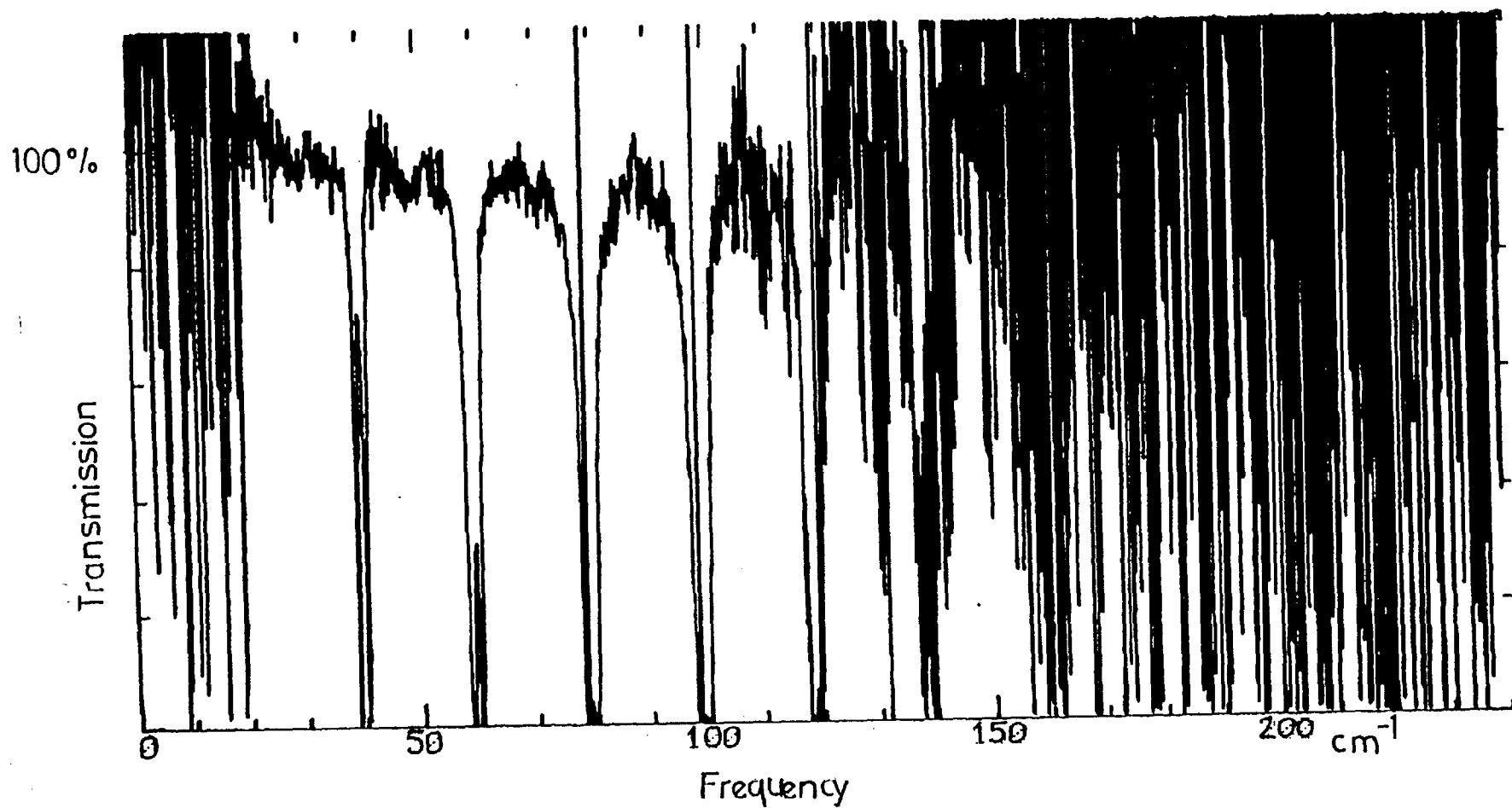


FIG 26a₃ NH_3 Transmission Spectrum (see 26a₁ for expanded horiz scale)

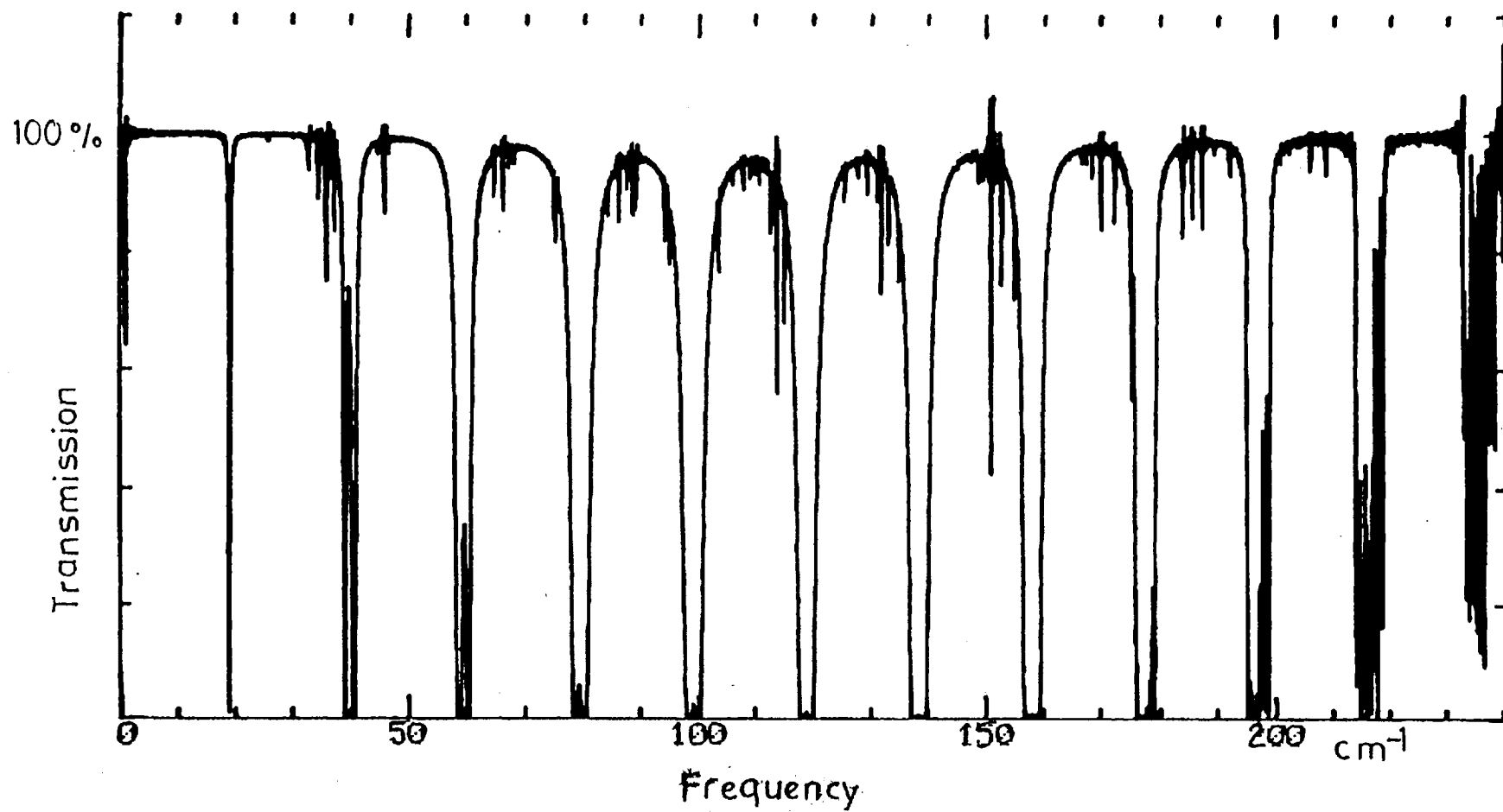


FIG 26a₄ NH₃ Theoretical Transmission Spectrum c.f 26a₃

Pressure = 25 Torr
Temperature = 252K
Path Length = 130 cm
Resolution = 3 cm^{-1}

266_{1,2,3,4}

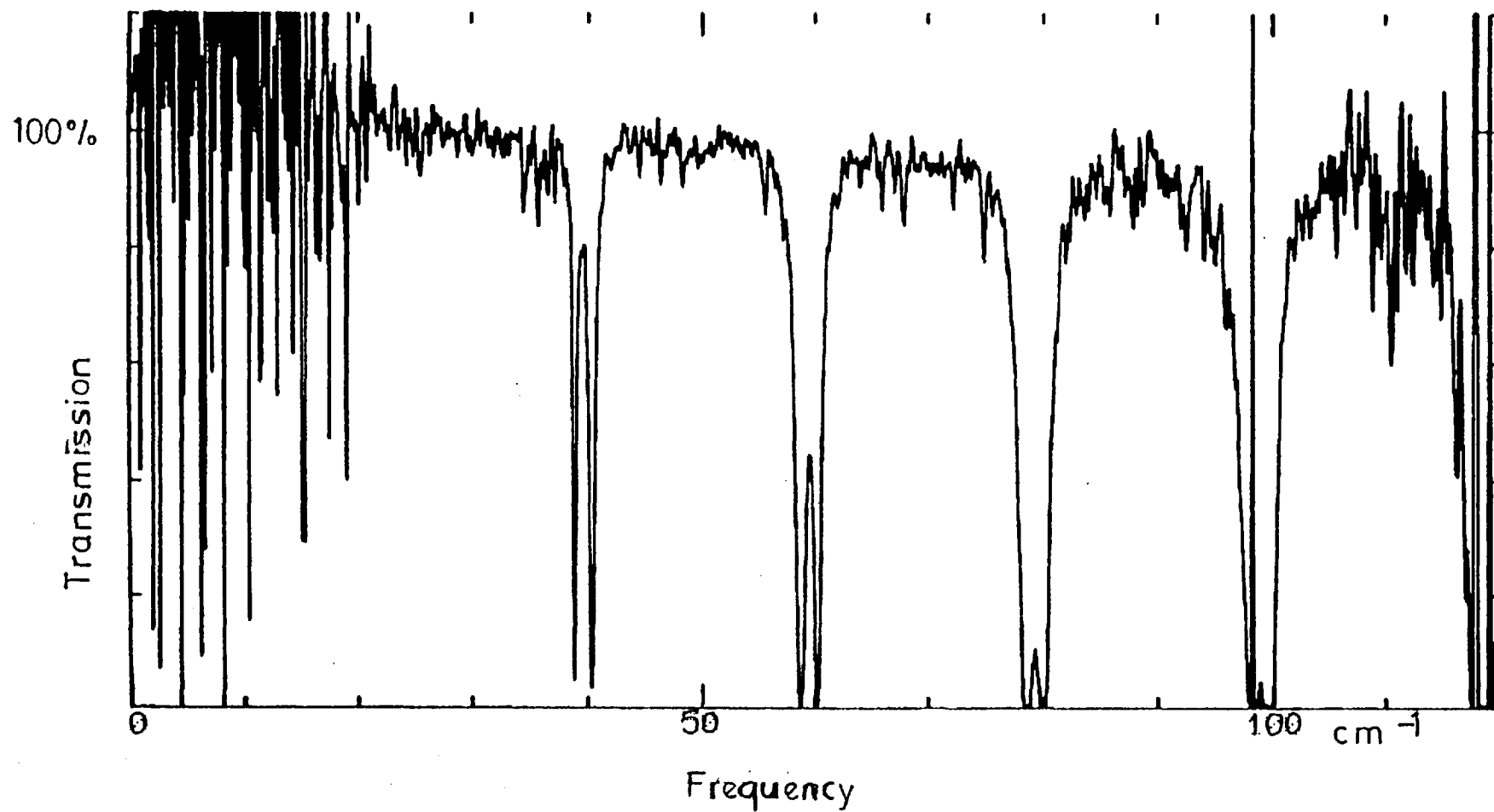


FIG 26b₁ NH_3 Transmission Spectrum

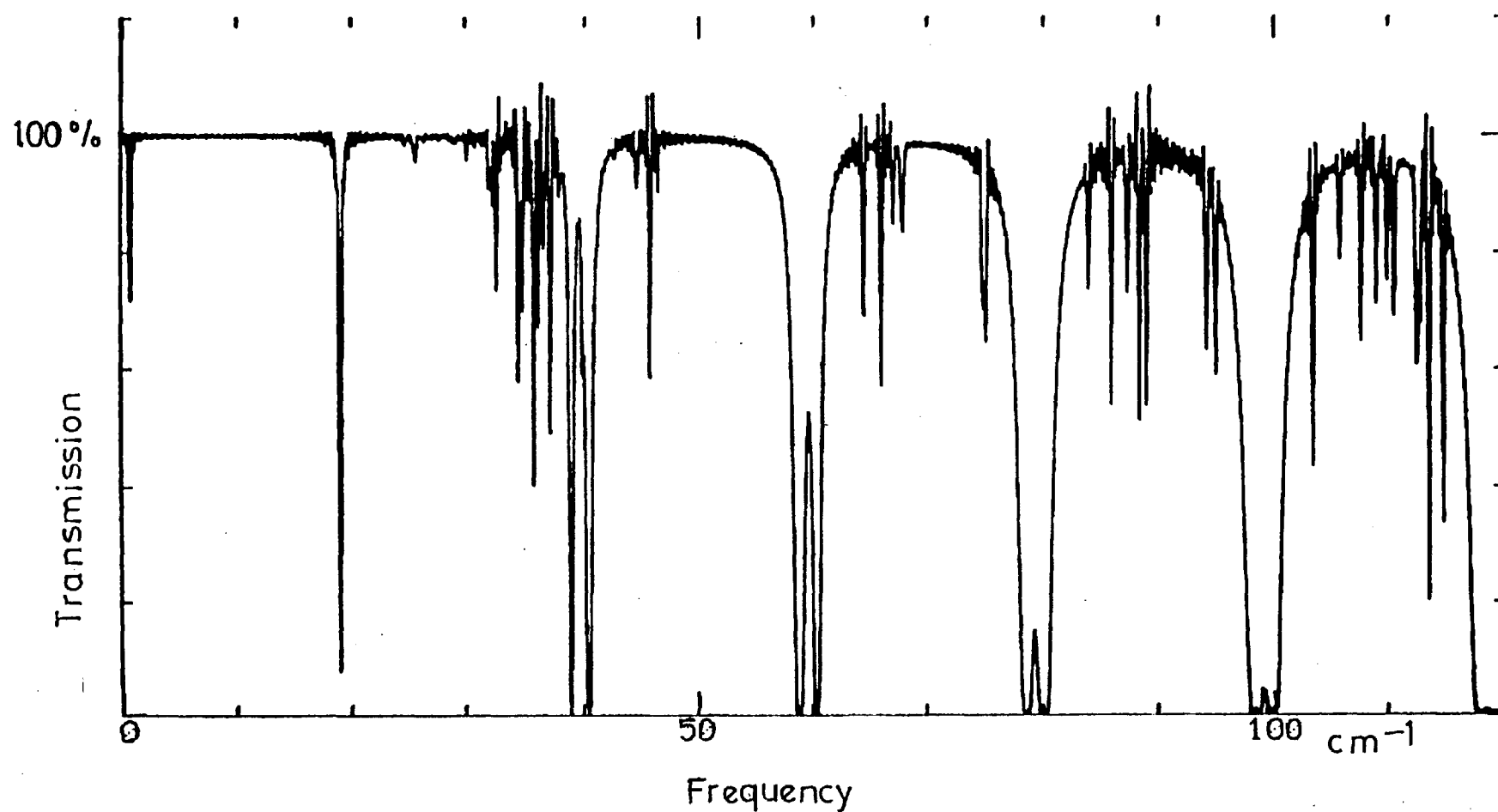


FIG 26b₂ NH₃ Theoretical Transmission Spectrum c.f 26b₁

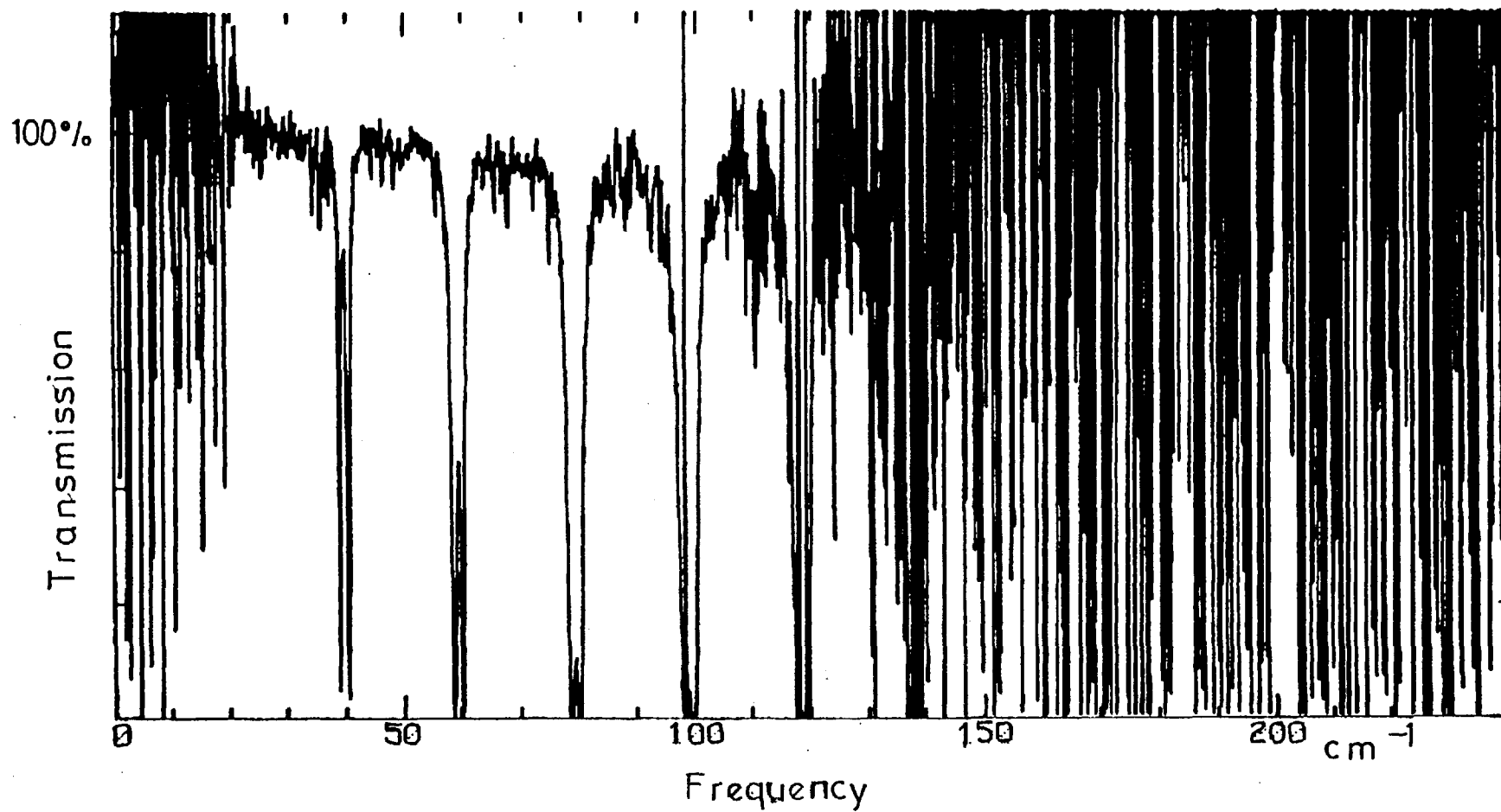


FIG 26 b₃ NH₃ Transmission Spectrum (see 26b₁ for expanded horiz scale)

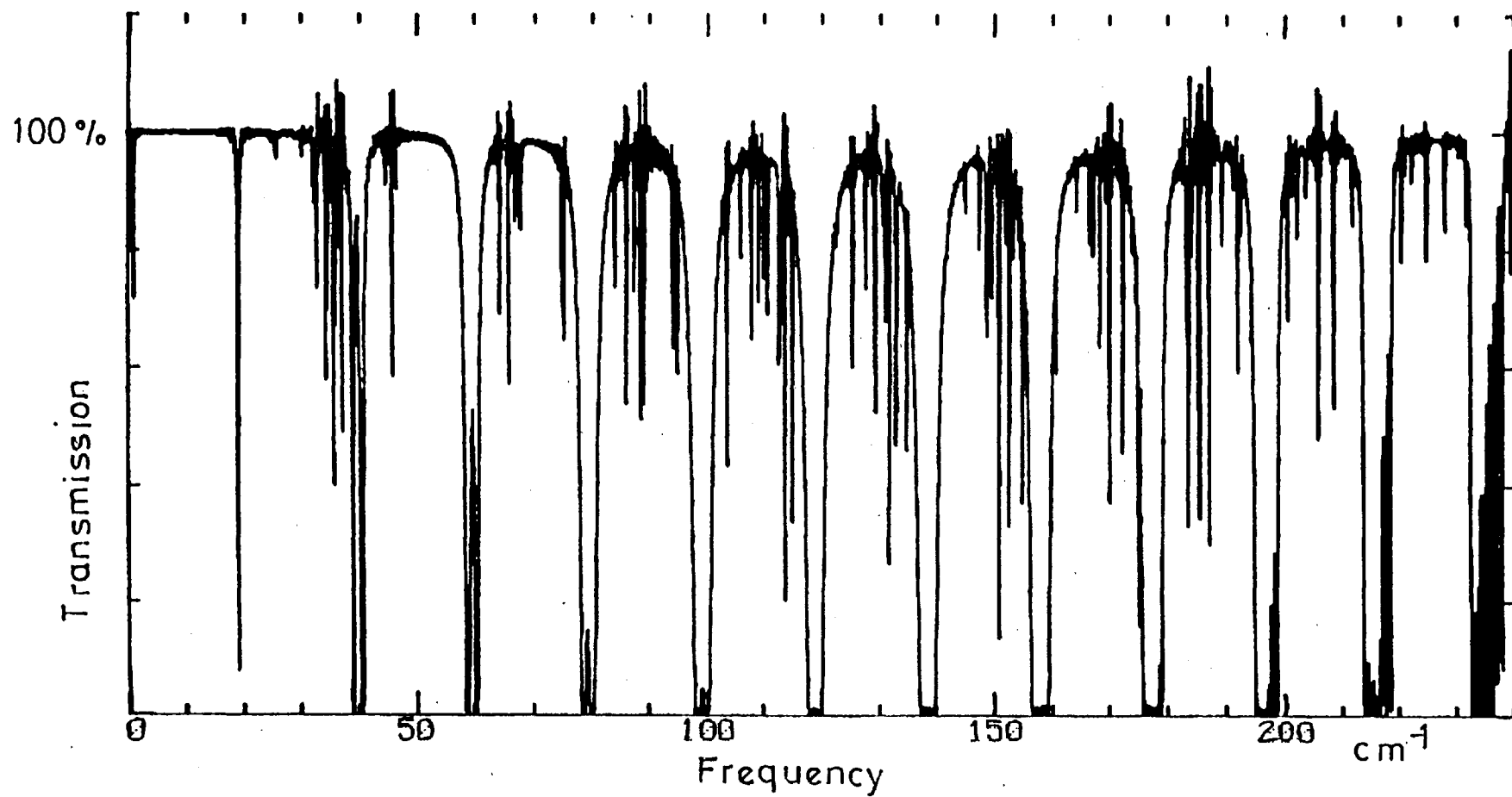


FIG 26 b₄ NH₃ Theoretical Transmission Spectrum -c.f 26 b₃

Pressure = 29 Torr
Temperature = 298 K
Path Length = 130 cm
Resolution = 3 cm^{-1}

} $^{26}\text{C}_{1,2,3,4}$

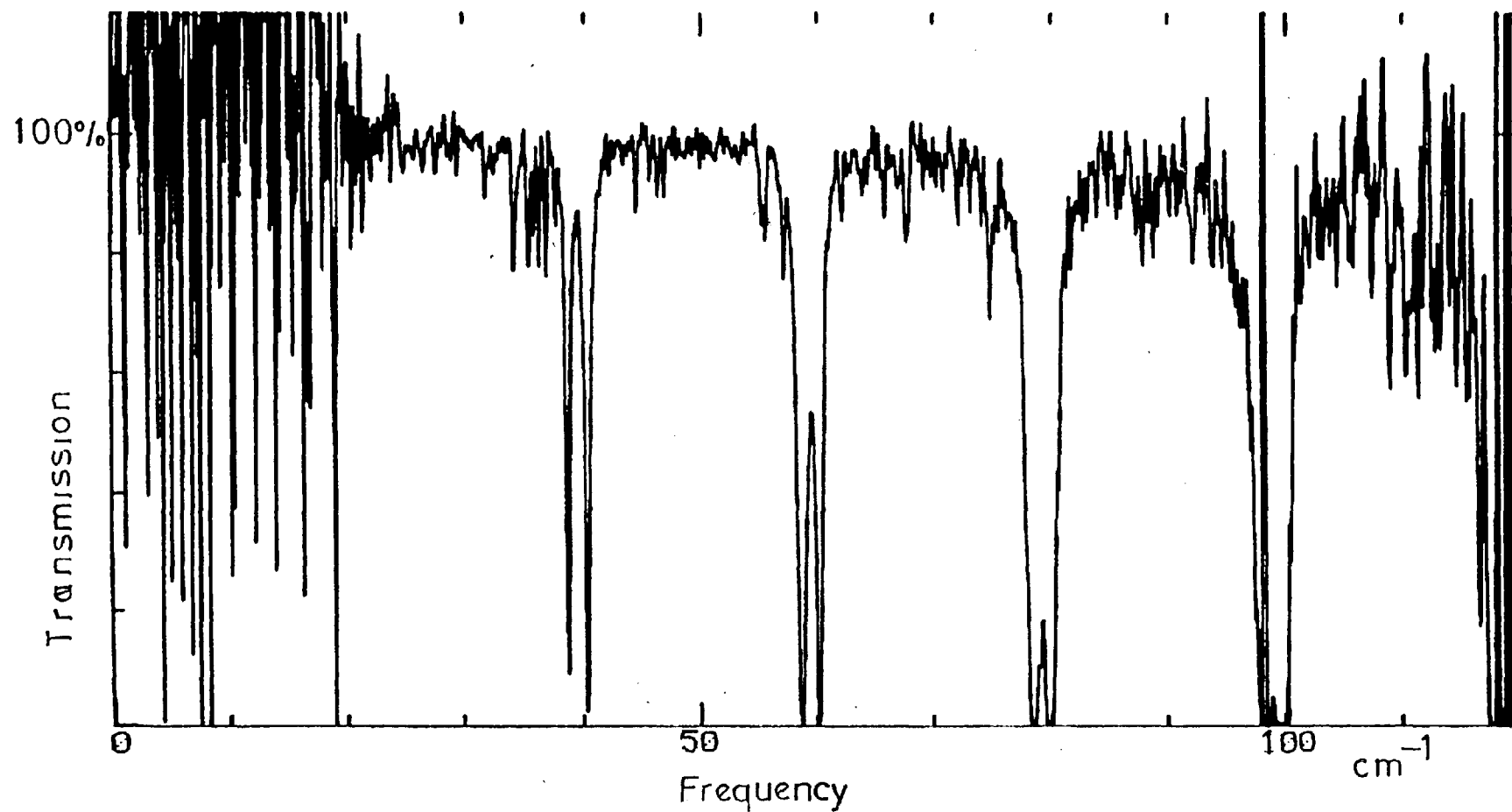


FIG 26 c_1 NH_3 Transmission Spectrum

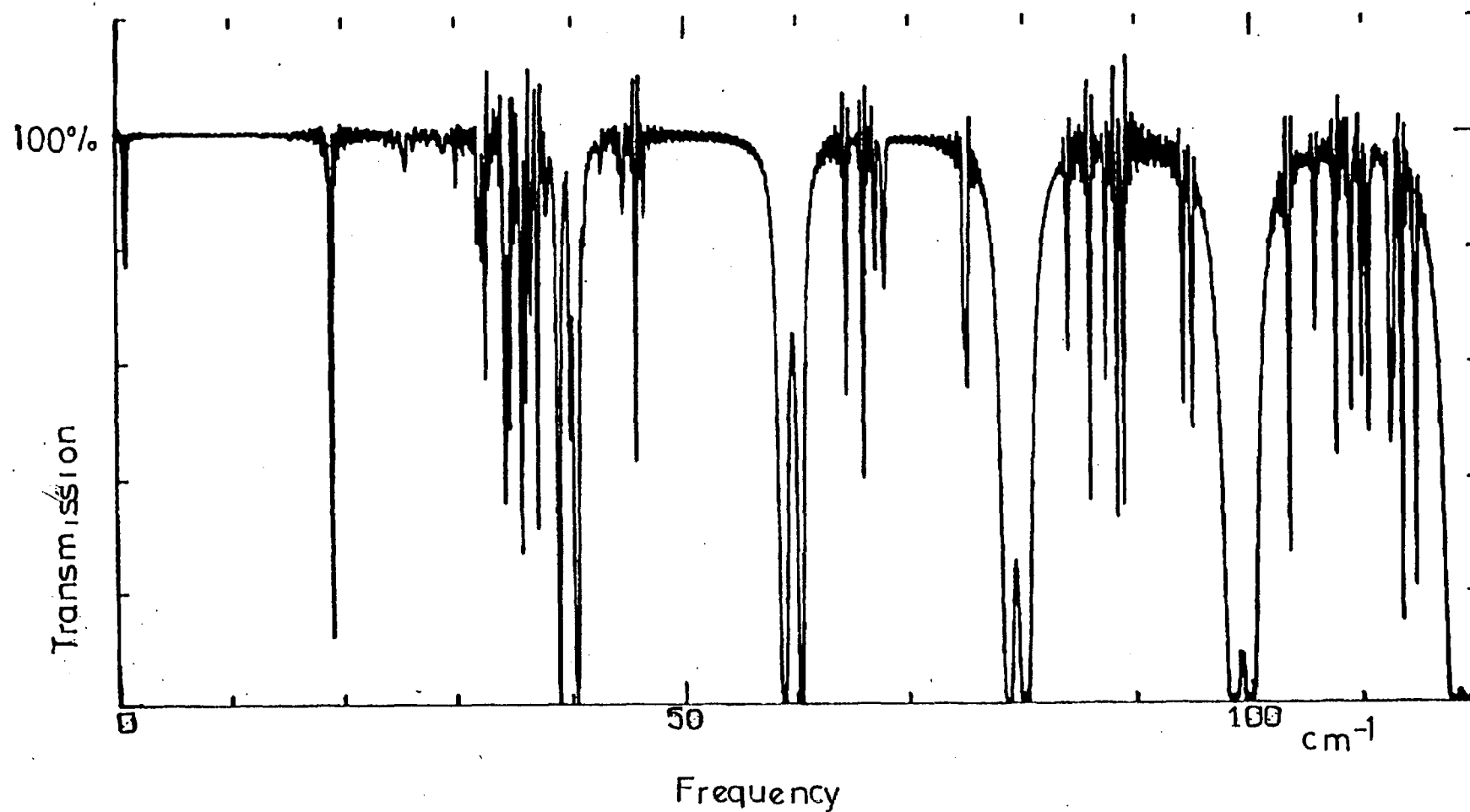


Fig 26c₂ NH₃ Theoretical Transmission Spectrum cf 26c₁

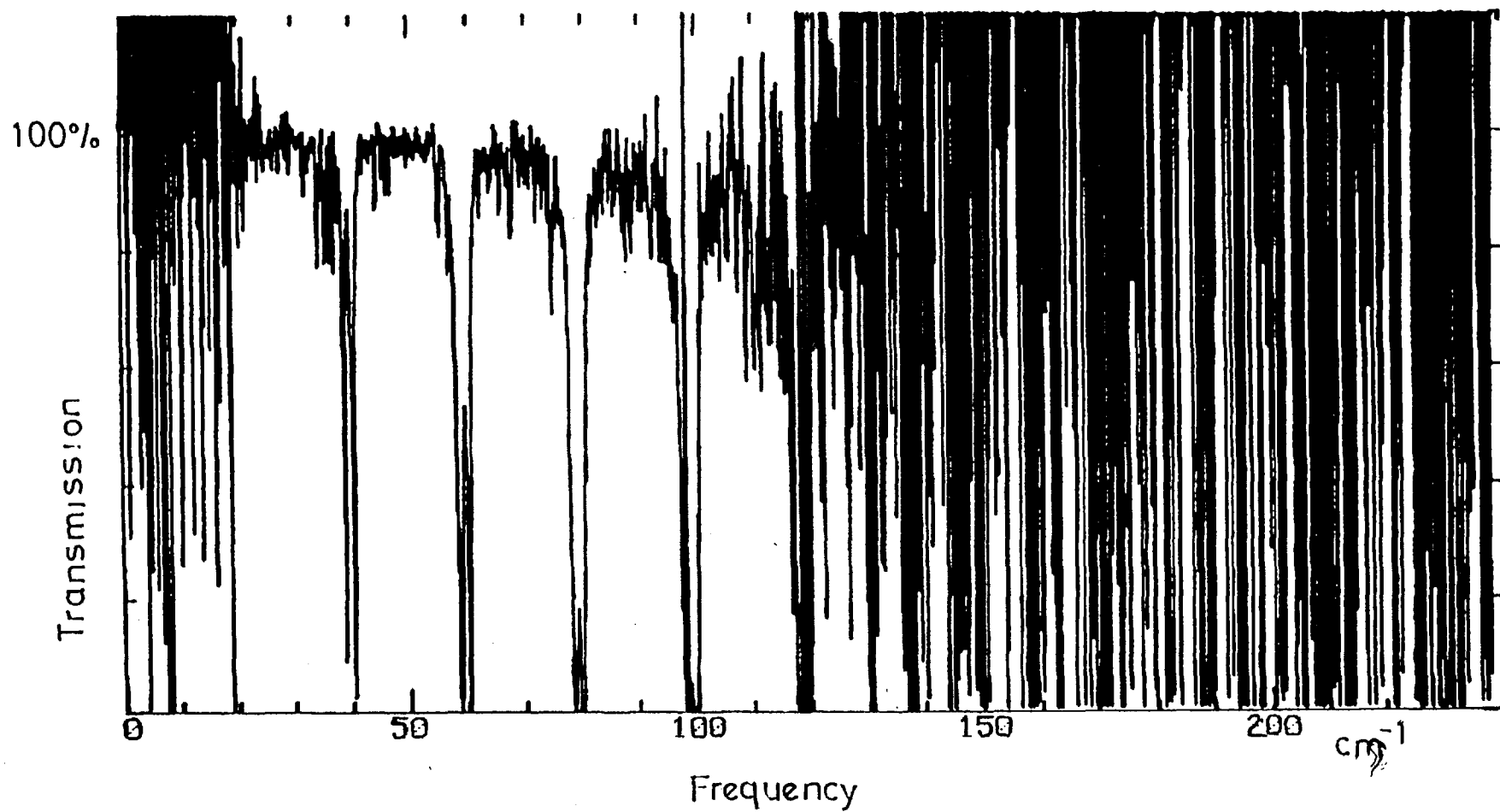


Fig 26c₃ NH₃ Transmission Spectrum (see 26c₁ for expanded horiz scale)

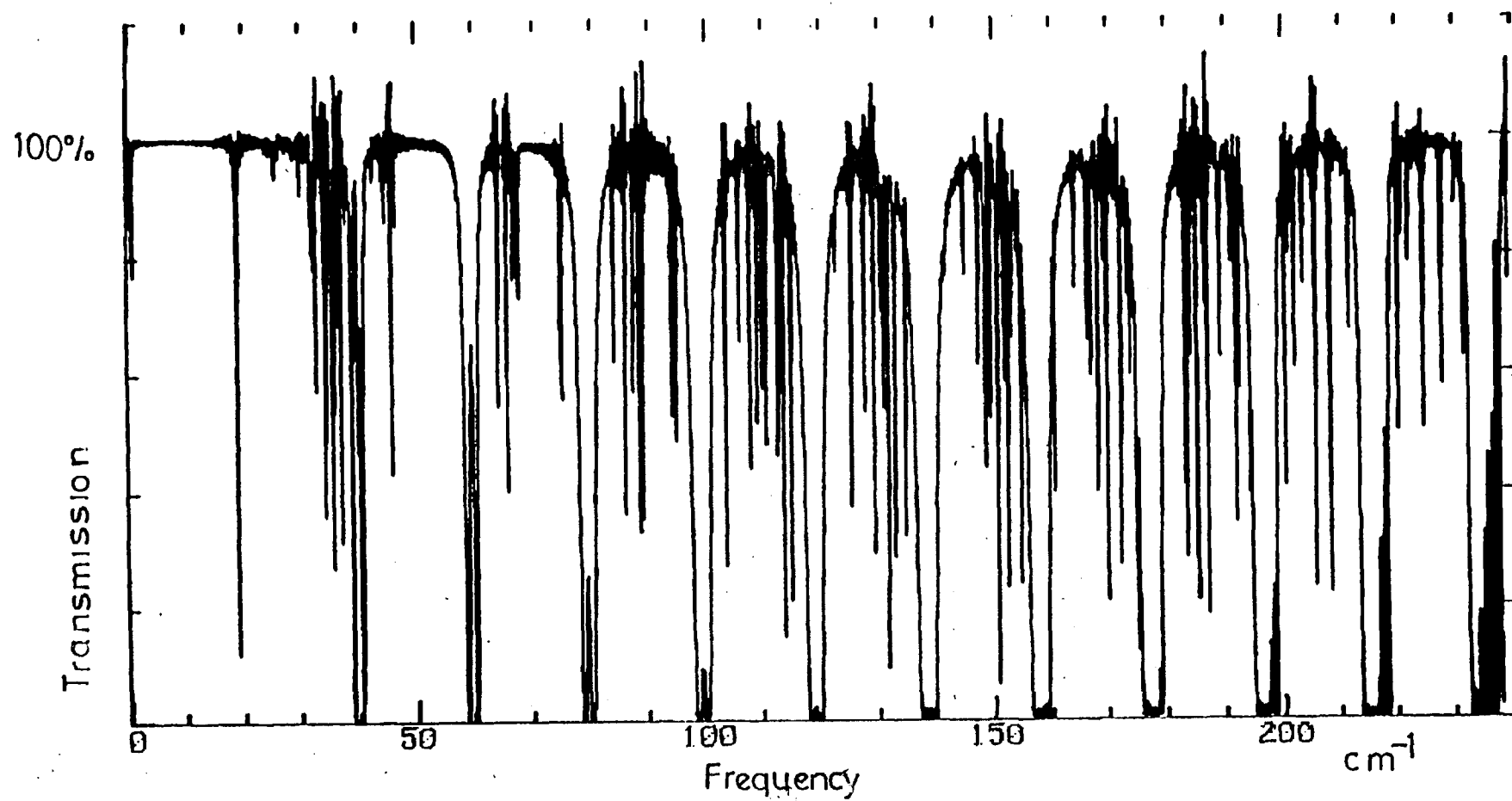


Fig 26c₄ NH_3 Theoretical Transmission Spectrum c.f 26c₃

Pressure = 21 Torr
Temperature = 210K
Path Length = 130 cm
Resolution = 0.3 cm^{-1}

} $26d_{1,2}$

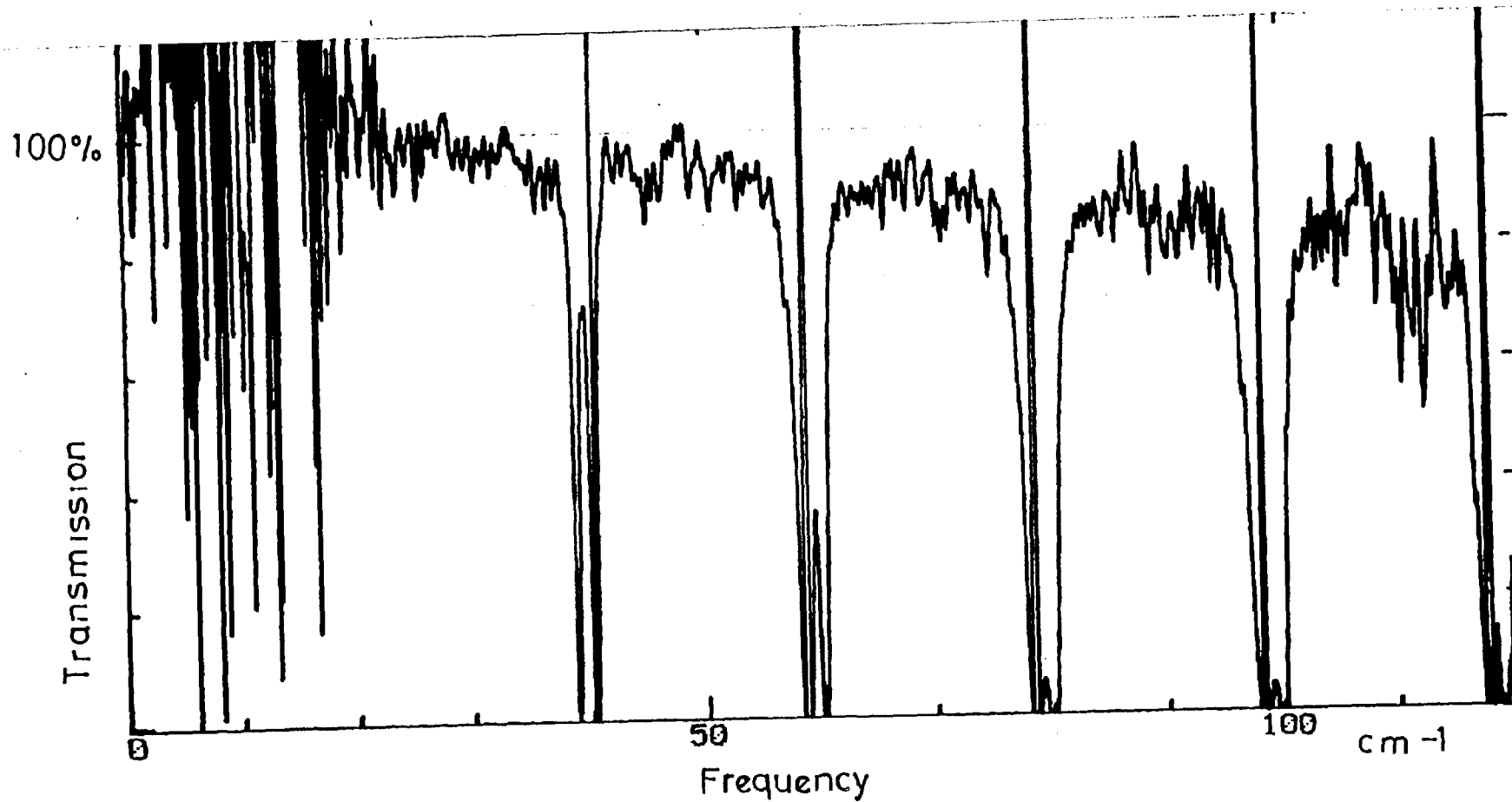


Fig $26d_1$ NH_3 Transmission Spectrum

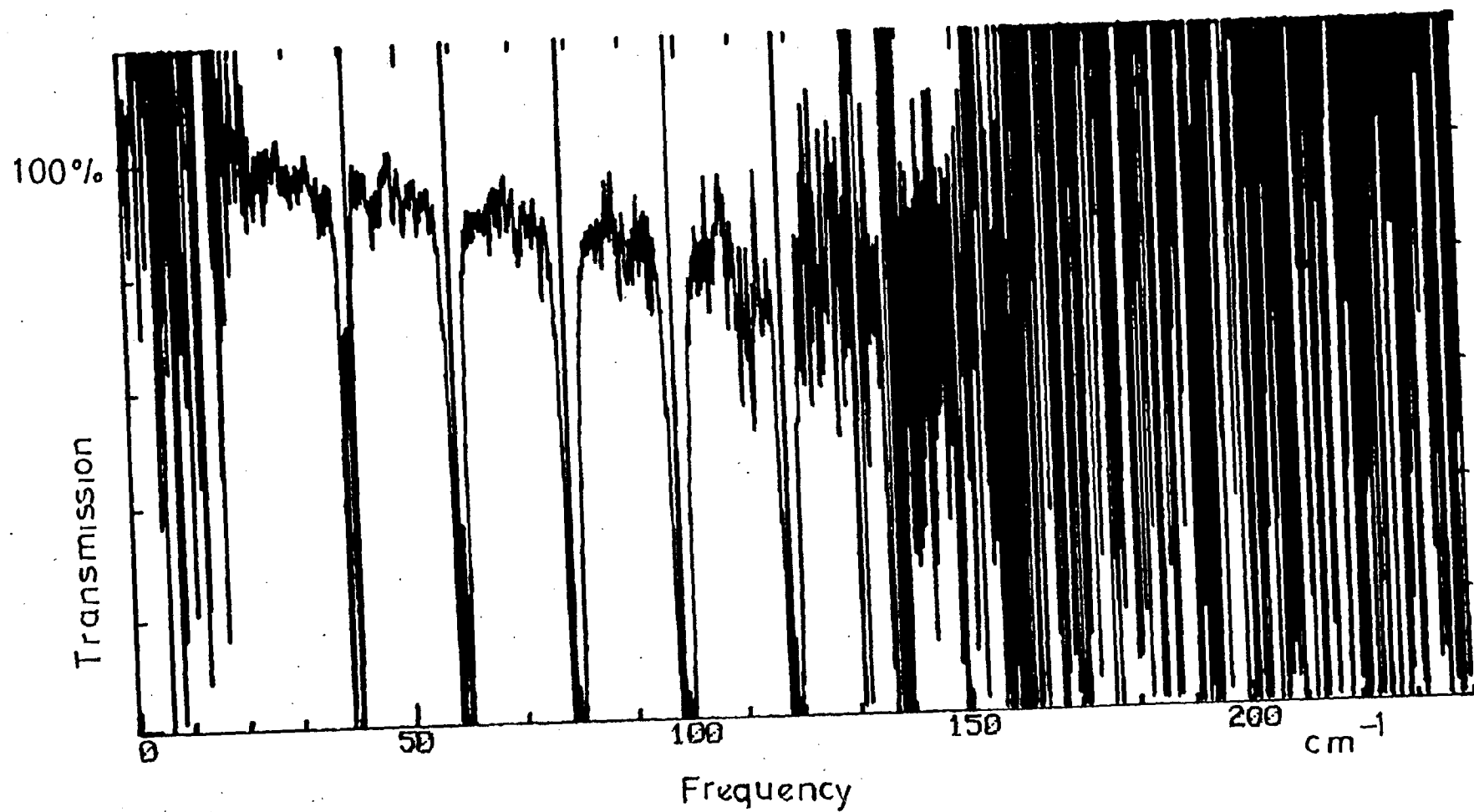


Fig 26d₂ NH_3 Transmission Spectrum (see 26 d₁ for expanded horiz scale)

Pressure	= 22 Torr	} 26e _{1,2}
Temperature	= 225 K	
Path Length	= 130 cm	
Resolution	= 3 cm ⁻¹	

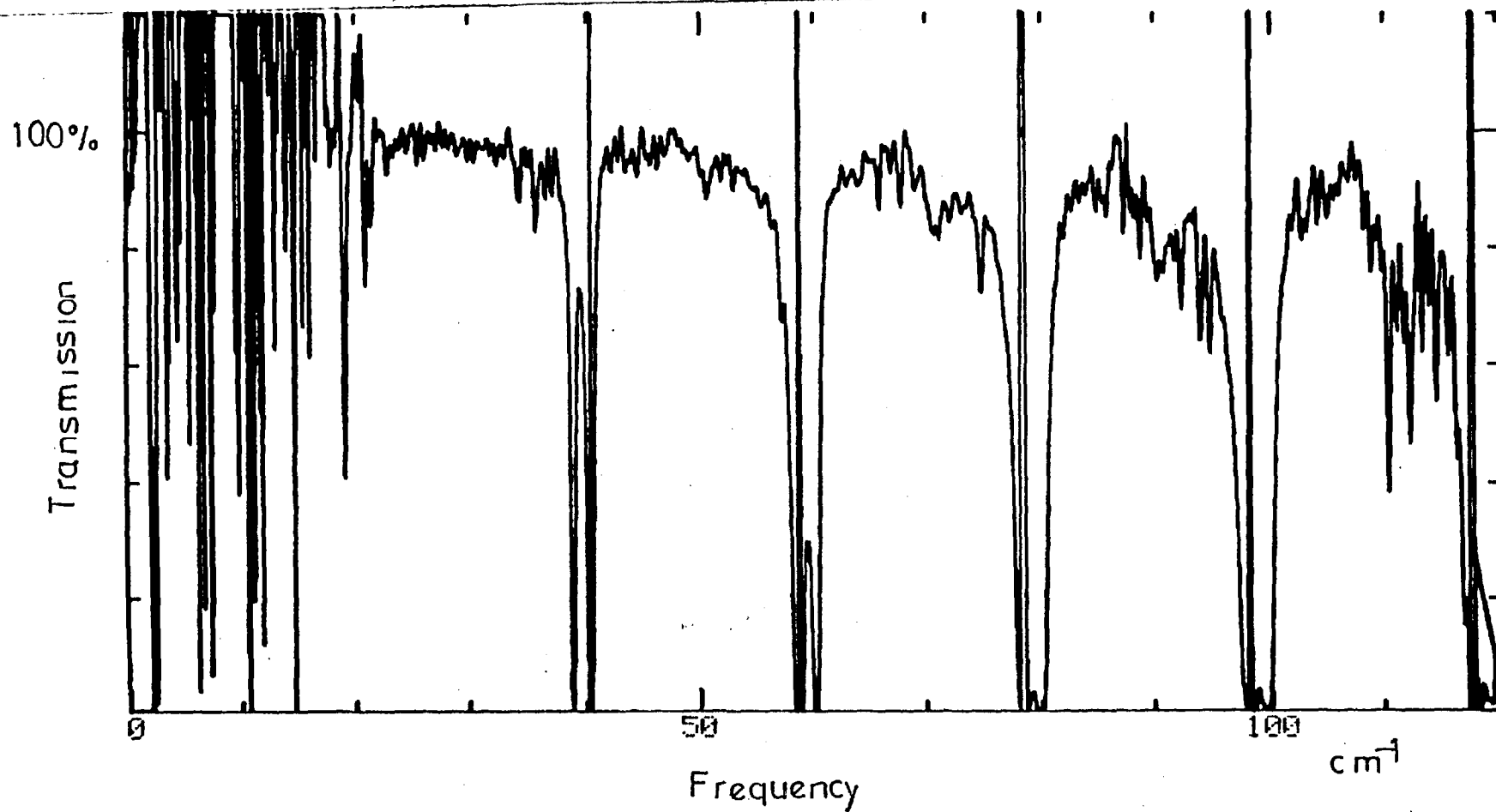


Fig 26e₁ NH₃ Transmission Spectrum

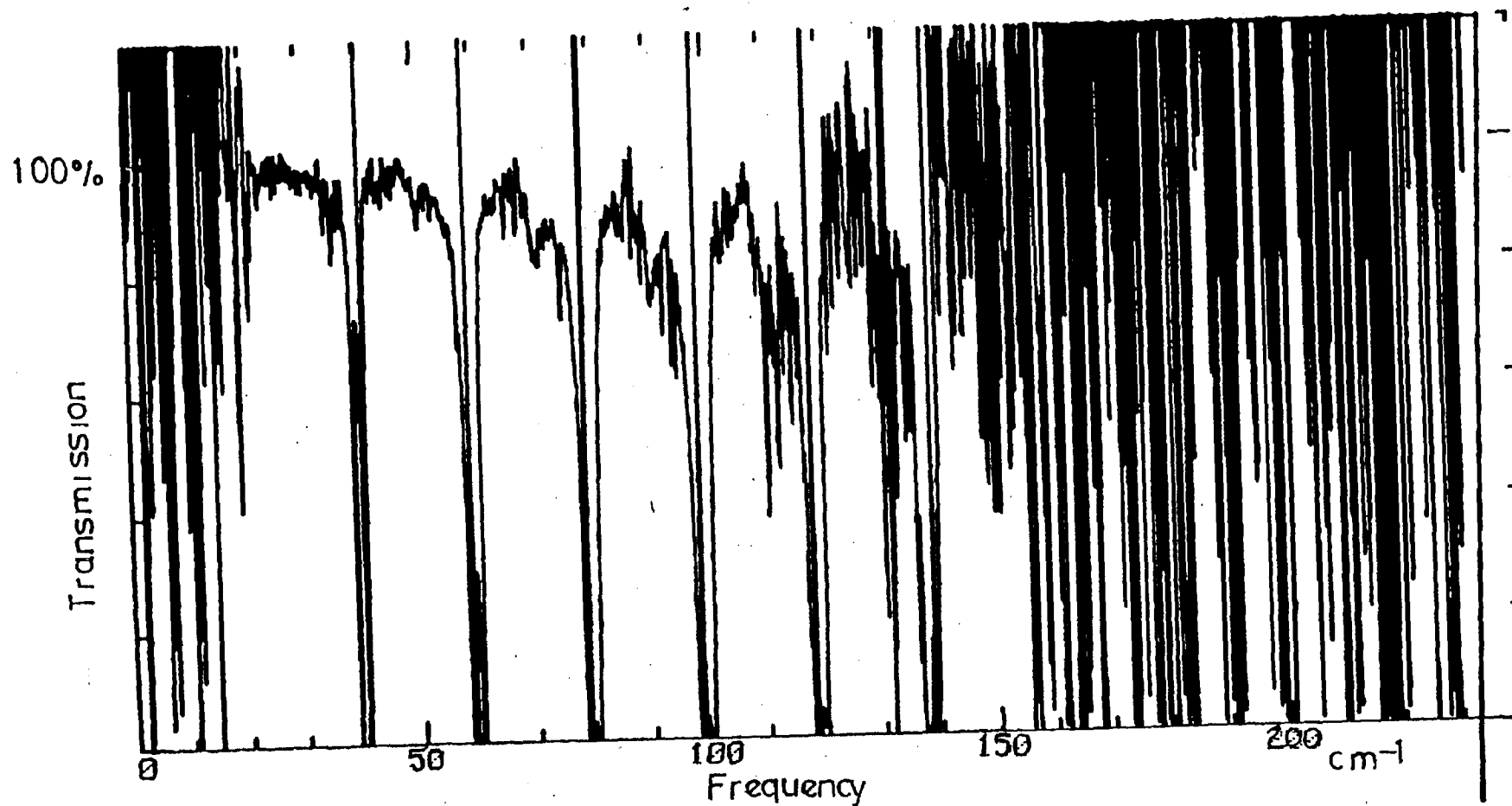


Fig 26e₂ NH₃ Transmission Spectrum (see 26e₁ for expanded horiz scale)

Temperature = 298 K

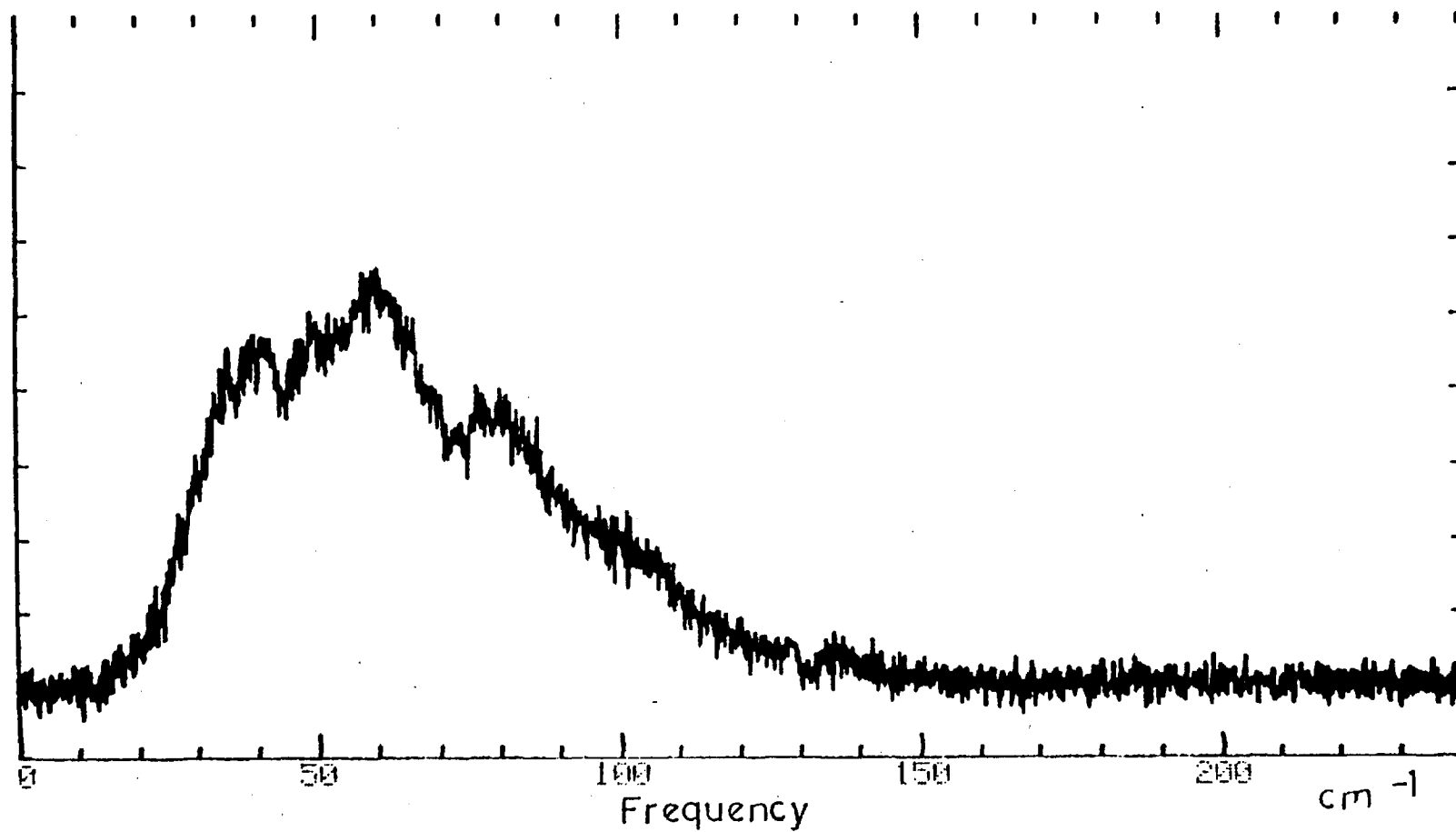


Fig 27a Background Spectrum Showing Teflon Absorption Bands

Temperature = 257K

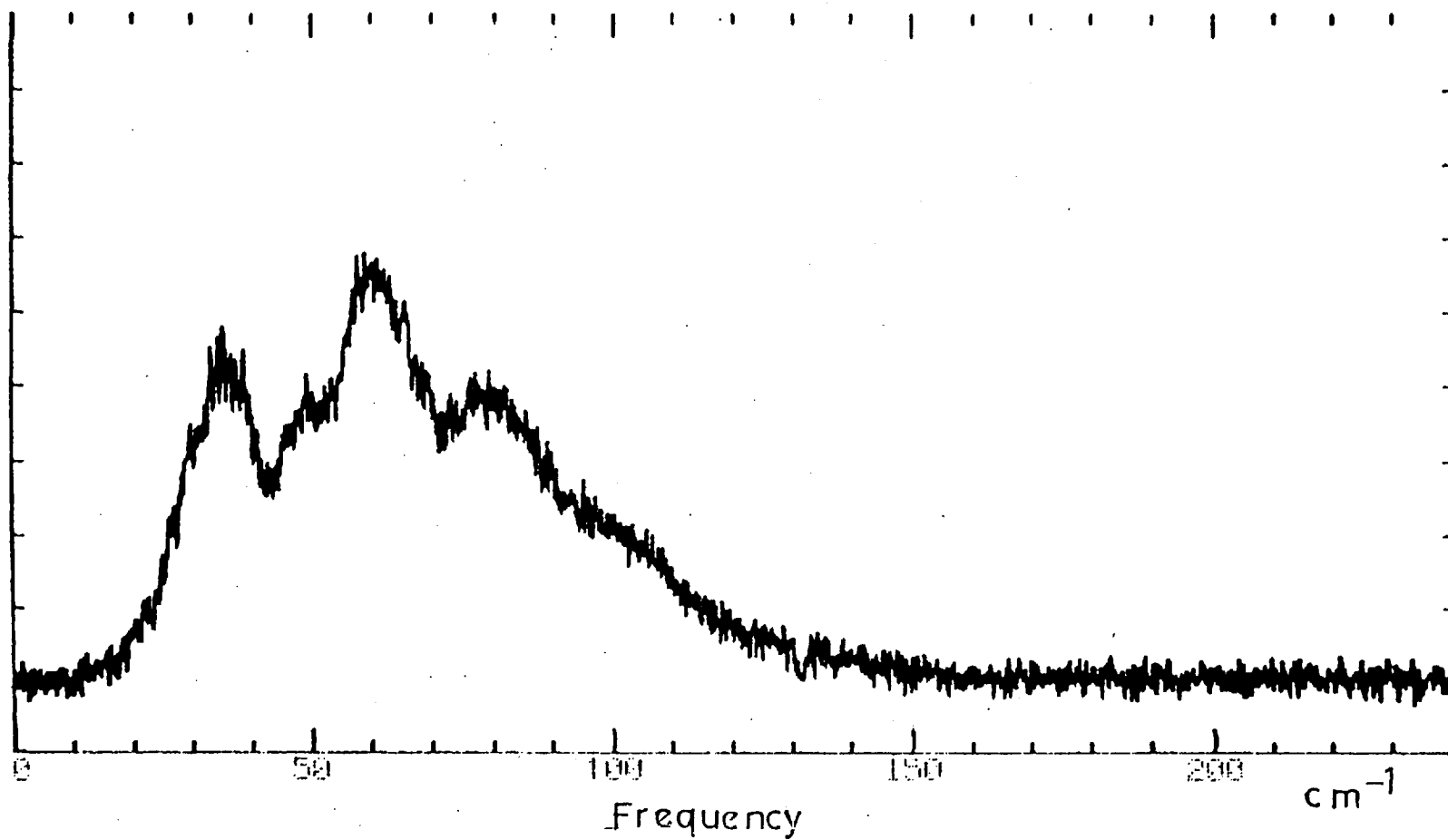


Fig 27b Background Spectrum Showing Teflon Absorption Bands

Temperature = 193 K

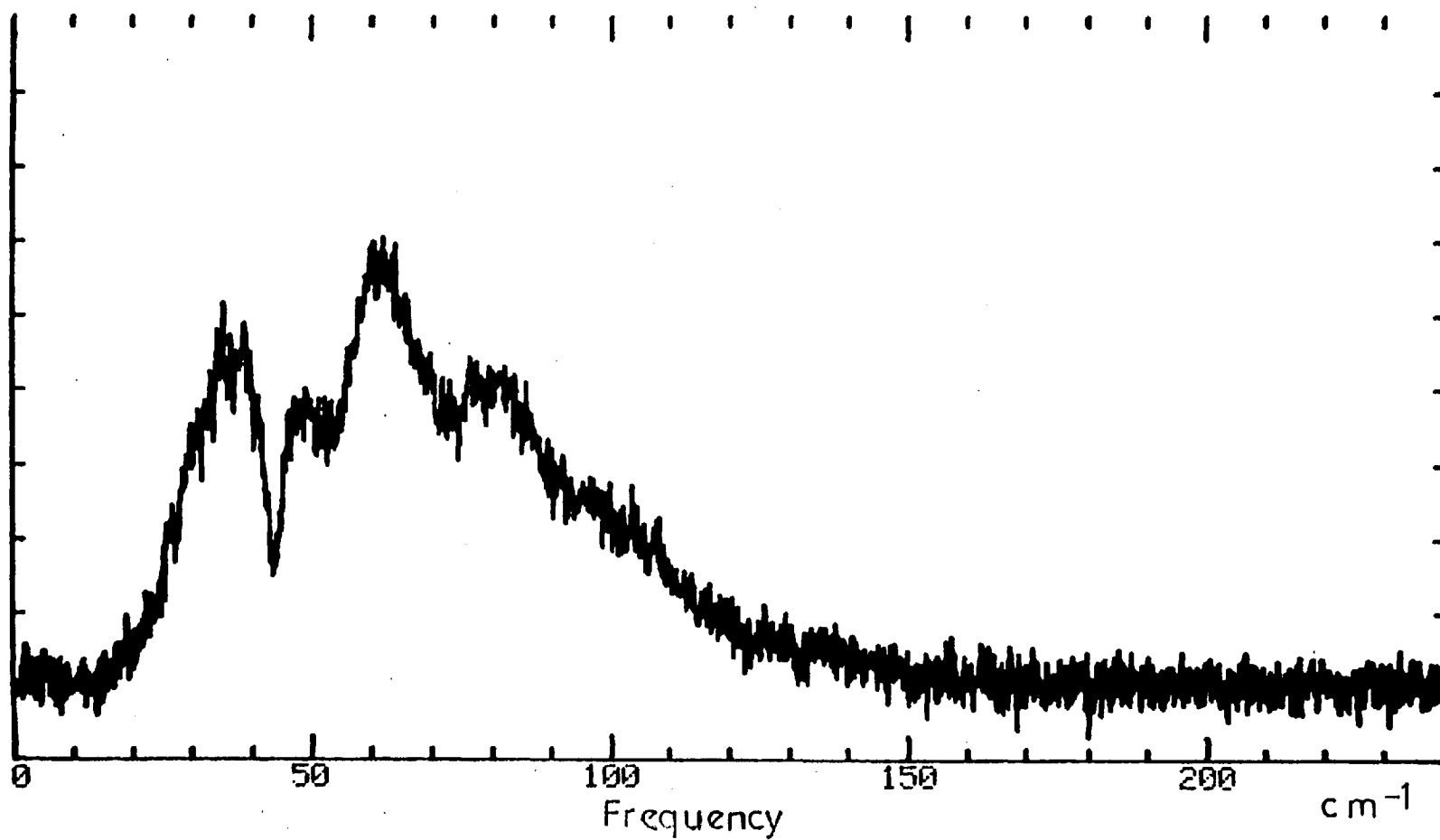


Fig 27c Background Spectrum Showing Teflon Absorption Bands

Because of these bands special care was taken to ensure that foreground and background spectra were recorded at a constant temperature.

The obvious source for these absorption bands had to be the Teflon windows of the cavity. A survey of the literature produced a paper⁸ reporting these bands. According to the paper Teflon at 4.2°K has strong absorption bands at 46.5 and 56 cm⁻¹ (see fig 28). These must be the bands that have been observed.

A comparison of the observed background and transmission spectra shown that the absorption feature at 50 cm⁻¹ (attributed to dimers) cannot be explained in terms of the Teflon absorption bands.

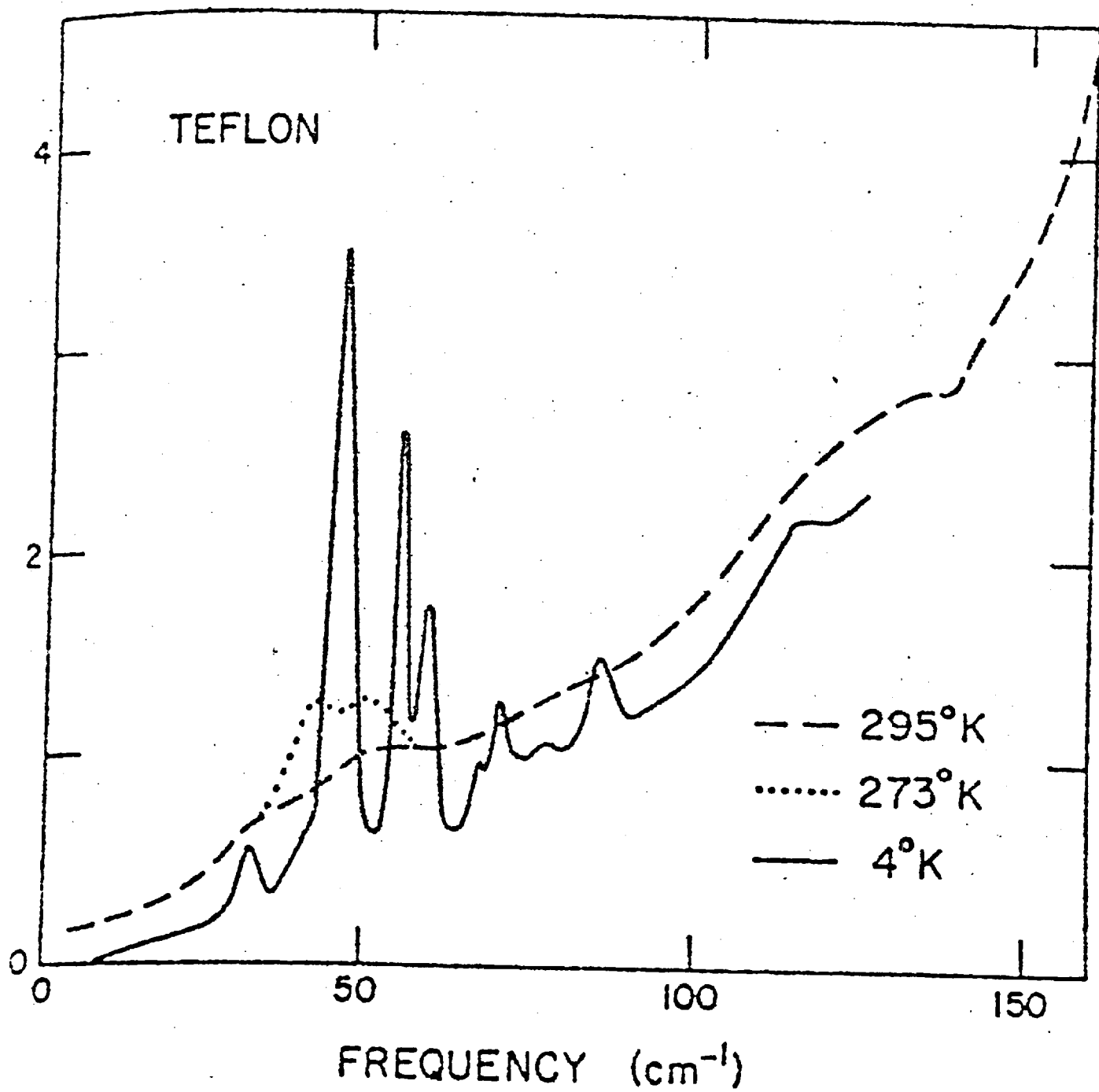


Fig 28

CHAPTER 7

Summary and Suggestions for Further Extensions to this Work.

The experimental work reported in this Thesis has shown the existence of spectral absorption features near 5ϕ , 7ϕ and 9ϕ cm^{-1} whose temperature dependencies, and resulting binding energies, at constant density of NH_3 molecules, are consistent with them using associated with NH_3 dimers. More supporting evidence comes from the binding energies calculated from the temperature dependence of broad band spectral absorption in the region of 2ϕ to 55 CM^{-1} . These calculated binding energies are in close agreement with those calculated by other workers¹³⁶. The binding energy calculated from the temperature dependence of broad band spectral absorption in the region of 4 to 18 CM^{-1} (between the ground state inversion time and the first rotation time) was found to be less than the other calculated binding energies reported in this thesis. As it has been mentioned in section 5.2.3 it would be rewarding to determine which line shape would be needed for the ground state inversion absorption band in order to calculate a binding energy in agreement with those previously mentioned.

In order to make a detailed analysis of the spectral features, which would yield information concerning the structure, dipole moment etc., of the NH_3 dimer, the path length would have to be increased by an order of magnitude or more (so that the features are stronger). A possible method of achieving this would be to use a white cell (a multi-pass absorption gas cell) which should be capable of giving path lengths greater than $1\phi\text{M}$.

Of course if NH_3 dimers are atmospheric constituents of Jupiter and Saturn then it should be possible to observe these features because of the large effective path lengths and low temperature afforded by these planets.

APPENDIX A

Stannic Chloride - An exercise in Fourier Transform Spectroscopy

An investigation of the ν_4 vibrational band of SnCl_4 was undertaken as an exercise to show the relationship between an interferogram and its fourier transorm, the spectrum.

A.1 The SnCl_4 Molecule

SnCl_4 is a tetrahedral molecule with point group T_d . The molecule is composed to 5 atoms and therefore has nine $(3n-6)$ normal vibrations (see fig. 29).

The dipole moment of the point group T_d (XY_4 type molecule) has the triply degenerate species F_2 and therefore only the vibrations of species F_2 are active as fundamentals is the infrared, i.e. ν_3 and ν_4 .

A publication by F. KONIGER and A. MULLER⁹ has reported the observation of the ν_4 vibrational band and some of its isotopes. The observed frequencies are shown in the following table.

Observed Fundamental Frequencies

Branch	SnCl_4	^{116}Sn	$^{35}\text{Cl}_4$	^{116}Sn	$^{37}\text{Cl}_4$
R	$130.8 \pm .5$	$131.8 \pm .3$		$129.0 \pm .3$	
Q	$126.8 \pm .5$	$127.5 \pm .2$		$125.1 \pm .2$	
P	$122.8 \pm .5$	$123.2 \pm .3$		$121.2 \pm .3$	

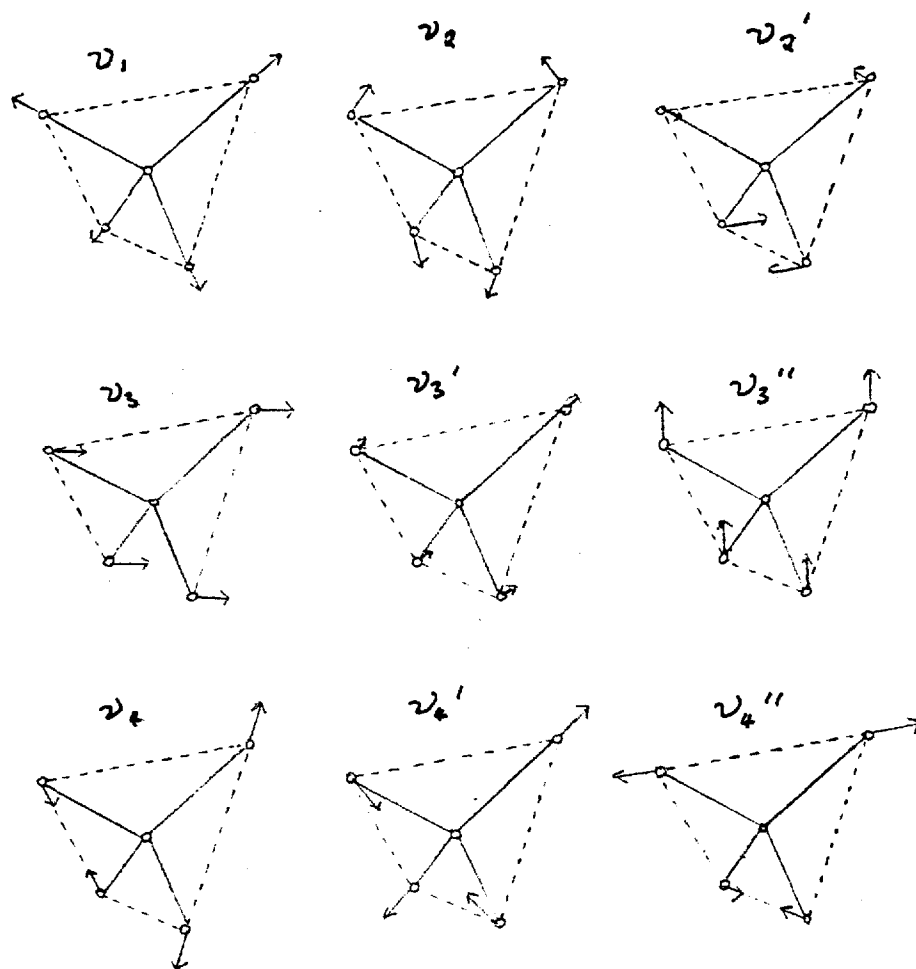


Fig 29 Normal Vibrations of the SnCl_4 Molecule

A.2 Apparatus

In order to make observations in the frequency range of 1000 to 2000 cm^{-1} it was necessary to remove all atmospheric water vapour from the apparatus as it is strongly absorbing in this region. Therefore Mark 1 was converted into a completely pumpable system (to be known as Mark 1a) (Figure 30). The brass gas cell, and the adjoining gas handling system, of Mark 1 was not used as Sn Cl_4 is extremely reactive and would attack these items. Instead a stainless steel cell was used which could be filled with Sn Cl_4 liquid or vapour and then placed in the radiation path in the vacuum tank.

A.2.1 Method of Filling Cell

Sn Cl_4 is a dangerous substance. Because of this the cell was filled in a fume cupboard. To prevent contamination of the Sn Cl_4 when the bottle top was taken off, a finger from a rubber glove was fitted over the top of the open Sn Cl_4 bottle (fortunately this was a good tight fit). When the cell was ready to be filled a small hole was cut into the top of the rubber finger and the tube from the cell was inserted (see fig. 31)

The syphon (see fig. 31) produced a gentle suction which sucked Sn Cl_4 into the cell. A small light bulb situated behind the cell enabled the level of the Sn Cl_4 in the cell to be observed (when using polypropylene on T.P.X windows it was impossible to see the level without using a light bulb), and by careful manipulation of the taps it was possible to fill the cell to the required amount.

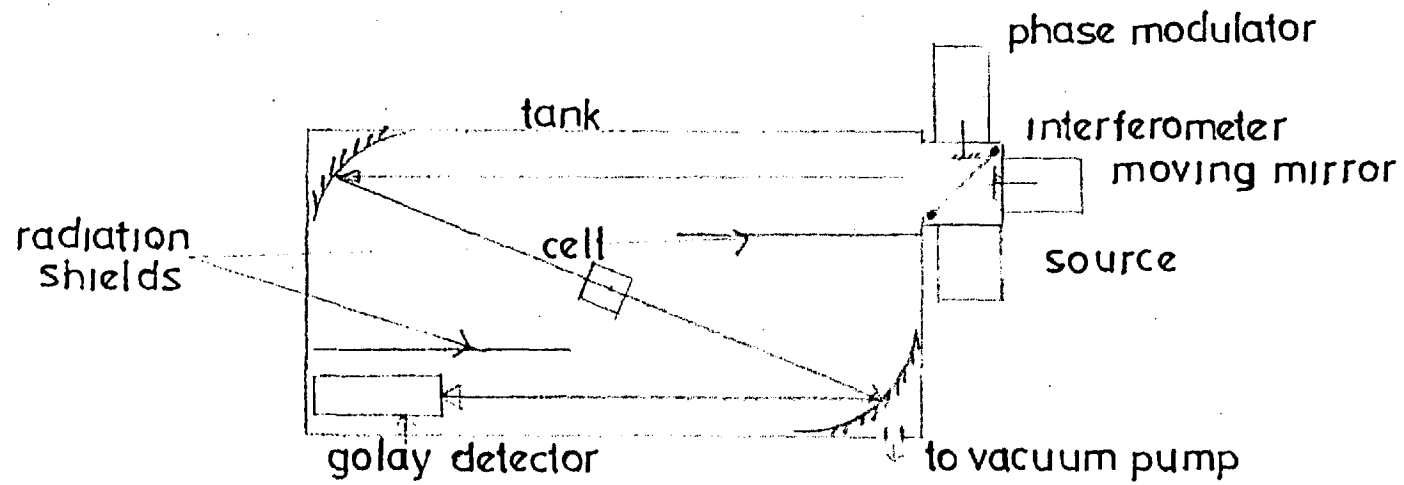


Fig 30 Mark 1a

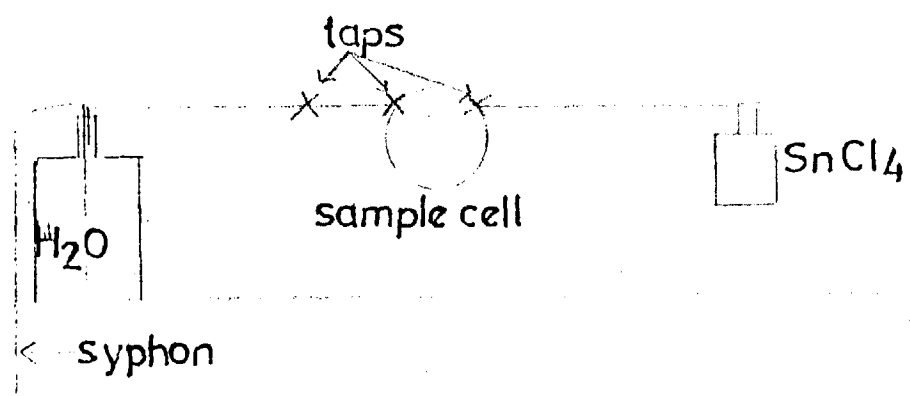


Fig 31 Filling of $SnCl_4$ Cell

In order to make observation of Sn Cl₄ vapour, instead of completely filling the cell with Sn Cl₄ liquid it was one third filled, and then using a vacuum pump the Sn Cl₄ was pumped off until the liquid level was halved i.e. there was now saturated SnCl₄ vapour in the cell

A.3 Observations

The observations can be separated into two sections because of the different cell windows used.

In fact four different types of cell windows were tried, which were, polypropylene, high density polythene, Teflon, and T.P.X. T.P.X. windows proved to have the highest transmission and subsequently the highest signal to noise ratio in the region.

Initial results had shown that Sn Cl₄ liquid was too strong an absorber in this region and so all the subsequent observations were of the saturated vapour.

A.3.1 T.P.X. Windows

A background interferogram was recorded over night and a foreground interferogram recorded the next day.

The resulting observed transmission spectrum (see Fig 32) shows the absorption due to the ν_4 vibrational mode with apparent strong P and R branches.

The background spectrum (see fig 33) shows the presence of a channel spectrum which peaks in intensity around 125 cm^{-1} . This channel spectrum was removed by a method which will be described in section A.4

Path Length = 4 mm

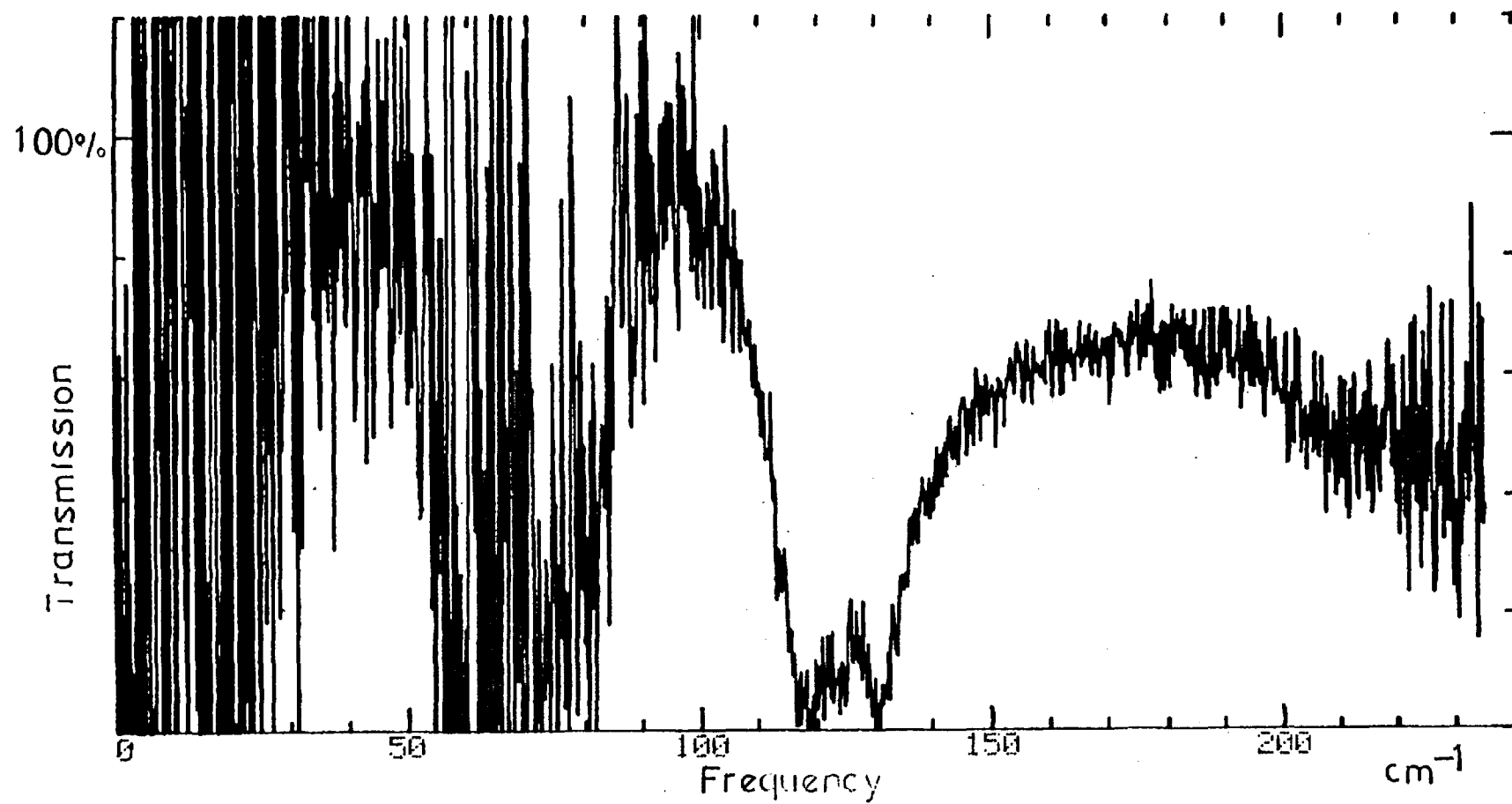


Fig 32 Saturated SnCl_4 Vapour Transmission Spectrum

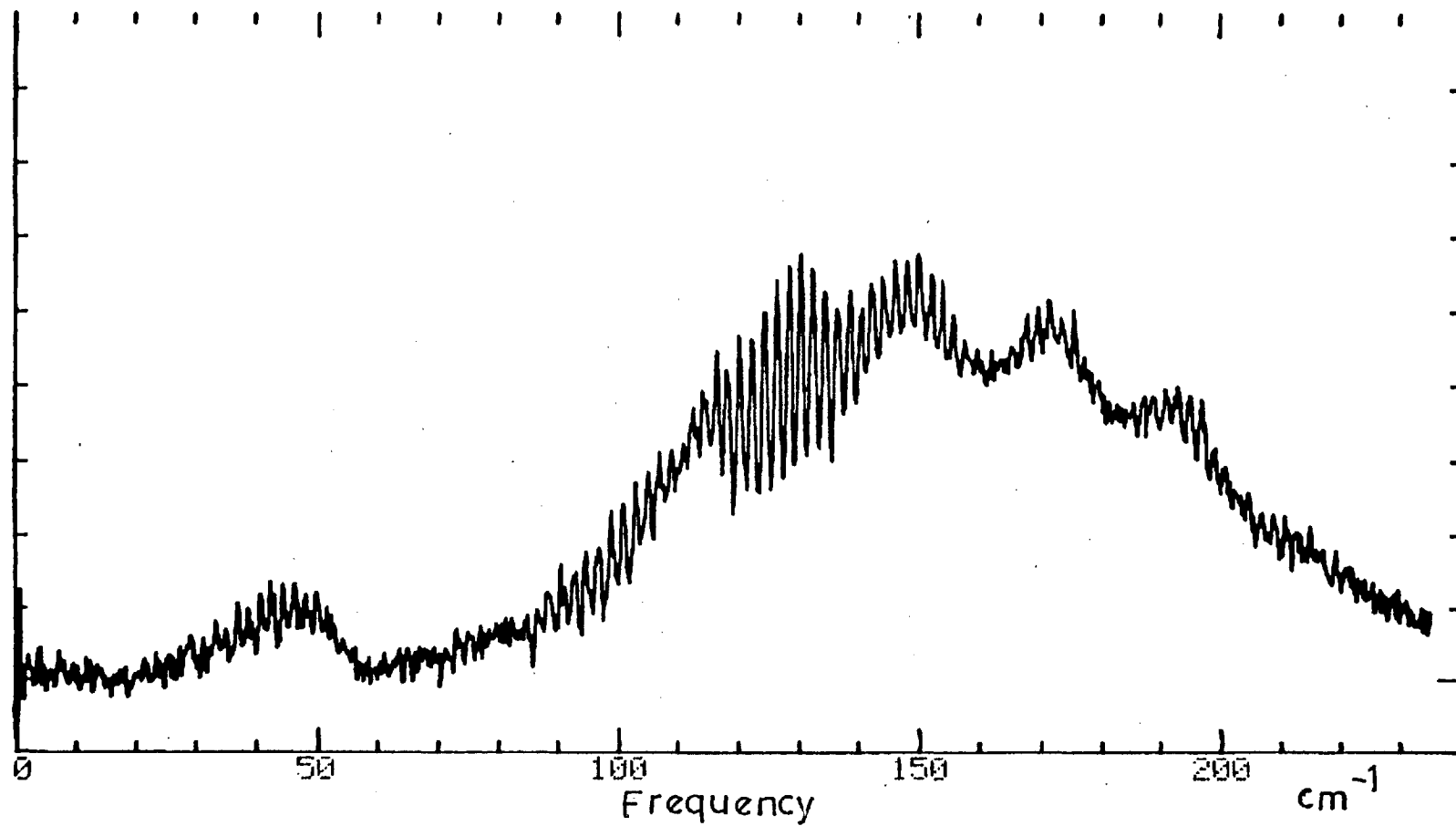


Fig 33 Background Spectrum Showing a Channel Spectrum

When the cell was taken apart (and washed in distilled water, as it was after each filling) it was apparent that the SnCl_4 had attacked the T.P.X. windows. Hence the measurements were repeated using polypropelene windows.

A.3.2 Polypropelene Windows

This time instead of recording foreground interferogram the day after recording a background interferogram during the night, several foreground interferograms were recorded during the day. The resulting foreground spectra were checked for consistency and then their average was ratioed to the background spectrum.

The resulting transmission spectrum (see fig. 34) is consistent with that obtained in section A.3.1. (the increased absorption seen beyond 1400 cm^{-1} in A.3.1. is most probably due to the substance formed by the reaction of SnCl_4 on T.P.X.).

The periodicity of signal seen in the foreground interferograms (see Fig. 35) correspond to wavelengths around 125 cm^{-1} as observed in the resulting spectra. This is analogous to the fourier transform of a dirac function.

A4 Removal of Channel Spectra

Analysis of the background spectra showed the existence of two channel spectra of spacing 2.2 and 1.2 cm^{-1} . Subsequent study of the interferograms showed the fourier transforms of these channel spectre (see figs. 36). The channel spectra corresponded to path differences of $.4$ and $.8\text{ cm}$ which were comparable to the widths of the cell windows and therefore the cell windows were, initially, thought to be the cause of the channel spectra. Hence the surfaces of the windows were mechanically

Path Length = 4 mm

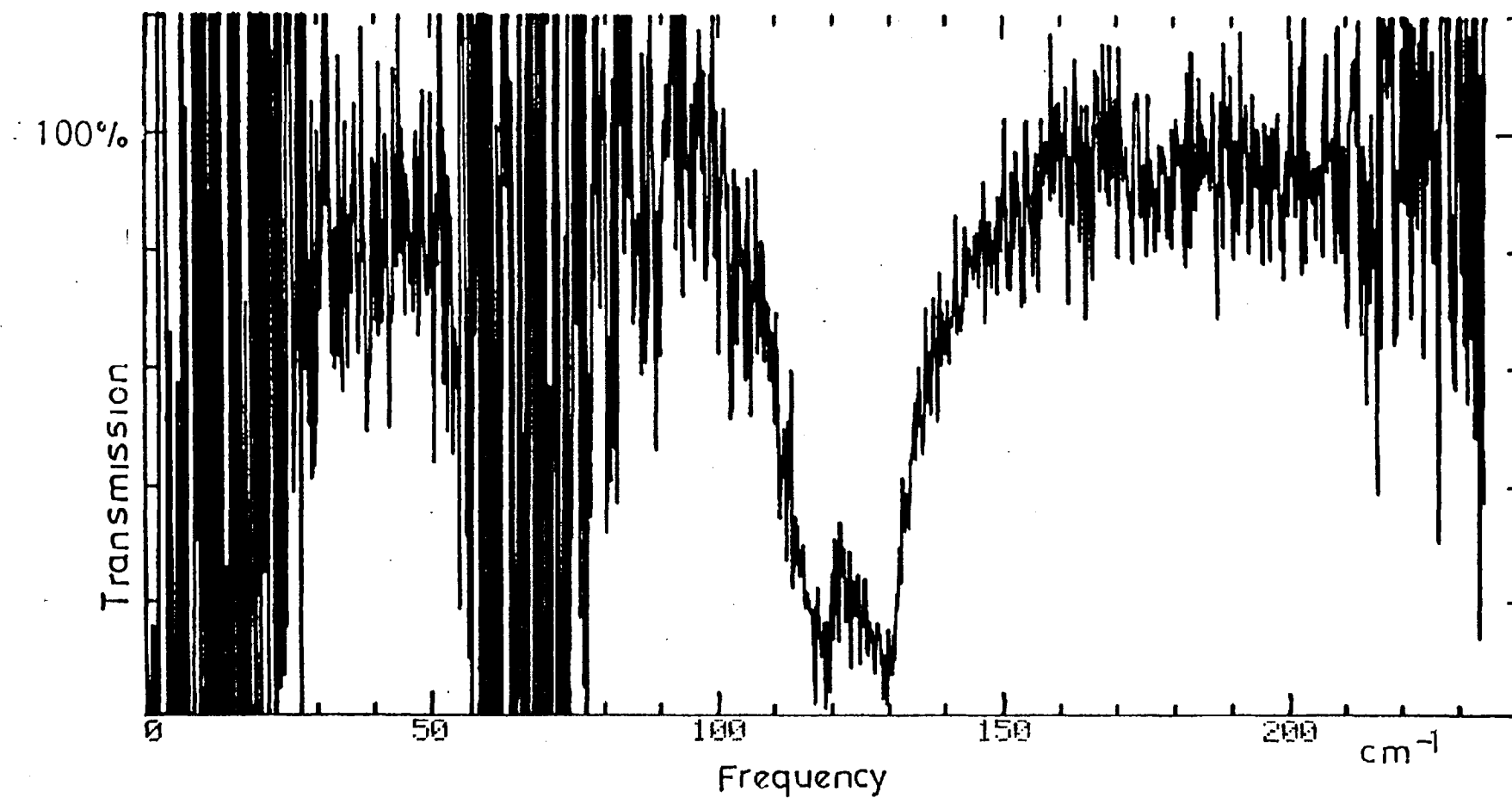


Fig 34 Saturated SnCl_4 Vapour Transmission Spectrum

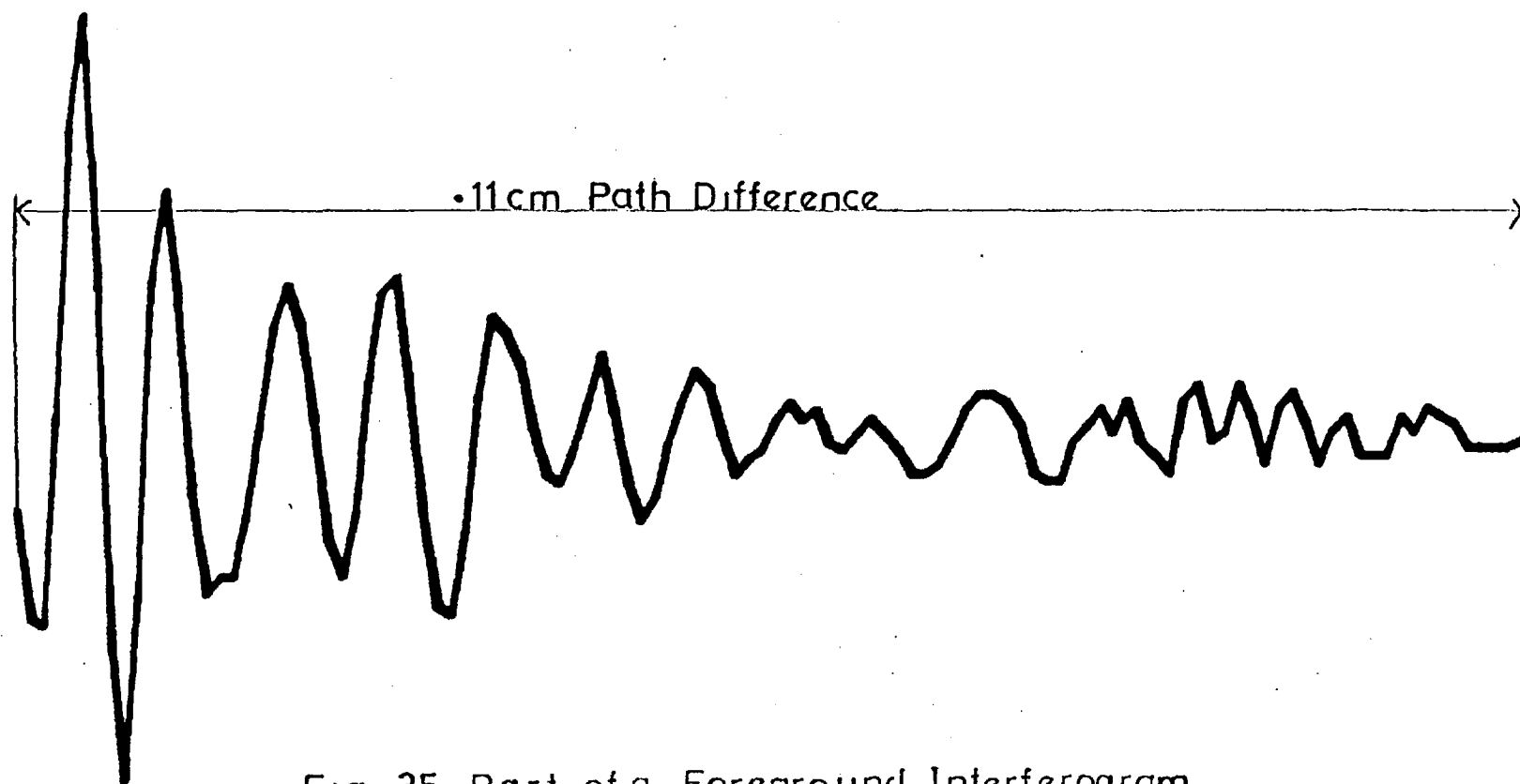


Fig 35 Part of a Foreground Interferogram

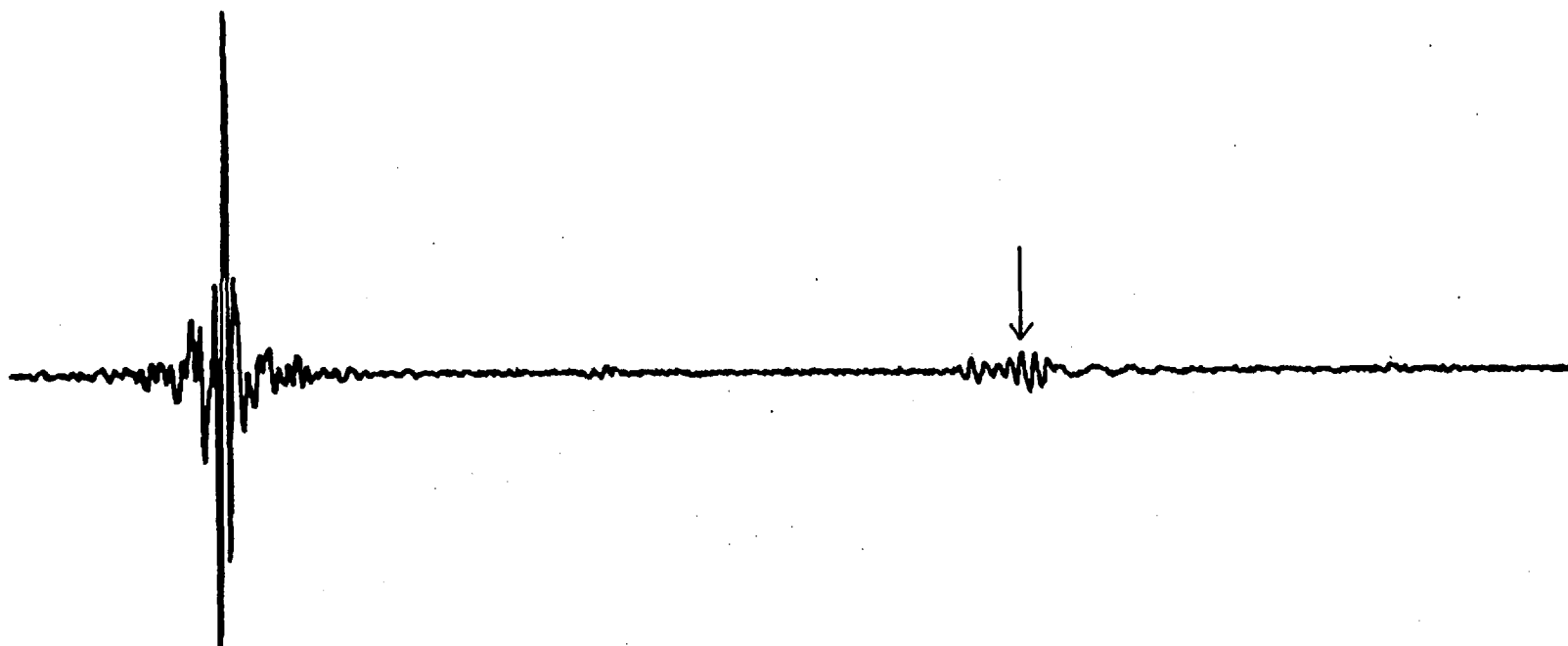


Fig. 36 This Interferogram Indicates the Presence of a
Channel Spectrum (see arrow)

scratched in such a way so as to prevent the interference of internal reflections. This procedure made no difference to the channel spectra whatsoever.

Another possible source for the channel spectrum was the window in the silicon golay detector. But as replacing the window (or wedging it) would have been a difficult operation it was decided to alter the interferogram itself. Hence the data points associated with the channel spectra were substituted by data points from the end of the interferogram. This procedure was justified because of the expected shape of the SnCl_4 ν_4 absorption band which would have meant that the major part of the information in the interferogram would be situated near zero path difference. One can see from figure 36 that the feature associated with the channel spectra are quite far from zero path difference.

As can be seen from the transmission spectra obtained from altered foreground and background interferograms, (Figs 32, 34) they have a slightly better signal to noise ratio otherwise they are no different from the transmission spectra obtained in the normal analysis (Fig 38).

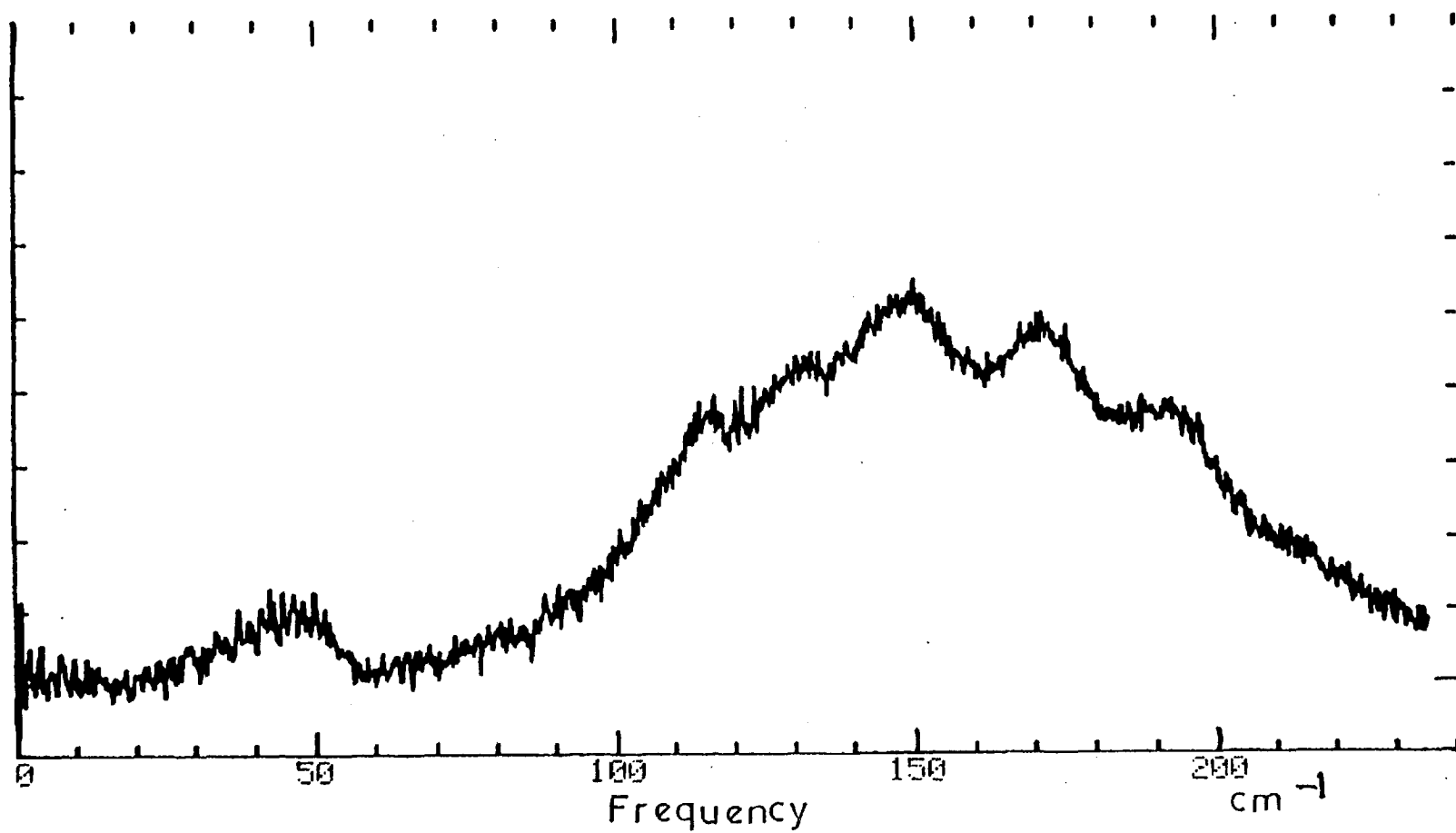


Fig 38_a Spectrum obtained from altered Interferogram(cf Fig 33)

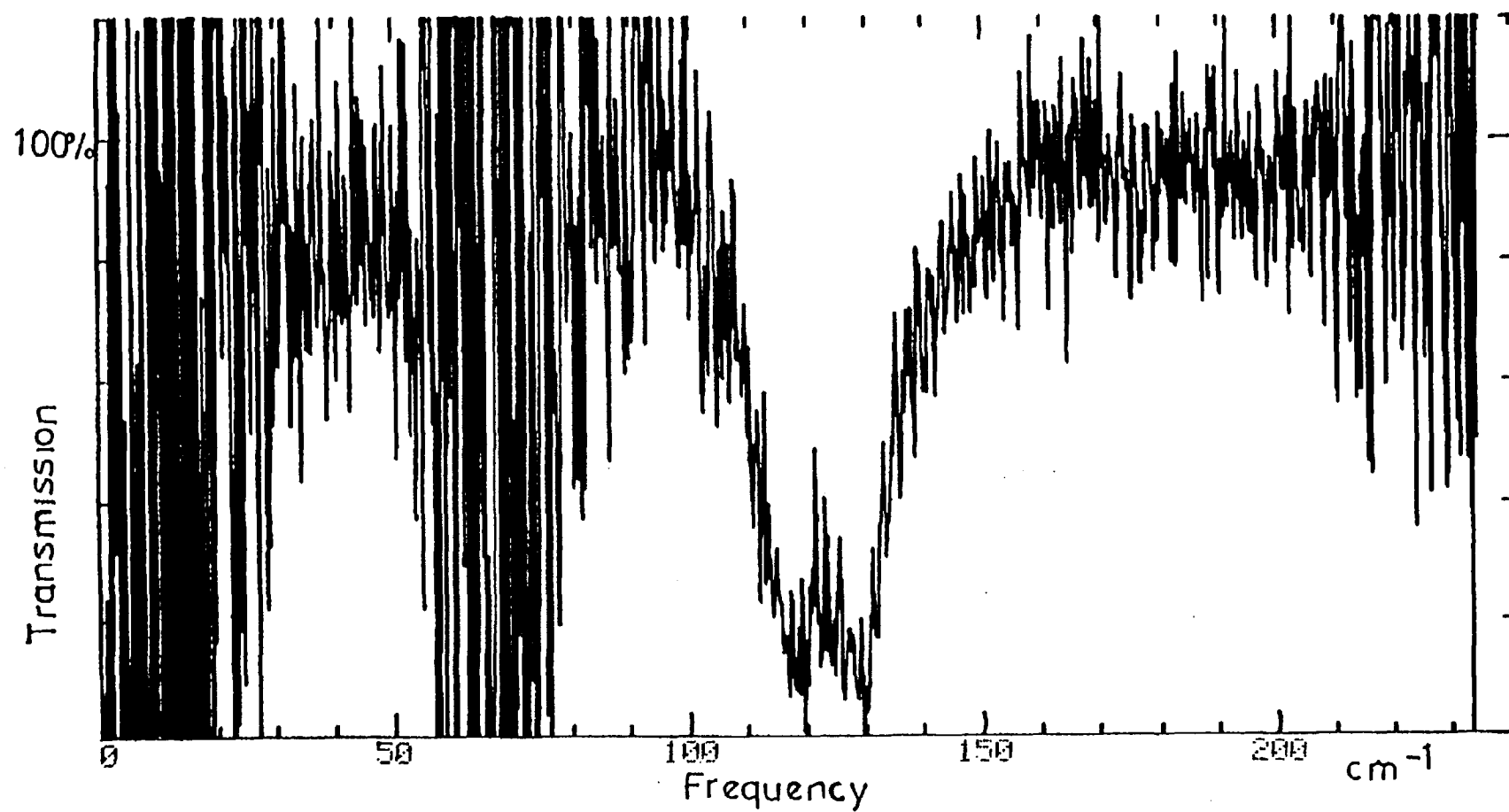


Fig 38b Transmission Spectrum obtained from unaltered Interferograms
c.f figs 32+34

APPENDIX B

The Pure Rotation Spectrum

The ammonia molecule is a symmetric top, possessing a rotation spectrum characterized by a quantized total angular momentum P equal to $\frac{h}{2\pi} J(J+1)$ about an axis fixed in space. The component P_z (see fig. 1) of the angular momentum along the figure axis of the molecule is also quantized proportional to K (obviously $J \gg K$)

The expression for the pure rotational energy levels can be written as follows:- DOWLING 1968) $F(J, K) = BJ(J+1) + (A-B)K^2$

$$\begin{aligned} & D_J J^2 (J+1)^2 - D_{JK} J(J+1) K^2 \\ & - D_K K^4 + FJ^3 (J+1)^3 + GJ^2 (J+1)^2 K^2 + HJ (J+1) K^4 \\ & \pm \frac{1}{2} E_{inv} (J, K) \quad \text{CM}^{-1} \dots \dots \dots B.1 \end{aligned}$$

where A and B are the rotation constants, D_J and D_{JK} are first order constants to represent the effect of centrifugal stretching, and F , G , and H are constants of higher order.

E_{inv} gives the energy splitting due to inversion. Because of the inversion splitting the following applies:-

For $K = \text{even}$, the wave functions which belong to the lower energy level of the inversion split are symmetrical (+) with respect to the inversion (the lower sign in the above expression B1 has to be used). The wave functions which belong to the upper energy level are antisymmetrical (-) with respect to inversion (the upper sign must be used).

For $K = \text{odd}$, the symmetries are reversed.

For $K = \emptyset$, and $J = \text{even}$, the symmetrical levels are missing.

For $K = \emptyset$ and $J = \text{odd}$, the anti-symmetrical levels are missing.

Costain's formula for E_{inv} was used for the inversion splitting

$$\begin{aligned} E_{inv} = & \emptyset .793455 \text{ EXP } (-6.3699 \times 10^{-3} J (J + 1) \\ & + 8.88986 \times 10^{-3} K^2 + 8.6922 \times 10^{-7} J^2 (J + 1)^2 \\ & + 1.7845 \times 10^{-6} J (J + 1) K^2 + 5.3075 \times 10^{-7} K^4) \text{ cm}^{-1} - B.2 \end{aligned}$$

The line positions are given by the expression

$$(J, K) = F(J', K') - F(J'', K'') \quad (\text{where the ' indicates the upper and'' the lower level of the transition}), \text{ using the selection rules } \Delta J = +1 \text{ and } \Delta K = \emptyset \text{ (see LEUPOLT 1973)}.$$

The ν_2 and $2\nu_2$ Inversion bands

The energy levels of the inversion bands were calculated from the expression, (GILLE 1969)

$$\begin{aligned} F(J, K) = & \nu_0 \left\{ \begin{array}{l} S \\ a \end{array} \right\} + B_J (J + 1) + (A - B) K^2 - D_J J^2 (J + 1)^2 \\ & - D_{JK} J(J + 1) K^2 - D_K K^4 \text{ cm}^{-1} \quad B.3. \end{aligned}$$

$$\left\{ \begin{array}{ll} \text{For } \nu_2 & \nu_{os} = 932.436 \text{ cm}^{-1} & \nu_{oa} = 968.076 \text{ cm}^{-1} \\ \text{For } 2\nu_2 & \nu_{os} = 1597.494 \text{ cm}^{-1} & \nu_{oa} = 1882.194 \text{ cm}^{-1} \end{array} \right.$$

Because of the selection rules

$$\Delta K = \emptyset \text{ and } \Delta J = \begin{cases} +1 & R - \text{branch} \\ \emptyset & Q - \text{branch} \\ -1 & P - \text{branch} \end{cases}$$

we obtain for the line position three branches namely,

$$\left\{ \begin{array}{lll} \nu_0 (J, K)_{s,a}^R & = & F(J + 1, K)_{a,s} - F(J, K)_{s,a} \quad - B.4 \\ \nu_0 (J, K)_{s,a}^Q & = & F(J, K)_{a,s} - F(J, K)_{s,a} \quad - B.5 \\ \nu_0 (J, K)_{s,a}^P & = & F(J - 1, K)_{a,s} - F(J, K)_{s,a} \quad - B.6 \end{array} \right.$$

Again the following levels are missing,

Symmetrical: $K = \emptyset$ for $J = \text{even}$

Anti-symmetrical: $K = \emptyset$ for $J = \text{odd}$ (see LEUPOLT 1973).

Line Intensities

The line intensities were given by the following expression (GILLE 1969)

$$I(\nu) = \frac{8 \pi^2 F N \nu^2 |\langle \mu \rangle_{m_0}|^2}{3 c K T} S(\nu, \delta \nu) \quad -B.7$$

where, N is the total number of molecules per unit volume, F is the fraction of molecules in the state ψ_0

c is the speed of light,

$|\langle \mu \rangle_{m_0}|^2$ is the square of the dipole matrix elements.

K is the boltzman constant

T is the absolute temperature

$\delta \nu$ is the half-width

$S(\nu, \delta \nu)$ is the shape factor

The kinetic line shape (Gross 1955) gives the best theoretical fit to the observed transmission spectra. This is given by the expression

$$S(\nu) = \frac{4 \nu^2 (\delta \nu)}{\pi [(\nu_0^2 - \nu^2)^2 + 4 \nu^2 (\delta \nu)^2]} \quad -B.8$$

The Van Vleck and Weisskoff shape is given by the expression (Van Vleck and Weisskoff 1950)

$$S(\nu) = \frac{\nu^2 (\delta \nu)}{(\nu - \nu_0)^2 + (\delta \nu)^2} + \frac{\nu^2 (\delta \nu)}{(\nu + \nu_0)^2 + (\delta \nu)^2} \quad -B.9$$

APPENDIX C

Experimental Calibration of Cavity

Using a known fixed path length cell (16.45 cm) the transmission of the 19.6 cm^{-1} ammonia monomer line, broadened by nitrogen, for different ammonia pressures was measured, the broadening pressure being kept constant i.e.

$$P_{\text{NH}_3} + \frac{P_{\text{N}_2}}{6} = \text{constant (22}\phi \text{ torr)}.$$

Transmission is given by the expression $T = \text{EXP} (- K_B PL)$ where K_B is the pressure broadened absorption coefficient, and L is the path length.

From the results a graph of $\text{LOG}_e T$ against P was plotted and knowing L, K_B was determined. This procedure was repeated for the cavity i.e. K_B was kept constant by keeping the broadening pressure constant. This time a graph of $\text{LOG}_e T$ against P was plotted from which knowing K_B , L was determined $L = 129.7 \text{ cm}$.

From chapter 4, equations 15 can be written

$$\frac{C}{\nu^{\frac{1}{2}}} KP = \frac{1}{T} - 1 \quad \text{.....} \quad \text{C.1}$$

where $\alpha = \frac{C}{\nu^{\frac{1}{2}}}$, and T is transmission.

Knowing the effective path length L at 19.6 cm^{-1} and the measured transmission, the value of KP could be found and so the value of the constant C, the "cavity constant" (this is constant at all frequencies).

Having determined the cavity constant values of KP could be determined at all frequencies using equation C.1. Then by using the expression $T = \text{EXP} (- KPL)$ a new transmission spectrum could be obtained i.e. the initial cavity spectra were adjusted to fixed path

length (13 ϕ cm)

$$C = 2.6328 \times 10^8$$

NOTE:

The nitrogen gas was dried by storing the gas for about twenty minutes in a reservoir containing phosphorus pentoxide

It was found that P_2O_5 was not suitable for drying

NH_3 .

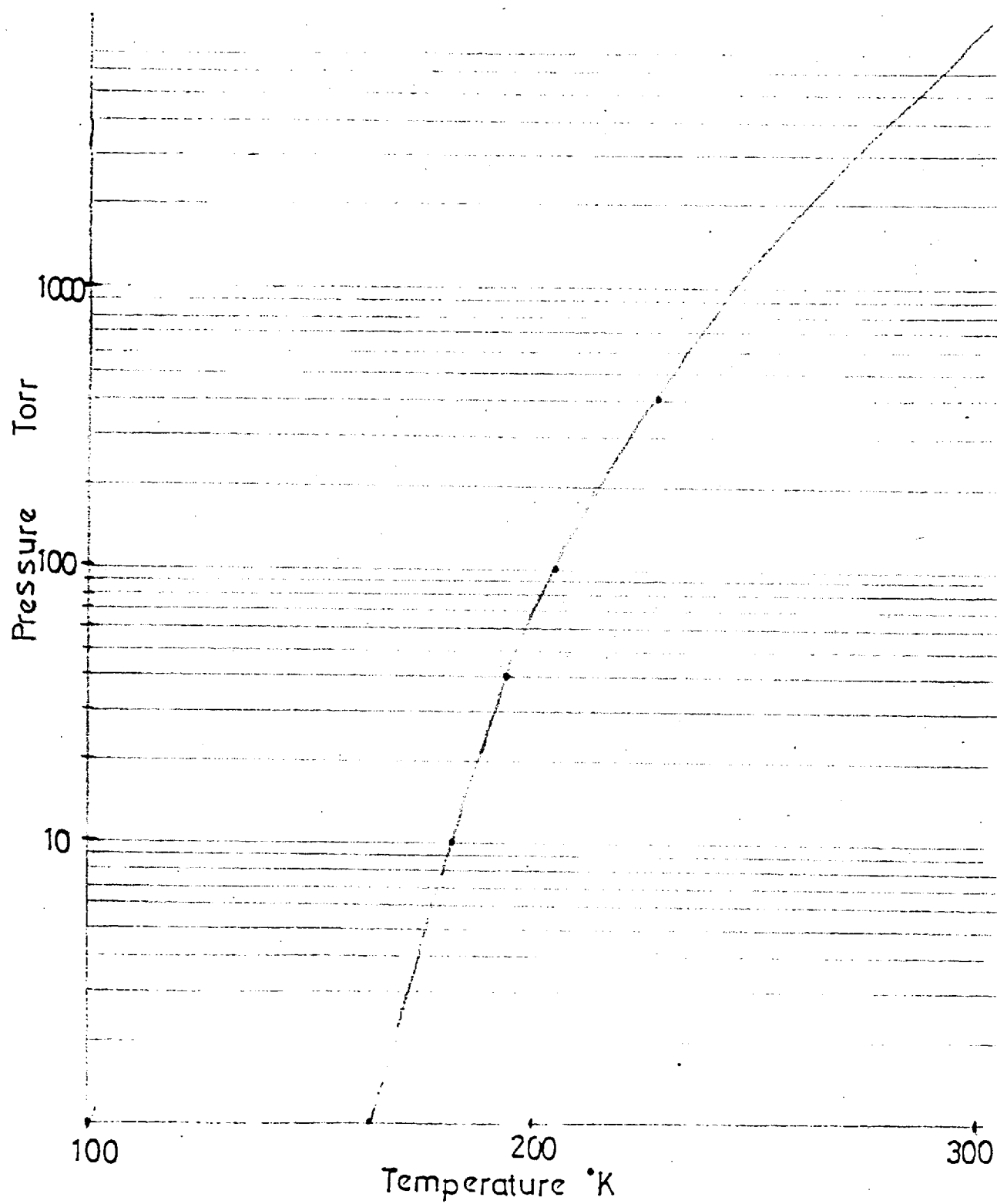


Fig 37 Vapour Pressure of Ammonia

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