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Temperature effects on the far-infrared absorption spectra of simple organic molecules

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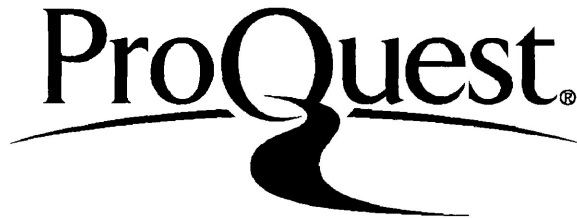
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TEMPERATURE EFFECTS ON THE FAR-INFRARED ABSORPTION SPECTRA
OF
SIMPLE ORGANIC MOLECULES

A THESIS SUBMITTED BY

C.K. McLellan

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS OF THE DEGREE
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Summary

The recent development of interferometers operating in the far-infrared frequency region, coupled with the use of modern high-speed digital computers for processing the interferometric data, has made this frequency region more readily available for investigation. It became apparent quite early that most, if not all, compounds exhibit absorptions in this region, confirming the speculations of earlier dielectrics studies. For polar molecules, the existence of these absorptions has been attributed to a variety of causes, several of which have in common a concept of a short-lived pseudo-lattice or cage of molecules surrounding a central trapped molecule which could absorb energy from an applied oscillating electromagnetic field in order to move within the potential energy well created by the cage members.

In the present work, an attempt has been made to examine this concept by varying the temperature of the sample, with a view to altering the size and rigidity of the cage. The type of motion exhibited by the central molecule has also been considered.

In general, both the intensity and frequency of maximum absorption increased smoothly with decreased temperature within the liquid phase, and within certain solid phases in which molecular rotational motion was allowed. On passing into non-rotator solid phases, however, the broad, featureless absorption curve of the liquid was replaced abruptly by one containing several sharp, narrow

and intense absorption peaks.

It has been suggested that the broad absorption bands of the liquid phase are composed of several overlapping bands due to different types of molecular motion. Further, each of the component bands was suggested to arise from the differences between the kinetic energy possessed by a central molecule, and the energy barrier created by the molecular cage. The kinetic energy of the central molecule was suggested to be governed by a continuous distribution. Similarly, the energy barrier might also be governed by a second continuous distribution.

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CHAPTER I

Introduction

Introduction

The definition of the "far-infrared" frequency range of the electromagnetic wave spectrum is an arbitrary one based primarily on apparatus and experimental techniques, and not on any fundamentally distinctive aspect of the range which sets it apart from the rest of the infrared region or from the lower-frequency neighbouring microwave range. Brasch⁴ quotes the IUPAC specification that the far-infrared region falls between 10 and 200 wavenumbers. The limits have been approached from both sides, the most recent advance on the microwave side being the development by Garg *et al.*²³ of a free-space interferometer operating at 5 wavenumbers (2 mm. wavelength) for the determination of the complex dielectric permittivity of liquids. On the other side, most infrared spectrometers available commercially are limited to frequencies above approximately 200 wavenumbers by poor source output and detector sensitivity and by absorptions by atmospheric gases.

The region has become more accessible recently with the development of far-infrared Fourier transform spectrometers, to be detailed later, bringing together these two fields of research, infrared spectroscopy and dielectric studies. The result has often been considerable controversy arising from the different approaches to the absorption phenomena. This has been, and no doubt will continue to be, valuable, for dispute and controversy are key elements of the maelstrom from which emerges scientific understanding.

Infrared spectroscopists have inferred molecular motion against small energy barriers from the broadening of high-frequency absorption bands in condensed phases as compared to the gaseous phase. For example, Ewing¹⁹ has investigated these effects particularly on the ν_3 (stretching) fundamental (of F_2 symmetry) of methane in liquid and solid phases. He states that the intermolecular interactions occurring in these phases may be regarded as giving rise to potential energy barriers which, if small, may be treated as perturbations on the energy levels of the first-approximation model of independent rotors. Jones and Sheppard³⁸ suggested that line broadening was due to the increased contribution to overall band shape from branches activated by symmetry-distorting forces on the absorbing molecule which were due to intermolecular forces.

As the far-infrared region became directly accessible, infrared spectroscopists applied their techniques of spectral analysis to some data. Hadni *et al.*²⁶ have analyzed the rather sharp absorption bands of naphthalene, durene and anthracene crystals and assigned them to translational molecular motions. Hunt *et al.*³⁵ have used far-infrared data in part to obtain the hindering potential to intramolecular rotation in hydrogen peroxide. Durig *et al.*¹⁸ have analyzed the far-infrared and Raman spectra of several "globular molecules" in terms of molecular translations and group torsional motions occurring in solid phases. Savoie and Fournier⁴⁸ have analyzed the absorption spectra of methane and methane-d₄ in their

solid phases as arising from molecular translations, but noted that the spectra of the liquid and of a warmer solid phase were suggestive of predominantly rotational molecular motions.

In dielectrics studies, one is concerned with the information on molecular motions and structures derived from measurements of the complex dielectric constant (or permittivity), ϵ^* , as a function of frequency. For a system undergoing relaxation characterized by only one relaxation time, the relation is:²⁷

$$\epsilon^* = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau} = \epsilon' - i\epsilon'' \quad (\text{I-1})$$

where ϵ^* is the complex dielectric constant (permittivity),

ϵ_{∞} is the high-frequency dielectric constant,

ϵ_0 is the low-frequency dielectric constant,

ω is the angular frequency of the applied field,

τ is the relaxation time,

ϵ' is the real part, often called simply the dielectric constant, and

ϵ'' is the complex part, often called the dielectric loss factor.

Separating real and imaginary parts, one obtains

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + (\omega\tau)^2} \quad (\text{I-2})$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty})\omega\tau}{1 + (\omega\tau)^2} \quad (\text{I-3})$$

The low-frequency dielectric constant, ϵ_0 , is measured at frequencies so low that the molecular reorientation by rotation necessary to follow the electric field's change of direction is accomplished easily and with no absorption of energy from the field (i.e., $\epsilon''=0$ and $\epsilon_0 = \epsilon'$). The high-frequency dielectric constant, ϵ_∞ , is measured at frequencies so high that reorientation by molecular relaxation is not fast enough, so that the molecules do not get a chance to follow the field. Again, $\epsilon''=0$ and $\epsilon_\infty=\epsilon'$, but of course this is a new ϵ' since it is measured at a different frequency. In fact, the frequencies associated with ϵ_∞ are so high for many molecules of interest that the measurement is not made because the experimental method is difficult. Instead, a series of measurements at lower frequencies are made and fitted to a Cole-Cole plot which is then extrapolated to give ϵ_∞ . The Cole-Cole plot of ϵ'' vs. ϵ' is a semi-circle, as may be seen from Eqn. I-4 below, derived by eliminating $\omega\tau$ from Eqns. I-2 and I-3.

$$\left[\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2} \right]^2 + (\epsilon'')^2 = \left[\frac{\epsilon_0 - \epsilon_\infty}{2} \right]^2 \quad (\text{I-4})$$

The dielectric constant of a medium is equal to the square of its refractive index, n , measured at the same frequency. Hence, ideally, ϵ_∞ should be obtained from the square of the refractive index in the infrared region, since this is the range of frequency at which molecular rotations cannot follow the alternating field. Most

commonly, the infrared refractive index is approximated by the refractive index in the visible light region (often as measured at the sodium D lines, and hence symbolized n_D). One finds, then, that much interest has centred around the existence or non-existence of significant differences between ϵ_∞ and $(n_D)^2$.

From Eqn. I-3 one sees that the maximum loss factor, $\epsilon''_{\max.}$, occurs when $\omega\tau=1$. Hence $\tau=1/\omega_{\max.}$, where $\omega_{\max.}$ is the angular frequency of maximum dielectric loss factor. This is the relaxation time associated with molecular rotational reorientation, and is typically of the order of 10^{-11} sec. (For example, for chloroform in dilute solution in cyclohexane at 25°C , τ is approximately 4×10^{-12} sec., or 4 picosec.)⁴³ By contrast, if the maximum absorption observed in the far-infrared occurs at a frequency of 20 wavenumbers, the corresponding time is at least one order of magnitude smaller. It would seem unlikely that such a time could be associated with whole-molecule rotations of the type associated with dielectric relaxation.

Accumulated Data

In 1950, Whiffen⁵³ reported the results of dielectric measurements on six non-polar liquids (benzene, carbon tetrachloride, trans-decalin, cyclohexane, tetrachloroethylene and carbon disulphide) in the range 0.3 to 1.2 wavenumbers. Graphs of $\tan \delta$ vs. frequency, where $\tan \delta = \epsilon''/\epsilon'$, were found to be linear, whereas one would expect such a graph to show a maximum⁵² when $\omega\tau=1$, for polar molecules,

and one would expect $\tan \delta = 0$ for these non-polar species, since there is no permanent molecular dipole which could interact with the applied field to produce a torque causing molecular rotation. Whiffen considered four possible explanations. Firstly, there could exist a small non-zero dipole moment due to the presence of isotopes. This was rejected because the resulting dipole moments would be too small to account for the absorption, and isotopic abundance factors would further decrease this effect. Secondly, the absorption might be due to molecular quadrupolar moments, but these would have been too small. Further, absorptions from this source should not be linear with frequency. Thirdly, the absorptions could have been the tails of infrared bands. However, any such tails would be too small to account for the magnitude of $\tan \delta$ observed, and the direction of the temperature effect was wrong for rotational absorption. Finally, the absorptions could arise from the existence of small dipoles produced by molecular distortions, with decay of the dipolar polarization due both to slight molecular reorientation and to further distortions caused by subsequent collisions. For CCl_4 , bending of one $\text{Cl}-\text{C}-\text{Cl}$ bond angle by 6° would produce a dipole moment of $0.1 D$, sufficient to account for the absorption. For benzene, such a process is more difficult to envisage, but Whiffen cited the views of LeFèvre and LeFèvre that, by a suitable arrangement of $\text{C}-\text{H}$ bonds in neighbouring molecules, it was possible to have induced in benzene an appreciable dipole moment.

Whiffen estimated the relaxation time associated with this process as $\tau = 1$ picosec. which, he noted, was of the order of the time between molecular collisions.

In 1957, van Eick and Poley⁵¹ reported data for chloro- and bromobenzene which indicated that the extrapolated $\epsilon_{\infty} > (n_D)^2$. Further they found that this difference was strongly temperature-dependent, falling sharply as temperature was increased from 10°C to 50°C but relatively constant below or above this range. They suggested that there existed a second dipolar dispersion at higher frequencies, the intensity of which might show a strong and unusual dependence on temperature.

In 1962, DiCarlo and Smyth¹⁷ examined several symmetrical aromatic molecules and concluded that their apparent molecular dipole moments were less than 0.1 to 0.2 D for most. These values were based on estimates of the experimental error, since they were indistinguishable from zero. The authors suggested that perhaps the dipole moment really was zero, and that the previous values of up to 0.5 D could be based on erroneous values of P_A , the atomic polarization, of the molecules investigated.

Early in 1965, Garg and Smyth²² obtained dielectric data for several liquids at 4.5 wavenumbers frequency by an oblique-incidence interferometric method developed previously, finding that these data fit a Cole-Cole plot well to give an ϵ_{∞} not significantly different from $(n_D)^2$, so that there was no evidence of the higher-frequency dispersion indicated earlier by other workers. Later the same year, however, Garg *et al.*²³ reported the development of a new Michelson

interferometer operating at nearly the same frequency with which they were able to confirm the existence of non-zero dielectric loss factors for benzene, carbon tetrachloride, n-heptane and possibly cyclohexane.

Also in 1965, Gebbie *et al.*²⁵ reported measurements on the four mono-halobenzenes at 29.7 wavenumbers which gave values of ϵ' well below those predicted from lower-frequency data using a simple Debye expression, indicating the existence of an additional higher-frequency absorption process. This was confirmed later that year with the publication by Chantry and Gebbie¹⁰ of far-infrared absorption spectra in the range 10 to 400 wavenumbers for liquid and crystalline chlorobenzene obtained by Fourier transform of interferometric data. The liquid showed a broad, featureless absorption centred near 45 wavenumbers, while the solid showed two sharp peaks at 36 and 57 wavenumbers. From the similarity of these frequencies they suggested that the liquid-phase absorption arose from a "pseudo-lattice".

One year later, Bradley *et al.*³ published absorption spectra in the range 10 to 150 wavenumbers for liquid and solid phases of chlorobenzene and carbon disulphide, where the phases were obtained by the application of pressure. The spectra of the solids tended to be more intense than those of the liquids, and to be composed of sharper peaks. The authors declined to discuss their significance in this short note beyond mentioning the pseudo-lattice concept. The existence of far-infrared absorptions, as well as some strange

effects of temperature, pressure and phase changes, was now well established. Their interpretation, however, awaited further data upon which to construct hypotheses.

In 1966, Hassell and Walker²⁸ reported results for four mono-alkylbenzenes from the microwave region. The absorptions of all could be described by two relaxation times using the Budó equations for two overlapping Debye-type dispersions. The values of τ_2 , the shorter relaxation time, decreased with dilution for toluene to a constant value of 1.6 picosec., with a corresponding increase in apparent molecular dipole moment from 0.31 to 0.36 D . The authors considered three sources of absorption. The longer relaxation time, τ_1 , was assigned to molecular reorientation. For the shorter relaxation time, they considered the possibility of relaxation of aggregates of polar solute molecules within the solvent. This was further subdivided. Because of the rather small values of τ_2 , it was not seen possible for the process to be reorientation of entire aggregates. The other possibility, the association-dissociation rate process, was viewed as possible but unattractive for the observed energy barrier associated with the τ_2 was too small to fit such a model. These workers favoured an intramolecular relaxation mechanism for τ_2 , possibly a shift of the mesomeric moment along the $C_{\text{alkyl}}-C_{\text{aryl}}$ bond as the alkyl group rotated. It was noted that the solvent could affect such a process by its interaction with the rotating alkyl group of the solute molecule.

An examination of pure liquid toluene was reported in 1967 by

Santarelli *et al.*⁴⁷ in the microwave region up to 4 wavenumbers. They analyzed their results in terms of two overlapping Cole-Cole dispersions and got $\epsilon_{\infty} = 2.222$, $\tau_1 = 5.8$ picosec., and $\tau_2 = 0.20$ picosec. They also investigated toluene saturated with water, since water contamination had previously been proposed as the source of the anomalous higher-frequency dispersions observed, and concluded that the water could not nearly account for the observed data. They pointed out that, despite the fact that relaxation theory fit their experimental data, it was not necessary that the origin of the high-frequency absorption lay in dipolar relaxation.

Crossley and Walker¹² in 1968 reported their investigation of several symmetrically-substituted benzenes. They found non-zero absorptions for all, corresponding to short relaxation times and small dipole moments. The absorbance was rather insensitive to temperature. They obtained a roughly linear graph by plotting the frequency of bimolecular collisions (estimated by an equation for gas-phase collisions) against the inverse of the short relaxation times observed, and therefore suggested that the relaxation might involve molecular collisions.

Chamberlain *et al.*⁹ reported in 1967 a definite absorption at 29.7 wavenumbers for several polar and non-polar liquids, although the absorbance of cyclohexane was so small ($\alpha = 0.11$ neper-cm.⁻¹) that it might be zero.

In the same year, Gabelnick and Strauss²¹ reported that CCl_4 exhibited an absorption peak at approximately 40 wavenumbers in the

far-infrared region. They deduced from their data that the apparent dipole moment was $0.18 D$, with a relaxation time of 1 picosec. The effective moment of inertia, however, was found to be only about 4% of the value for CCl_4 as calculated for the whole molecule. The absorbance could not be accounted for by the tails of known infrared and Raman-active bands, and was ascribed to molecular distortions of the order of 10° on one $Cl-C-Cl$ bond. The authors also noted that their results for gaseous CCl_4 showed no absorption feature below 315 wavenumbers. Hence, the 40 wavenumber feature appeared to be a property of the liquid state, and not of the molecule itself.

The Resonance Approach by Hill

In 1963, Hill³² proposed a model in which a polar solute molecule was temporarily trapped in a cage of nearest neighbours. As it rotated, it encountered potential energy minima not necessarily due to dipolar forces (e.g., steric factors might play a part). Such a molecule could undergo reorientation, characterized by a longer relaxation time, and/or oscillations about its equilibrium position at one potential energy minimum, characterized by a shorter relaxation time. She stated that, for the latter case, the potential energy barrier between minima must be greater than kT , the thermal energy, or a considerable switching between minima would occur, obscuring the effect. The author suggested that certain molecules which exhibit a rotator phase in the solid state cannot meet this condition, and pointed out that several of these molecules,

which she grouped as "Class II" liquids, showed ϵ_{∞} approximately equal to $(n_D)^2$. By contrast, she placed the halobenzenes in "Class I" and noted that ϵ_{∞} was appreciably greater than $(n_D)^2$ for these.

The model, then, involved a type of resonance absorption damped by the non-rigidity of the temporary cage. The equation she obtained is shown as Eqn. I-5. The author stated that at high frequencies where $\omega\tau \gg 1$, one can say $\omega/\omega_0 \ll 1$, and make

$$\frac{\epsilon_{\infty} - n^2}{\epsilon_0 - n^2} = \frac{1 + j\omega\tau(2kT/I\omega_0^2)(a-jb)}{1 + j\omega\tau} \quad (\text{I-5})$$

where

$$j = \sqrt{-1}$$

$$a = \frac{1 - (\omega/\omega_0)^2}{[1 - (\omega/\omega_0)^2]^2 + (r\omega/\omega_0)^2}$$

$$b = \frac{r\omega/\omega_0}{[1 - (\omega/\omega_0)^2]^2 + (r\omega/\omega_0)^2}$$

and r is a damping coefficient

the approximation of Eqn. I-6, from which ω_0 may be calculated, since all other quantities are experimentally measurable.

$$\frac{\epsilon_{\infty} - n^2}{\epsilon_0 - n^2} = \frac{2kT}{I\omega_0^2} \quad (\text{I-6})$$

For the halobenzenes, she calculated that ω_0 is in the range 3 to 6×10^{12} rad./sec., which corresponds to a range of 17 to 33 wavenumbers. One might note with interest the approximation that $\omega / \omega_0 \ll 1$ in the development of Eqn. I-6, in view of the facts that for chlorobenzene, the absorption maximum occurs at 45 wavenumbers, while Eqn. I-6 predicts 22 wavenumbers. These data might suggest that the use of the approximation is inappropriate.

In 1968, Hill³³ examined qualitatively the implications of assuming a model liquid containing a continuous distribution of damped resonance systems. The examination was done by taking algebraic sums for only three overlapping absorption curves of equal amplitude. It was noted that the frequency at maximum absorption coefficient (α) was greater than that for maximum dielectric loss factor (ϵ''), and less than the value calculated from Eqn. I-6. The author also suggested that the broad nature of far-infrared bands pointed to a considerable spread of resonance frequencies and/or heavy damping.

In a 1969 paper, Hill³⁴ considered the types of absorption and refractive index curves which would result from assuming a continuous distribution of resonance frequencies. She used both Debye and Gaussian forms for the distribution of systems with resonant frequencies within a small range of frequencies, and integrated the appropriate expressions to obtain the total absorption or refractive index increments as a function of frequency. The resulting curves fit experimental data well in both cases, provided that the

damping coefficient was close to unity. She concluded that the experimentally-observed absorptions in the far-infrared could be represented satisfactorily by a distribution of resonant frequencies, but that it was not possible at present to determine experimentally whether a Debye or a Gaussian expression for the distribution function was more appropriate.

Molecular Field Approaches

In 1962, Birnbaum and Maryott² showed that non-polar CO_2 had an absorption at frequencies above 30 Gigahertz (1 wavenumber) which varied with the square of the gas pressure (i.e., density). Similar results were obtained for nitrogen and ethylene. These absorptions were all attributed to "transient dipoles induced by molecular quadrupole fields during binary encounters".

Rosenburg and Birnbaum^{4,6} reported in 1968 a pressure-induced absorption in gaseous CF_4 . The region below 250 wavenumbers showed two peaks. The one near 200 wavenumbers had an intensity linearly dependent on gas density, and was assigned to a combination band of higher-frequency vibrational levels which should occur at 197 wavenumbers. The lower-frequency band near 50 wavenumbers was composed of two overlapping contributions, the intensity of one being dependent on the square of the gas density, while that of the other was linear with density. It was speculated that the linear term might, similarly, be a difference band. The quadratic term was ascribed to a transient dipole moment created by molecular

octupolar fields and/or bond angle distortions during bimolecular collisions.

Chantry *et al.*¹¹ reported in 1967 a study of liquid and crystalline phases of CCl_4 (spherical), CS_2 (linear), and C_6H_6 (planar), all non-polar. In the far-infrared region, all showed absorption in the liquid phase at frequencies similar to the main lattice vibration peaks in this range for their solids. They suggested that a liquid molecule is entrapped in a pseudolattice of neighbours which induce in the trapped molecule a small dipole whose magnitude and direction alters as the pseudolattice oscillates. They pointed out that the separation between induced and inducing dipoles is so small that it approaches the distance separating the charges comprising the dipoles involved, so that the 'point dipole' treatment is inadequate. Rather, one should consider the potential field at a point in terms of the multipole fields of the surrounding molecules. They further noted that the effects of multipole fields are strongly dependent on distance. (Perhaps a distribution of intermolecular distances and of bond dipole orientations is involved in the explanation of the width of far-infrared absorption bands.) Hildebrand³¹ had made a similar comment twenty years earlier to the effect that intermolecular forces must be treated on a highly localized basis rather than point approximations.

Davies *et al.*¹³ in a 1968 paper considered the far-infrared absorption of polar molecules in the liquid state, pointing out a number of significant features of the data. Firstly, peak intensity

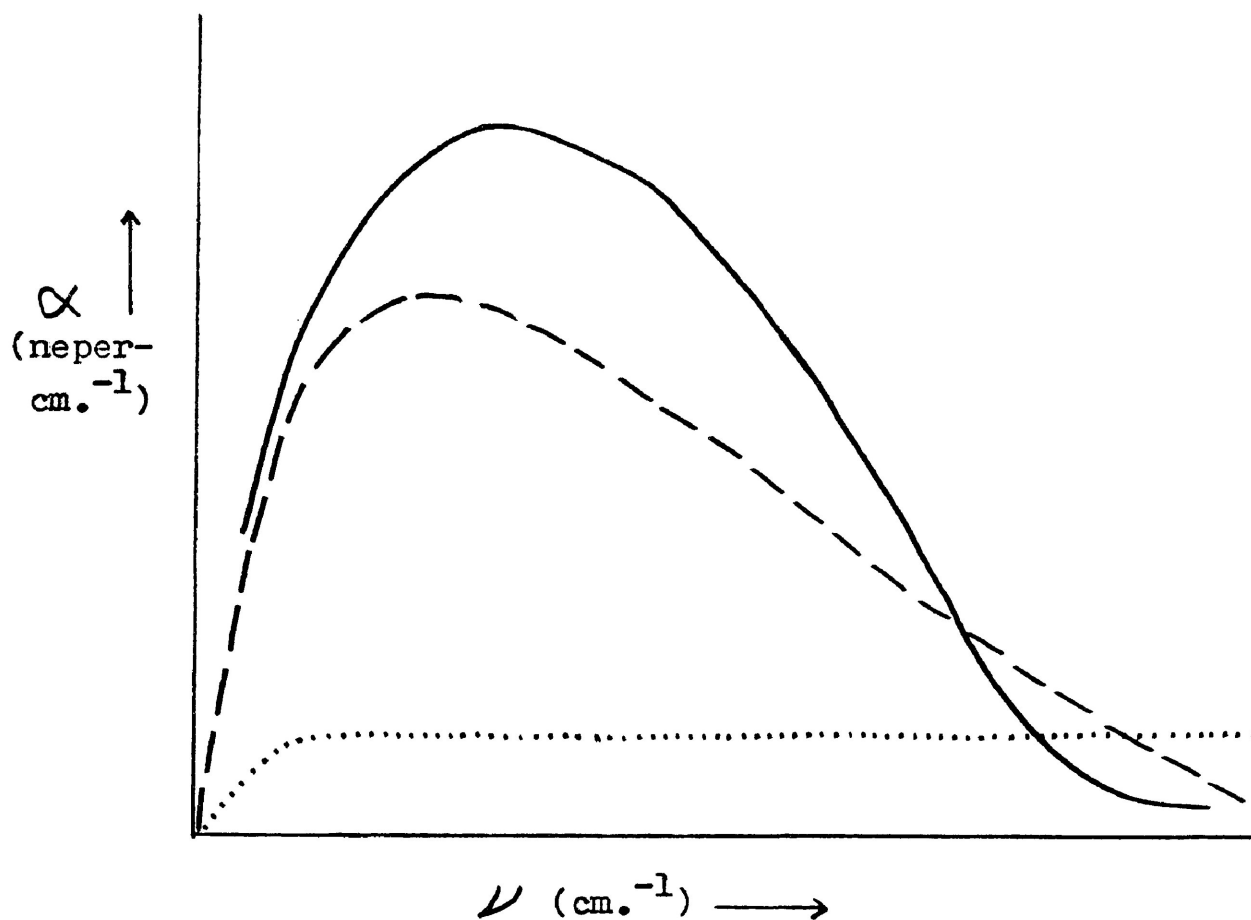


Figure I-1: Rough sketch to indicate the relationships between observed absorptions and the theories of Debye and of Rocard and Powles

- observed absorption in far-infrared
- Debye theory
- - - - Rocard and Powles theory

was considerably larger than that calculated by either the Debye or Rocard and Powles approaches. The commonly-used form of Debye theory says that the absorption coefficient, α , reaches a constant maximum value at high frequency given by Eqn. I-7:

$$\alpha_{\infty} = 21.1 (\epsilon_0 - \epsilon_{\infty}) / \tau \quad (\text{I-7})$$

Rocard and Powles had reconsidered the Debye equations for high frequency and, including the moment of inertia term which Debye had dropped in an approximation, derived an expression which showed α dropping to zero at high frequency. As one may see from Fig. I-1, however, even this treatment did not account for the far-infrared bands observed.

Secondly, the absorption peaks were quite broad. If $\nu_{(+\frac{1}{2})}$ and $\nu_{(-\frac{1}{2})}$ are the upper and lower frequencies, respectively, at which $\alpha = 0.5 \times \alpha_{\text{max.}}$, then for chlorobenzene, $\nu_{(+\frac{1}{2})} / \nu_{(-\frac{1}{2})}$ is approximately 21, whereas classical Debye theory says it should be 14.1.

Thirdly, many polar molecules exhibited far-infrared absorptions with the maximum absorption coefficient somehow related to the permanent molecular dipole moment.

Finally, there were several effects presumably related to local environment. Cooling the samples caused peaks to shift to higher frequency and to sharpen. The absorption did not appear to be abnormally affected by dilution, and seemed relatively insensitive to the choice of solvent.

From these observations, the authors drew three main conclusions. First, the Poley-Hill absorption was not dependent on collisions of two or more molecules. Second, any local molecular field which might affect the absorption was relatively independent of the type of neighbouring molecule, suggesting that perhaps the repulsive forces were most important in the molecular field. Third, the 'resonance frequency', ν_R , given by Hill's expression (Eqn. I-6), did not seem to correlate with the observed frequency of maximum absorption coefficient, nor with the relaxation times for molecular reorientation known from microwave dielectrics data.

In the same year, Davies *et al.*¹⁴ considered several non-polar molecular absorptions in this frequency region, and noted the following. All molecules, regardless of polarity, appeared to have some absorbance in this region. As molecular rigidity and symmetry increased, the absorption intensity decreased. Absorption intensity increased when there were more polar bonds within the molecule. The ratio of the frequency of maximum absorption observed to the frequency of bimolecular collisions in the liquid phase, as estimated from an equation due to Mie, was relatively constant for benzene, carbon disulphide, and carbon tetrachloride (although they did not remark on the fact that the ratio for 1,4-dioxane was considerably different). The ratio $\nu_{(+\frac{1}{2})} / \nu_{(-\frac{1}{2})}$, when calculated for dielectric loss factor data, rather than absorption coefficient, came very close to the value of 14.1 predicted from Debye theory.

The authors then proceeded to suggest origins for the absorptions.

The relationship to the frequency of bimolecular collisions suggested a collisional process. On the other hand, the peak half-width ratios suggested a relaxation mechanism. However, plots of dielectric loss factor vs. the logarithm of frequency were not symmetrical, as they should have been for relaxation. Further, plots of refractive index vs. frequency had shallow minima. (A minimum in such a plot suggests a resonance process. A relaxation process shows only a smooth fall from one value to another as frequency is increased.) This observation was supported by the publication previously by Chamberlain *et al.*⁸ of the refractive index spectrum in this region for 1,1,2,2-tetrabromoethane, which showed several distinct minima. It appeared to Davies and co-workers that the peak half-widths' ratios were merely a fortuitous circumstance. They concluded that the whole band was probably the superposition of overlapping translational-rotational resonance modes.

Also in 1968, Garg *et al.*²⁴ examined several non-polar liquids in the microwave and far-infrared regions, taking great pains to exclude water, and then adding this contaminant to examine the water absorptions. Most systems had relaxation times of about 1 picosec., and apparent dipole moments of about 0.1 *D*. The authors viewed the absorptions as being due to dipoles, μ_i , induced by the multipoles of the neighbours in the liquid state. They noted the results of Gabelnick and Strauss²¹ mentioned earlier, finally concluding that there were two types of absorption processes. Firstly, a relaxation absorption characterized by long relaxation times, and

hence observable in the microwave region, involved exponential decay of polarization during slow diffusion through the system by the molecule. Secondly, at higher frequencies one observed a broad resonance absorption by molecules possessing a multipole-induced dipole and trapped temporarily in a cage of neighbours for times of the order of the time between molecular collisions. The cage configuration lifetime was suggested to be short but variable, and they envisaged considerable coupling between molecular motions, giving rise to the very broad absorption peaks in the far-infrared.

Correlation Functions

In 1967, Leroy *et al.*,^{40,41} considered the absorptions exhibited by polar liquids in the range 0.001 to 20,000 Gigahertz (i.e., up to 200 wavenumbers). They began by outlining the flaws of the classical Debye theory at high frequency, particularly its prediction of a constant high-frequency absorption coefficient (see Fig. I-1) which would deny the possibility of transparency in, say, the visible region.

The complex dielectric constant (or permittivity), ϵ^* , was viewed as the Fourier transform of a time function, $\phi(t)$, called the decay function. That is,

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = - \int_0^\infty \exp(-i\omega\tau)\phi(t)dt \quad (\text{I-8})$$

For the Debye relaxation process, the decay function is given by

$$\phi(t) = \exp(-t/\tau_1) \quad (\text{I-9})$$

The authors went on to derive new expressions based on the auto-correlation function $\phi(t)$ and using a few experimental parameters, then took up two limiting cases. Their general expressions are shown in Eqns. I-10 to I-12.

$$(\epsilon_0 - \epsilon_{\infty 1}) = (\epsilon_0 - \epsilon_{\infty}) \exp C \quad (\text{I-10})$$

$$\frac{\epsilon_0 - \epsilon_{\infty 1}}{\epsilon_0 - \epsilon_{\infty}} = 1 + C \quad (\text{since } C \text{ is small}) \quad (\text{I-11})$$

$$B' = \frac{\epsilon_{\infty 1} - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = 1 - \exp C = -C \quad (\text{I-12})$$

where ϵ_0 = low-frequency dielectric constant,
 $\epsilon_{\infty 1}$ = the real high-frequency dielectric constant,
 ϵ_{∞} = the high-frequency dielectric constant obtained by
 assuming the Debye relations in fitting the data,
 B' and C are experimental parameters.

The first limiting case considered was that of dominance of the high-frequency dispersion by the inertial effect, in which case, C is small and positive. Under these conditions, the expression derived for the autocorrelation function was:

$$\phi(t) = \exp \left[\frac{-t + \tau_2(1 - \exp(t/\tau_2))}{\tau_1} \right] \quad (\text{I-13})$$

where τ_1 = the molecular relaxation time, and τ_2 = the correlation time of the angular rate of rotation. If, as a limiting situation

of this case, the molecular moment of inertia approaches zero, so does τ_2 , so that Eqn. I-13 reduces to Eqn. I-9, which is for simple Debye relaxation. That was why the authors chose the term "inertial effect". For purposes of calculation, provided $\tau_2 \ll \tau_1$, the authors derived Eqns. I-14 and I-15, with τ_2 derivable from τ_1 via Eqn. I-16.

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1 - \omega^2 \tau_1 \tau_2}{(1 + \omega^2 \tau_1^2)(1 + \omega^2 \tau_2^2)} \quad (\text{I-14})$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{\omega(\tau_1 + \tau_2)}{(1 + \omega^2 \tau_1^2)(1 + \omega^2 \tau_2^2)} \quad (\text{I-15})$$

$$\tau_1 \tau_2 = \frac{kT}{8\pi^4 c^2 I} \quad (\text{I-16})$$

where c = the speed of light, and
 I = the molecular moment of inertia taken in relation to a principal axis normal to that which contains the molecular dipole moment.

The equations predict that the absorption coefficient, α , drops off to zero at some higher frequency related to the molecular moment of inertia, so that large molecules might tend to be opaque in the visible region.

The other limiting case Leroy *et al.* dealt with was what they termed "excess sub-millimetre absorption", in which case, C was large and negative, and given by Eqn. I-17:

$$C = \frac{-2kT}{I\bar{\omega}_0^2} \quad (\text{I-17})$$

Recalling Eqn. I-12, which gave $B' = -C$, one obtains:

$$\frac{\epsilon_{\infty 1} - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{2kT}{I\bar{\omega}_0^2} \quad (\text{I-18})$$

It is interesting to compare Eqn. I-18 with Hill's expression, Eqn. I-6, reproduced here for reference.

$$\frac{\epsilon_{\infty} - n^2}{\epsilon_0 - n^2} = \frac{2kT}{I\omega_0^2} \quad (\text{I-6})$$

The parameter of $\bar{\omega}_0$ of Leroy *et al.* may be obtained by combining Eqns. I-17 and I-19:

$$C = \frac{-(\lambda_3')^2}{\lambda_1\lambda_2} \quad (\text{I-19})$$

where λ_1 and λ_2 are the wavelengths at which the absorption coefficient is half the maximum for the "excess absorption", and λ_3' is the wavelength for the maximum value of the dielectric loss factor.

To summarize, then, Leroy *et al.* hypothesized an anisotropic intermolecular potential characteristic of the polar molecule and of the solvent, and developed this using an autocorrelation function of the angular rate to give an explanation for the excess higher-frequency absorptions and the effect on absorption of the molecular moment of inertia.

Recent Data

Kroon and van der Elsken³⁹, in 1967, published some results of temperature and solvent effects in the far-infrared on mono-substituted methyl and phenyl groups. Briefly, they found that the methyl compounds absorbed more strongly than their phenyl analogues, that the band intensity increased with solvent polarizability, and that an increase in temperature shifted the band to lower frequency, but the integrated band intensity remained constant. They suggested that the major portion of the absorption was due to rotations, and used Eqn. I-20 below, derived by Gordon, for the integrated absorption cross-section due to pure rotations in liquid phase.

$$A = \int_0^{\infty} \sigma(\nu) d\nu = \frac{\pi}{3c^2} \sum_k (\mu_z)^2 \left[\frac{1}{I_x} + \frac{1}{I_y} \right] \quad (\text{I-20})$$

where μ_z = the component of the dipole moment along the molecule's long axis

I_x, I_y are molecular moments of inertia calculated perpendicular to the Z axis, and

$\sigma(\nu)$ is the optical absorption cross-section at frequency ν , derived from the absorption coefficient.

The sum is taken over all molecules. This equation accounted for the majority (i.e., 65% to 95%) of the observed absorption, and the rest was assigned to translational motion, which might be strongly

coupled to the rotational motions. The relative importance of the two processes was suggested to be temperature-dependent, which would account for the observed frequency shifts.

A paper by Ewing²⁰ in 1969 gave a simple, clear explanation of the mechanism of coupling of rotational and translational molecular motion, using the example of *HD*. In this molecule, the centre of mass does not occur at the centre of electronic charge. If the molecule rotates about its centre of mass within a cage of solvent atoms, the centre of electrical charge which is the basis of intermolecular interaction is displaced from its previous equilibrium position, so that the molecule must execute a translational motion to restore this equilibrium of intermolecular forces (i.e., to return to the minimum of the potential energy well defined by the interactions between cage and trapped molecules.) Hence any molecule in which the centres of mass and electronic charge distribution did not coincide could be expected to exhibit coupled rotational and translational motions in condensed phases.

A study of several polar and non-polar planar molecules, mostly benzene derivatives, has been completed by Jain and Walker.³⁷ The work demonstrated that, for polar molecules, $\alpha_{\max.}$, the maximum absorption intensity in the far-infrared band, is proportional to the quotient μ^2/I . Gordon's formula (Eqn. I-20) for the integrated intensity of a purely rotational band involves a similar quotient. However, actual observed values of the integrated absorption cross-

section in this work did not agree in any way with those calculated from Gordon's equation, suggesting that a rotational model was inadequate on its own.

For polar liquids, a temperature decrease produced sharper bands and increased values for both $\alpha_{\max.}$ and $\nu(\alpha_{\max.})$, the frequency at which the maximum absorption was observed. Such response to temperature is not characteristic of rotational bands, but suggested translational lattice modes. However, this effect appeared to be absent in non-polar liquids. The latter were presumed to absorb through small induced dipoles.

Brot *et al.*⁵ have reported far-infrared absorption spectra of tert-butyl chloride in the liquid and three crystalline phases. The absorptions of the solids decreased from those of the liquid, but remained broad and featureless for the two warmer phases, where partial molecular rotation was believed to occur. In the coldest solid phase, however, the band became differentiated into two rather broad peaks of intensity similar to that of the liquid. The authors suggested that sharp lattice bands would be observed in solids only when rigorous order prevailed.

In 1969, Bulkin⁶ examined the far-infrared absorption spectra of several pure liquids and solutions. He found that the band intensity for dimethyl sulfoxide, when adjusted for concentration according to the Beer law, was unchanged by considerable dilution with a range of non-polar solvents, and hence concluded that the molecular cage concept could not be involved, since there were no

permanent molecular dipole moments in the molecules comprising the cage which could interact with a trapped solute molecule. Instead, he favoured a mechanism of vibrations involving dipole-dipole complexes. This idea was supported by evidence that the bands of some aliphatic nitriles did change on dilution.

Burgiel *et al.*⁷ published in 1965 the results of an investigation of the far-infrared absorptions of gas molecules trapped in β -quinol clathrates. One might view such clathrates as very well-defined, more rigid molecular cages with a molecule trapped in the central hole. In these particular clathrates, the interior space is nearly spherical, with a diameter of 3 to 4 Angstroms. However, the actual volume within which a trapped molecule may move is less due to the volume taken up by the trapped molecule itself. Burgiel *et al.* investigated the absorptions for Ar, Kr, Xe, CO, NO, N₂, and O₂ in the range 20 to 150 wavenumbers, over temperatures from 1.2 to 170 °K, finding two main results. Monatomic and non-polar diatomic trapped molecules gave only one absorption peak for the trapped species, plus one for the host clathrate lattice. The guest peak was attributed to dipoles induced by the host lattice as the guest moved translationally. The polar diatomic guests exhibited a third peak, attributed to hindered rotation. In general, the frequencies of the peaks increased with increasing temperature, both for translational and rotational peaks. This temperature effect was opposite to what was observed by other workers using pure liquids and solutions.

Davies¹⁶ studied N_2 , CO_2 , HCl , HBr , SO_2 , and HCN gases trapped in β -quinol clathrates. The numbers of peaks found corresponded well to the general features discovered by Burgiel *et al.*, but the effect of temperature was not the same. In this study, as with other studies on different systems, the peaks tended to shift to higher frequency, to sharpen, and perhaps to intensify slightly as the temperature was lowered. Davies attempted to account for the absorptions using a modified Pöschl-Teller equation for the one-dimensional energy function of the U-shaped potential energy well in which the guest molecule moves. For this purpose, he calculated the linear freedom in various directions from the clathrate cage's diameter and the van der Waals radii of the atoms of the guest molecule. He eventually concluded that, although the data and some derived information was at least reasonably self-consistent, he could not derive any truly uniform picture of the guest molecule's behaviour, for the freedom available to a guest molecule varied considerably from one guest to the other, making the data difficult to interpret completely.

In 1970 Davies *et al.*¹⁵ published a paper on far-infrared absorptions which contained expanded discussions of the work they had published in their two 1968 papers, plus some newer data, particularly for water. They concluded that the absorptions in non-polar molecules are primarily of collisional origin, but

involve polarizabilities of the more readily accessible groups within the molecule, and not just the mean molecular polarizability. For polar molecules, they concluded that the overlapping of several features precluded their complete analysis, but that the main absorption mechanism was of a resonance character and involved movement of molecular and/or group dipole moments. They thus seemed to be suggesting that the mechanisms of absorption in polar and non-polar molecules are different, although they may have meant merely that there are several mechanisms, the relative contributions of each to the total absorptions being dependent on such things as dipole moments, polarizabilities, anisotropy of polarizability, and molecular shape and size.

Pardoe⁴⁴ in 1970 has reported some investigations of the far-infrared absorptions of non-polar species. For carbon disulphide he found that the frequency of the absorption peak decreased with decreasing temperature, opposite to the effect observed in polar species. In his study of three binary mixtures of non-polar molecules, the data fit reasonably well an expression for the absorption intensity at an arbitrarily-chosen frequency vs. the mole fraction of the components, the expressions having been derived assuming there to be a contribution from a bimolecular collisional process. In the pure liquids, the integrated band intensities were used with the Kramers-Krönig relationship and the Debye expression to yield an effective molecular dipole moment. The moments so obtained were larger than either of the dipole moments

which could be produced by bond distortion or inductive effects, suggesting that both processes are involved in creating the apparent molecular dipole moment during a bimolecular collision.

The Present Work

In the present work, the experimenter sought to examine the molecular cage or "pseudolattice" approach by altering the size and rigidity of any such cage through variations of temperature, both for polar and non-polar materials. Particular emphasis has been placed on some molecules which are nearly spherical in shape, and which therefore exhibit in one or more solid phases relatively unhindered molecular rotation, in an attempt to shed more light on the importance of molecular rotations to the absorption phenomena observed in the far-infrared region. An examination has also been made of the linear relationship between the absorption coefficient, α_{max} and the quotient, μ^2/I , found by Jain and Walker.³⁷

CHAPTER II

Experimental

Experimental

Theory

There are no strong sources of far-infrared radiation available presently which cover the whole range. The most commonly used source is a mercury arc lamp which, as an approximation to a black body radiator, provides a spectral output containing a small proportion of far-infrared radiation. The intensity of this source, however, is very low. At the same time, there are few detectors available for this frequency range, all of which lack either sensitivity or wide frequency range response, or both. The most commonly used detector is the Golay cell which responds reasonably well over the range under discussion, although its sensitivity is poor. This combination of poor detector sensitivity and weak source output makes it very difficult to construct a conventional grating spectrophotometer with a signal-to-noise ratio sufficient to differentiate the desired information from background noise. Instead, interferometry is used, followed by Fourier transform of the interferogram to yield a conventional spectrum of transmitted intensity as a function of the frequency of the incident radiation. In this technique, all of the output from the source over the entire frequency region to be investigated falls upon the detector, rather than a small portion of it contained in a narrow band of frequencies selected by a monochromator. The result is a

considerably stronger signal produced at the detector.

The relevant mathematical equations have been shown by Strong and Vanasse⁵⁰ and by Hurley³⁶. They are summarized in the following material.

If two interfering beams of radiation, of amplitudes a_1 and a_2 and with identical frequencies ν' wavenumbers, fall upon a detector after traversing paths differing by x cm., the aggregate intensity, $I(x)$, a function of x , is given by:

$$I(x) = a_1^2 + a_2^2 + 2a_1a_2\cos(2\pi x\nu') \quad (\text{II-1})$$

Provided the amplitudes are equal, as they should be in an interferometer for these purposes, $a = a_1 = a_2$, and we obtain:

$$I(x) = 2a^2(1 + \cos(2\pi\nu'x)) \quad (\text{II-2})$$

Letting $I(\nu') = 2a^2$, a constant,

$$I(x) = I(\nu')[1 + \cos(2\pi\nu'x)] \quad (\text{II-3})$$

For polychromatic radiation, Eqn. II-3 must be integrated over all frequencies, whence

$$I(x) = \int_{-\infty}^{+\infty} I(\nu)d\nu + \int_{-\infty}^{+\infty} I(\nu)\cos(2\pi\nu x)d\nu \quad (\text{II-4})$$

At $x = 0$, the intensity $I(0)$ is given as:

$$I(0) = 2 \int_{-\infty}^{+\infty} I(\nu)d\nu \quad (\text{II-5})$$

Therefore, for larger values of x ,

$$I(x) = \frac{1}{2}I(0) + \int_{-\infty}^{+\infty} I(v)\cos(2\pi vx)dv \quad (\text{II-6})$$

Defining the "interferogram function", $F(x)$, as

$$F(x) = I(x) - \frac{1}{2}I(0)$$

we obtain

$$F(x) = \int_{-\infty}^{\infty} I(v)\cos(2\pi vx)dv \quad (\text{II-7})$$

The intensity, $I(v)$, at a frequency v is given by the Fourier transform of Eqn. II-7; specifically,

$$I(v) = \int_{-\infty}^{\infty} F(x)\cos(2\pi vx)dx \quad (\text{II-8})$$

Since, practically, x may be varied over only a finite range, symmetrical about $x = 0$, from $x = -X$ to $x = +X$, the integral of Eqn. II-8 is approximated by a truncated integral:

$$I(v) = 2 \int_0^X F(x)\cos(2\pi vx)dx \quad (\text{II-9})$$

Calculation of the spectrum may be performed readily by modern high-speed digital computers. The interferogram function, $F(x)$, cannot be expressed analytically, so the truncated integral of Eqn. II-9 is replaced by a finite summation suitable for computer processing:

$$I(\nu) = 2 \sum_{x=0}^X F(x) \cos(2\pi\nu x) \Delta x \quad (\text{II-10})$$

From information theory one finds that, in order to obtain all the information in a spectral region $0 < \nu < \nu_{\text{max.}}$, the interferogram must be sampled at intervals of path length difference

$$\Delta x = 1 / (2\nu_{\text{max.}}) \quad (\text{II-11})$$

The theoretical resolution, $\Delta\nu$, is given by:

$$\Delta\nu = 1/X \quad (\text{II-12})$$

In order to avoid contributions from false energies of frequencies higher than $\nu_{\text{max.}}$, it is necessary to place in the interferometer beam filters to absorb all radiation above this maximum frequency. Suitable materials for the present purpose, which absorb radiation at frequencies above about 150 wavenumbers, are crystalline quartz and black polyethylene.

Instrumentation

All spectra were obtained using a Beckmann-R.I.I.C. model LR-100 Fourier Transform Spectrometer of the lamellar grating type. The equipment is shown in Fig. II-1. The source was a high-pressure mercury arc lamp consuming 150 watts power, as supplied by a stabilized power source. The beam chopper, operating at 15 hertz, also supplied the reference phase signal to the phase-locked amplifier via a magnetic reed switch. The

lamellar grating had a "grating constant" of 0.95, making the system useful for the range 8 to 70 wavenumbers, although on occasion the spectra seemed reasonable down to 5 wavenumbers. To eliminate higher-frequency radiation, several filters were used. The Golay detector window was crystalline quartz, and a black polyethylene sheet was mounted on the front of the light cone which gathered the beam for the detector. An additional filter, consisting of a ruled polyethylene disk, was located in the beam path between the sample and the detector, which limited the range to less than 80 wavenumbers.

The lamellar grating movement was controlled by the FS-MC1 step drive module, visible at the right-hand side of Fig. II-1. The lamellar grating could be moved over a maximum distance of ± 2.50 cm. from the position of zero path difference, in steps of 2.5, 5, 10, 20, or 30 microns. In general, the system was operated to yield a double-sided interferogram by scanning the lamellar grating equivalent distances on either side of the zero path difference point. At the manufacturer's suggestion, scanning was always done with the moveable portion of the grating travelling inwards. A path difference increment of 20 microns (corresponding to grating movement of 10 microns) was used in most cases. From Eqn. II-11, one finds that this would allow information to be obtained up to 250 wavenumbers, well beyond maximum frequency available with this instrument. In a few

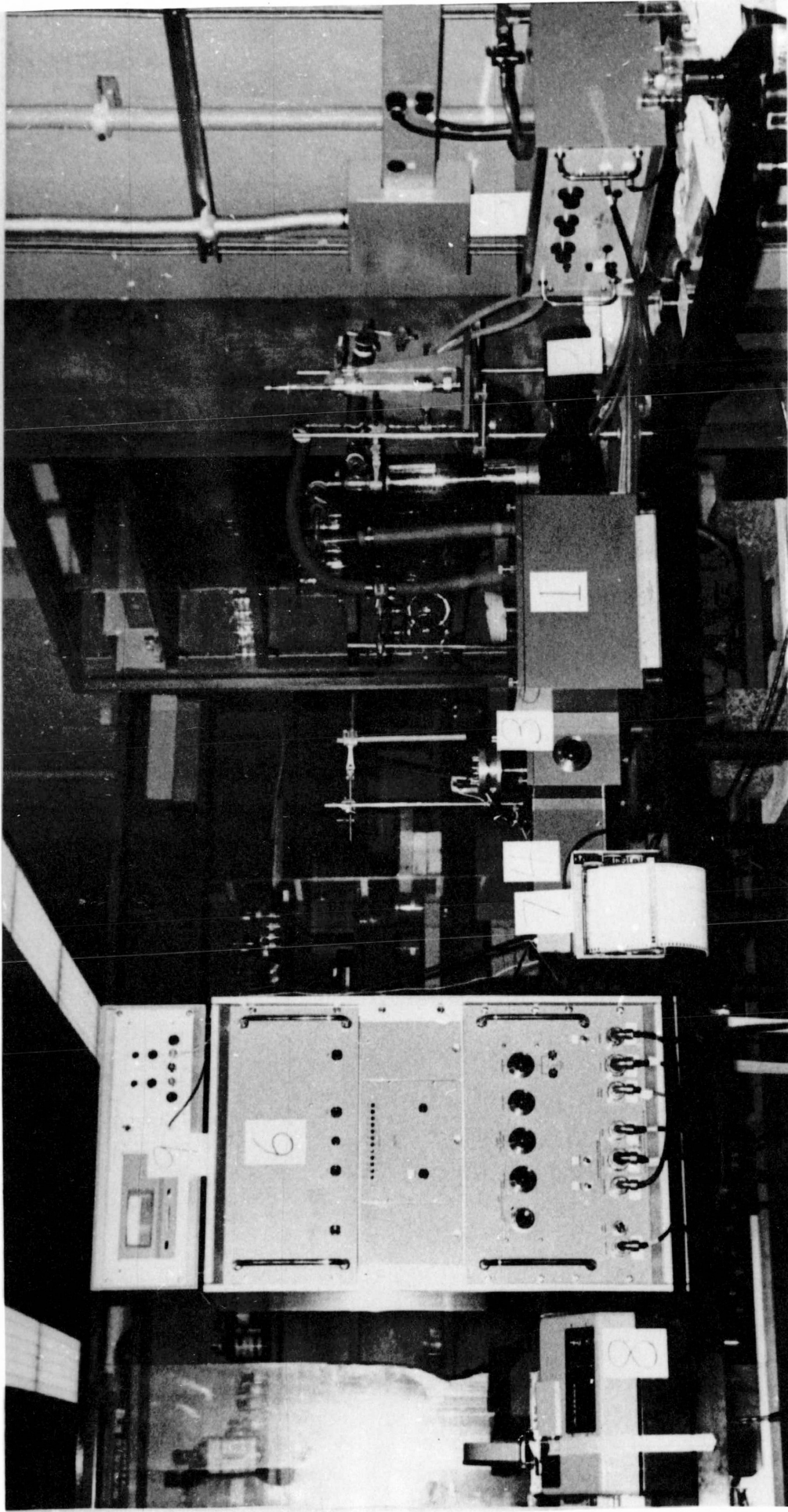


Figure II-1: General View of Far-Infrared Interferometer

- | | |
|-------------------------------------|--------------------------------------|
| 1 Interferometer Optics Module | 6 Electronics Module |
| 2 Lamellar Grating Micrometer Drive | 7 Strip Chart Recorder |
| 3 Sample Cell Compartment | 8 Paper Tape Punch |
| 4 Detector Module | 9 Sample Cell Temperature Controller |
| 5 Lamellar Grating Drive Controller | |

cases, path difference increments of 40 microns were used, corresponding to a maximum frequency of 125 wavenumbers. The lamellar grating was generally scanned from +0.2500 cm. to -0.2500 cm. from the zero path difference point, which, from Eqn. II-12, allows resolution of 2 wavenumbers (since the maximum path difference is twice the lamellar grating's maximum displacement of 0.2500 cm.). In some cases, this maximum path difference was doubled, yielding spectra of 1 wavenumber resolution. The time between stepping movements of the lamellar grating was 1.07 sec.

Fig. II-2 shows a closer view of the optical system of the interferometer. On the left-hand side is the detector module, containing the Golay cell fitted with a quartz crystal window. The signal from this detector was fed to a phase-locked amplifier housed in the FS-200/7 electronics module, which also contained the power supplies for the lamp, chopper motor, Golay cell, neon digital indicator lamps, and paper tape punch. This module is shown in Fig. II-3. The amplifier was operated with an output filter time constant of 1.0 sec., slightly shorter than the time between steps of the lamellar grating drive. The variable gain controls were set at an appropriate level in the range 30 to 55 db. The output of this amplifier was digitally coded, displayed by 12 neon glow lamps, and punched on paper tape by a type 4 Addo tape punch.

A low-level output from the amplifier was also displayed on

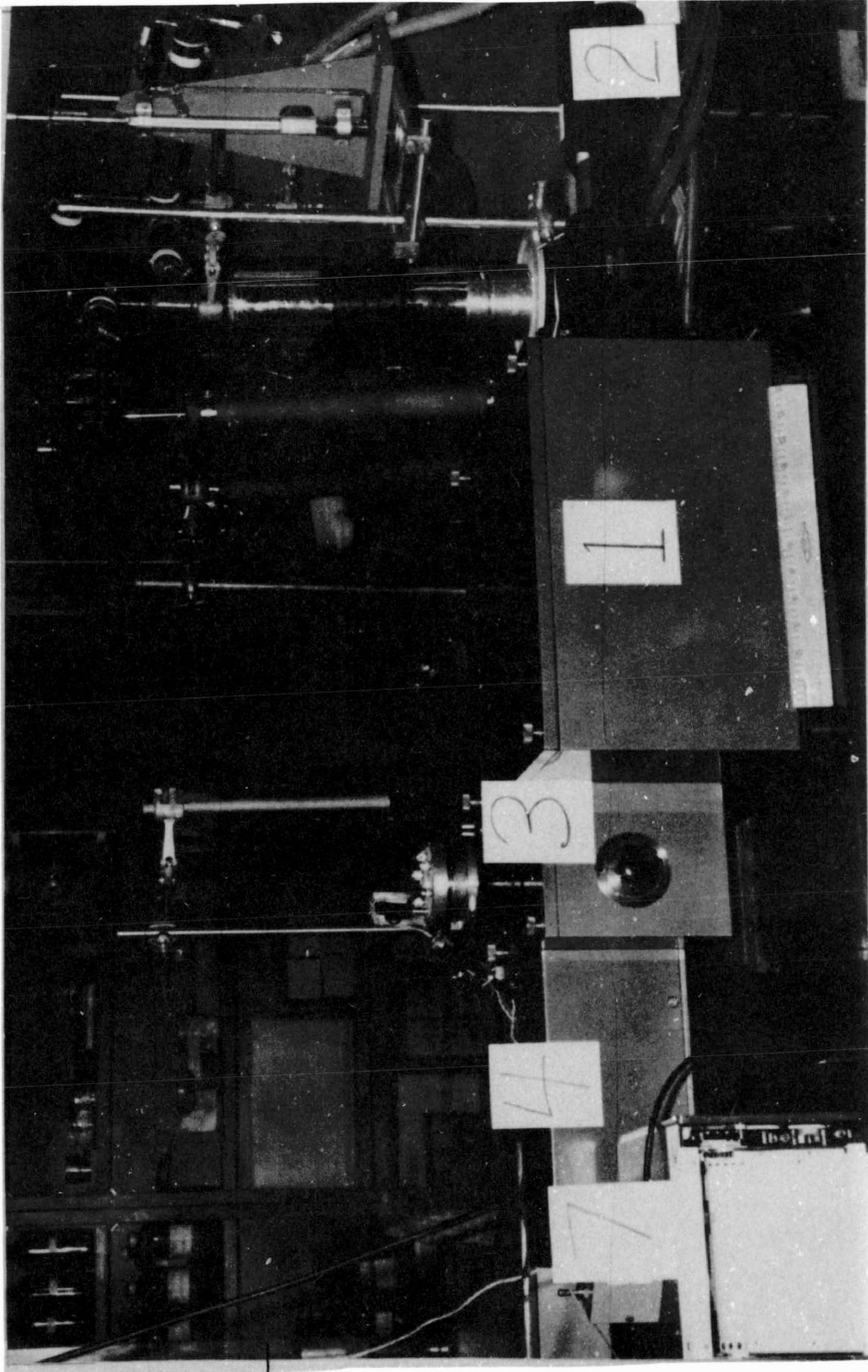


Figure II-2: Interferometer Modules

- | | |
|-------------------------------------|---------------------------|
| 1 Optics Module | 3 Sample Cell Compartment |
| (12 inch rule at lower edge) | 4 Golay Detector Module |
| 2 Lamellar Grating Micrometer Drive | 7 Strip Chart Recorder |

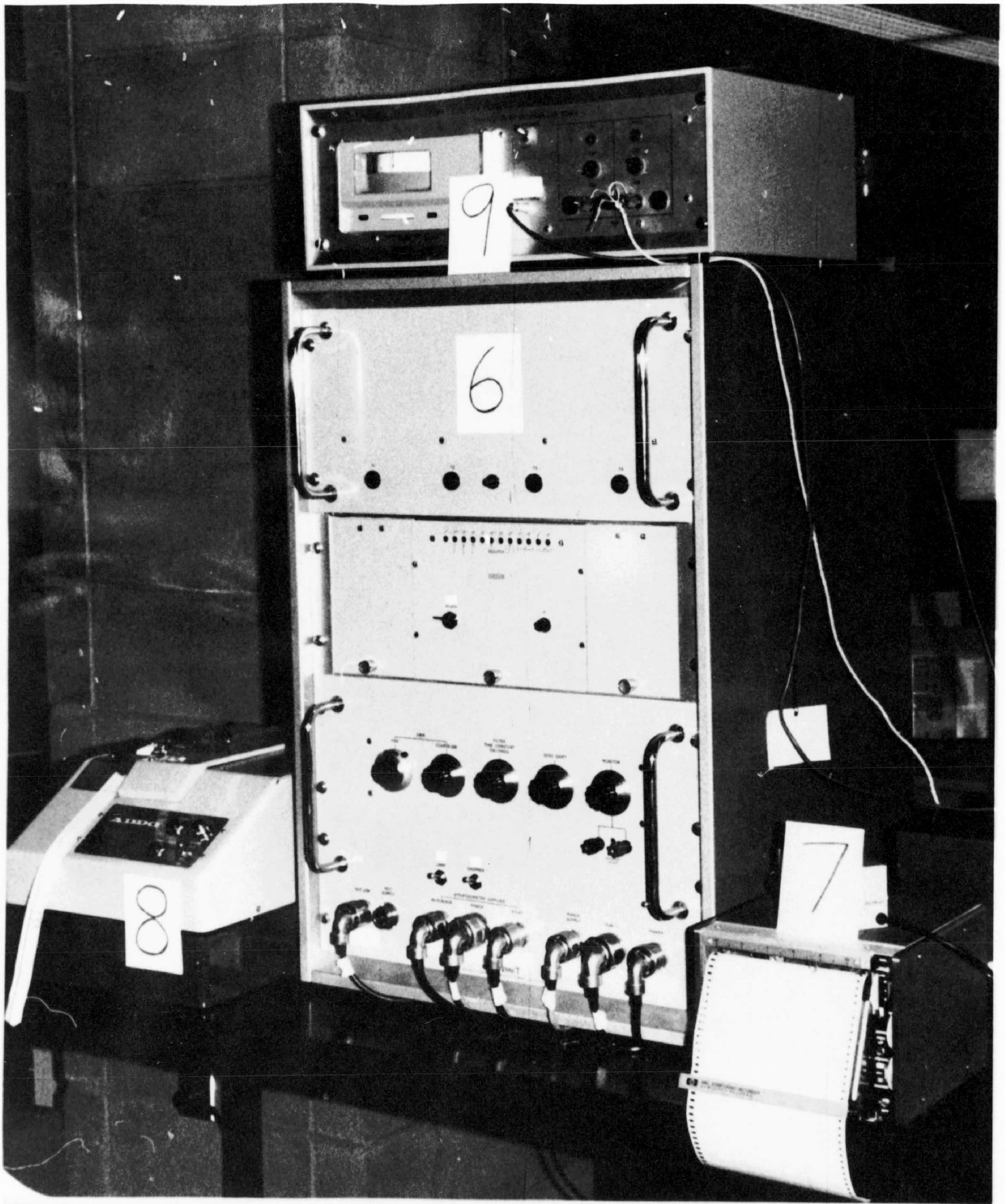


Figure II-3: Associated Electronic Equipment

6 Power Supplies, A/D Converter, and Amplifier

7 Strip Chart Recorder

8 Paper Tape Punch

9 Sample Cell Temperature Controller

a Hewlett-Packard model 680 strip chart recorder, which aided in the initial adjustment and in monitoring the recording of the interferogram. This unit is seen in the lower right-hand corner of Fig. II-3. The signal supplied to recorder for a fixed position of the lamellar grating may be viewed as a rough guide to the total radiation intensity transmitted by the sample over the entire frequency range. It is therefore related to the integrated absorption intensity of the sample. It was noted that, as a sample was cooled, the signal intensity displayed on the recorder usually decreased. Very abrupt changes in the recorder signal were observed at certain sample phase transition temperatures related to the loss of molecular rotational freedom as temperature was decreased. This phenomenon was very useful in ascertaining whether some phase transitions had occurred before starting to record the interferogram, and it also provided some interesting information in the case of carbon tetrachloride, to be detailed later. Indeed, the sensitivity of the absorptions to temperature as shown by the recorder signal often provided a more reliable indication of the stability of the temperature of the sample than did the indicator mechanism of the temperature controller, and in these cases a stable recorder trace was the criterion for judging when to begin recording the interferogram.

The sample cell was the Beckmann-R.I.I.C. model FH-01 fitted with polyethylene windows and a teflon spacer. The cell may be seen in Fig. II-4. The cell was fitted into the model VLT-2 cell holder, also shown in Fig. II-4. The holder consisted of a mounting

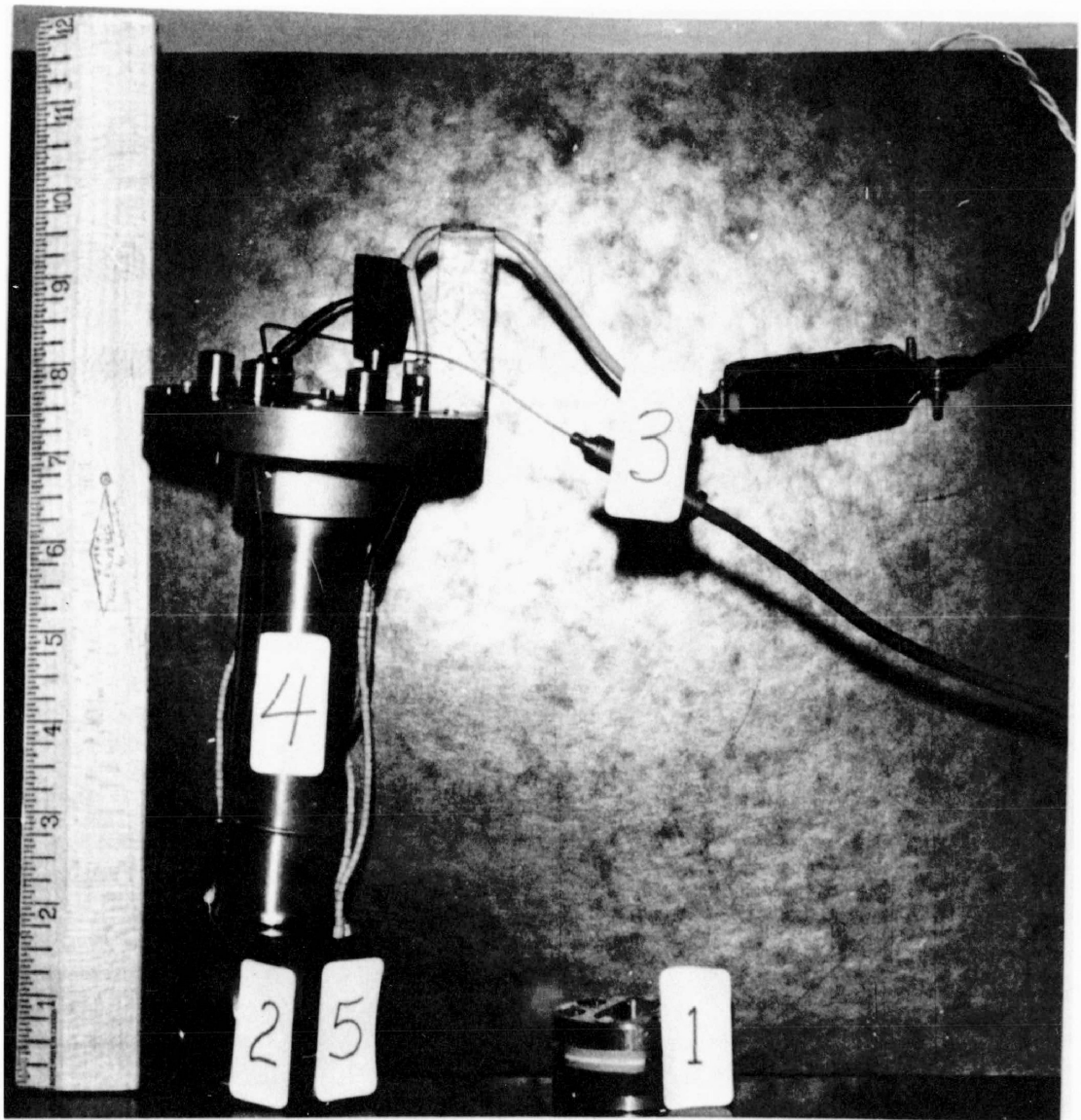


Figure II-4: Sample Cell and Cell Holder

- 1 Assembled Cell (note white spacer between windows)
- 2 Opening in Holder for Cell
- 3 Thermocouple and Heater Leads
- 4 Coolant Tube
- 5 Cell Heater (one of two)

block with electrical heaters on two sides, fastened to the lower end of a stainless steel well which contained an appropriate coolant. A small iron-constantin thermocouple rested in a shallow well in one of the cell windows. The thermocouple was connected to the model TEM-1 temperature indicator-controller with variable proportional band, which controlled the current to the cell heaters fastened to the two sides of the VLT-2 cell holder. In this way, the cell temperature could be observed and controlled to within $\pm 1^{\circ}\text{C}$ of the set point. The accuracy of the controller was checked against a calibrated thermocouple, and a calibration graph prepared enabling temperature set points to be accurate to within $\pm 0.5^{\circ}\text{C}$.

The coolant used varied with the temperature desired. None was necessary above 30°C . Ice was used down to 5°C , loosely packed solid CO_2 down to -25°C , tightly packed solid CO_2 down to -40°C , and either a dry ice-acetone slurry or liquid nitrogen for colder temperatures. Where the coolant temperature was very much colder than the desired temperature, insulating disks of plastic foam were placed at the bottom of the coolant tube and held in position by a "mushroom" plunger. These disks decreased the rate of heat transfer from sample cell to coolant so that lower cell heater currents could be used for more even temperature control. The assembled cell and holder are shown in Fig. II-5 suspended above the cell mounting system, with the insulating disks and plunger on the right.

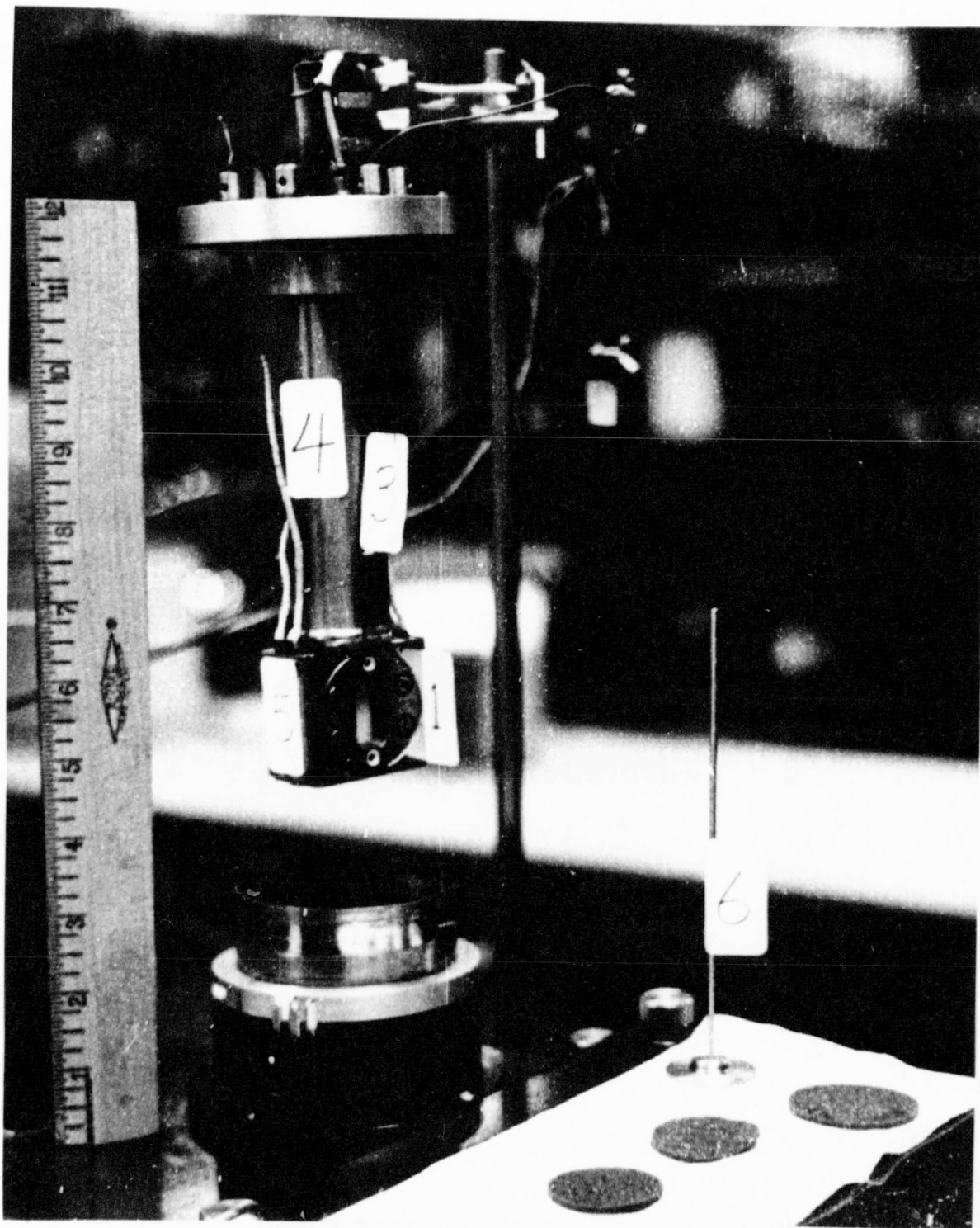


Figure II-5: Sample Cell and Holder Above Mount

- 1 Sample Cell in Holder
- 3 Thermocouple Lead
- 4 Coolant Tube
- 5 Cell Heater
- 6 "Mushroom" Plunger and Plastic Foam Insulating Disks

The polyethylene cell windows appeared to soften slightly at 50°C, so no sample temperatures above 37°C (310°K) were used.

Cell spacers were cut from sheets or blocks of teflon, and their thickness checked with a micrometer before and after a series of runs. The cells were filled using glass syringes, and were emptied, washed with cyclohexane, and dried after each run with a sample. When the cell was used at low temperatures, it was necessary to tighten the cell assembly screws after the cell had been cooled and before recording the interferogram, since contraction of the metal cell parts caused cell leakage if this was not done.

The entire interferometer was evacuated to a pressure of less than 50 microns mercury for all runs to eliminate absorptions due to atmospheric gases. Background (i.e., empty cell) and sample runs were always done at the same cell temperature, and as close together in time as was possible. This time separation was dependent on pump-down time (typically 5 min.) and on the speed with which temperature equilibrium could be established (in some cases, up to a few hours were required).

Data Processing

The punched paper tape records of the interferograms for background and sample were processed on an IBM System 360, model 40 (later, model 50) computer using a program in the PL/I language.

In addition to the two paper tapes, the input data contained a title for the spectrum, the lamellar grating drive parameters, the amplifier gain settings for background and sample runs, and the cell path length. For each interferogram tape, the computer created a single-sided interferogram from the double-sided one supplied by averaging the data points equidistant from the central grand maximum found at the position of zero path difference of the two beams. An apodizing function was applied to improve the estimate of the asymptotic value of the record at large values of x , the path difference, and the interferogram was then transformed to yield a graph of transmitted intensity vs. frequency. When this had been done for both tapes, the two resultant graphs were ratioed point by point to yield a graph of per cent, transmittance vs. frequency. Finally, this latter graph was converted to a plot of α , the absorption coefficient (in units of neper-cm.⁻¹) vs. frequency (in wavenumbers), where α is defined by Eqn. II-13 below.

$$\alpha(\nu) = \left[\frac{1}{L} \right] \log_e \left[\frac{I_0(\nu)}{I(\nu)} \right] \quad (\text{II-13})$$

where L = cell path length in cm.,

$I_0(\nu)$ = energy transmitted by background at frequency ν ,

and $I(\nu)$ = energy transmitted by sample at frequency ν .

The data points of the last graph of absorption coefficient vs. frequency were also punched out on computer cards which were

re-submitted under a different program to obtain the integrated absorption intensity. This program synthesized a polynomial of specified degree to fit the data points supplied using numerical methods. It then found the intercepts of this polynomial along the frequency axis, starting with initial estimates supplied as input data, and integrated the area under the curve between these two intercepts. The output provided a graph of the input data and the polynomial to give visual checks on the adequacy of the analysis results.

Values of the absorption coefficient are estimated by comparison with published results and by repeatability to be accurate to better than +/-10%. The accuracy of the frequency of maximum absorption is highly dependent on line shape. In some cases, the maxima were so broad that $\nu(\alpha_{\max})$ could be estimated to only +/-4 wavenumbers. In a few cases, notably in the very cold solids, the sharpness of the peaks allowed this frequency to be fixed to within +/-1 wavenumber.

In order to obtain the integrated absorption intensities, it was necessary to extrapolate the ends of the broad absorption bands via the polynomial synthesized in the computer. Extrapolations are hazardous tools to use, although the effects of the errors thus introduced were probably not too large, particularly at the lower-frequency end. Generally, the polynomial fit the observed spectrum well when the spectrum consisted of one smooth band, and sometimes not quite as well for spectra consisting of

distinguishable overlapping bands. Those spectra containing sharp peaks (e.g., very cold solids) and those which did not exhibit well-defined maxima in the frequency range examined, were not submitted to the integrated intensity program. In the former of these two situations, the program could not fit a smooth polynomial to a set of sharp peaks, and in the latter, it would be unreasonable to attempt to match a curve which is defined over less than half of its range. In view of these points, the accuracy of the integrated absorption intensities obtained was estimated at $\pm 20\%$, although it may be better in several cases.

Samples

Cyclohexane and 1,4-dioxane were distilled over sodium wire on a fractionating column filled with glass helices, and stored over sodium wire for drying. Other chemicals were used as commercially available in view of several studies (e.g., Davies *et al.*¹³ and Garg *et al.*²⁴) showing little effects from small amounts of impurities. Chloroform and carbon tetrachloride were spectrophotometric grades from Baker Chemicals. (Carbon tetrachloride was stored over activated molecular sieve to remove trace water.) Chloroform-d was obtained as "Silanor-C" from Merck, Sharpe, and Dohme. 1,1,1-trichloroethane was Fisher's Certified brand (catalogue no. T-391). 2-bromo-2-methylpropane (tert-butyl bromide)

was obtained from Aldrich Chemical Co. (catalogue no. 13,561-5; lot no. 082571). Bromoform was in reagent grade from British Drug Houses. α,α,α -trichlorotoluene was obtained from Eastman Chemicals (catalogue no. 779), and both 2,2-dichloro- and 2,2-dibromopropane were obtained from Chemical Procurement Laboratories, Inc.

CHAPTER III

Results and Discussion

Results and Discussion

The absorption spectra obtained are presented as graphs of the absorption coefficient, α , in neper-cm.⁻¹, vs. frequency, ν , in cm.⁻¹ (wavenumbers). In general, families of spectra for one compound at several temperatures are shown on the same graph to facilitate comparisons, but in some cases these have been separated into two graphs either because of considerable overlap or due to large differences in the magnitude of the absorption coefficient. In addition, tabulated data derived from the spectra for $\alpha_{\max.}$, the maximum value of α at a particular peak, $\nu(\alpha_{\max.})$, the frequency at which the peak occurs, $\Delta\nu_{1/2}$, the peak width at half height, and $\int\alpha(\nu)d\nu$, in units of neper-cm.⁻², are presented.

Chloroform - $CHCl_3$

The melting point of chloroform is -63.4°C (209.7°K). Spectra were obtained at four temperatures in the liquid phase, plus one in solid phase. Table III-1 contains the data derived

Table III-1: SPECTRAL DATA FOR CHLOROFORM

Temperature		Physical	$\alpha_{\max.}$	$\nu(\alpha_{\max.})$	$\Delta\nu_{1/2}$	$\int\alpha(\nu)d\nu$
°C	°K	State	(neper-cm. ⁻¹)	(cm. ⁻¹)	(cm. ⁻¹)	(neper-cm. ⁻²)
38	311	Liquid	18	33	75	1250
13	286	Liquid	17	36	80	1100
-55	218	Liquid	29	47	65	1600
-61	212	Liquid	37	46	--	2100
-70	203	Solid	38	56	~ 20	1700
			38	63	~ 20	
			26	36	(shoulder)	

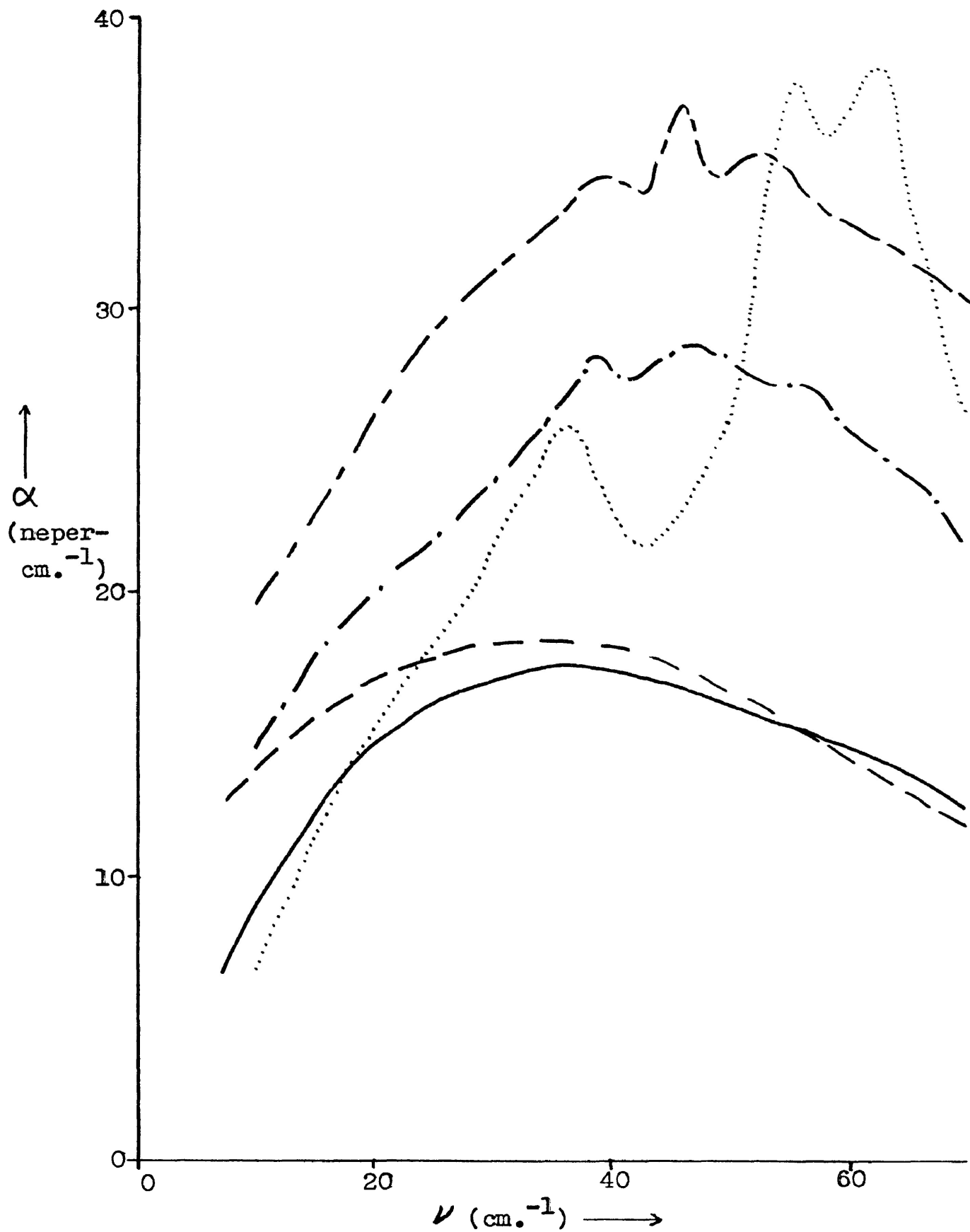


Figure III-1: Absorption Spectra of Chloroform

- | | | | |
|-----------|---------------|-------|---------------|
| ----- | 38°C (311°K) | ———— | 13°C (286°K) |
| - · - · - | -55°C (218°K) | ----- | -61°C (212°K) |
| | -70°C (203°K) | | |

from these spectra, which are shown in Fig. III-1. Several trends are immediately apparent. As the temperature was lowered, the absorption coefficient increased, the frequency of the peak increased, and the integrated intensity increased, until freezing occurred. In the solid phase, the spectrum altered drastically, becoming differentiated into three distinct and considerably narrower peaks. (The widths of these in the solid are approximate values because of the overlap, and that for the low-frequency shoulder could not be estimated.) It is apparent, however, that the value of α_{\max} in the cooled liquid approached that for the solid in a relatively continuous manner. Further, the spectra in the liquid phase appeared to become slightly differentiated at low temperatures into three broad, overlapping peaks. The sharp peaks of the solid are probably due to translational lattice vibrations, and the appearances of the cooled liquid spectra might suggest that such a process also occurred in liquid phase.

Chloroform-d - $CDCl_3$

At -64°C (209°K), the melting point of deuterated chloroform is very close to that of the undeuterated species, so that comparison of these two at similar temperatures meant also that the temperatures were similar distances from the melting points. Table III-2 and Fig. III-2 contain the appropriate data. The general trends of increasing absorption coefficient, peak frequency and integrated intensity were maintained.

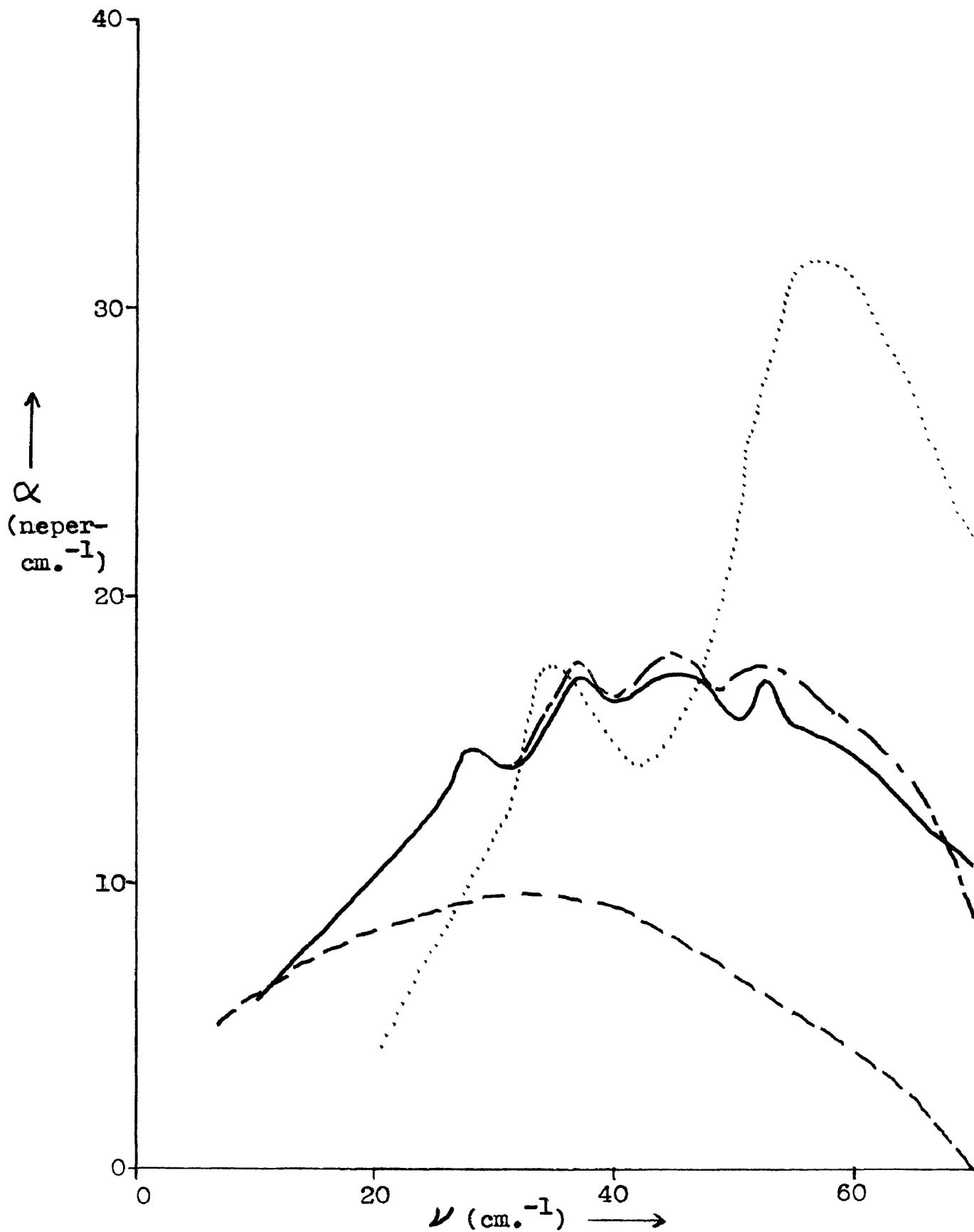


Figure III-2: Absorption Spectra of Chloroform-d

-----	37°C (310°K)	—————	-62°C (211°K)
- · - · -	-59°C (214°K)	·····	-70°C (203°K)

Table III-2: SPECTRAL DATA FOR CHLOROFORM-d

Temperature		Physical	$\alpha_{\text{max.}}$ (neper- cm. ⁻¹)	$\nu_{(\alpha_{\text{max.}})}$ (cm. ⁻¹)	$\Delta\nu_{\frac{1}{2}}$ (cm. ⁻¹)	$\int \alpha(\nu) d\nu$ (neper- cm. ⁻²)
<u>°C</u>	<u>°K</u>	<u>State</u>				
37	310	Liquid	10	32	50	470
-59	214	Liquid	18	45	50	850
-62	211	Liquid	17	45	60	900
-70	203	Solid	32 18	57 35	~ 20 (shoulder) }	1000

The strong absorption peak of the solid at 57 cm.⁻¹ did not appear to be split as was the case for chloroform. It is possible that it was split, but by a smaller amount, so that the separation was not observed in the scatter of experimental points. Although there was a small (1 wavenumber) shift to lower frequency, as compared to the undeuterated analogue, this shift was of the order of the resolution of the spectra, and cannot be reliably ascribed to an isotope effect. The peak intensities, however, were considerably reduced from those of chloroform, with the exception of the strong sharp peak of the solid, which was nearly equal to that for chloroform. In conjunction with this observation, it may be noted that this peak is appreciably more intense than those of the cold liquid, in contrast to the situation noted in chloroform. The integrated intensity data show this same difference.

Bromoform - CHBr_3

Bromoform has a melting point of 9°C (282°K), and only two spectra were recorded in the liquid phase, shown in Fig. III-3 and

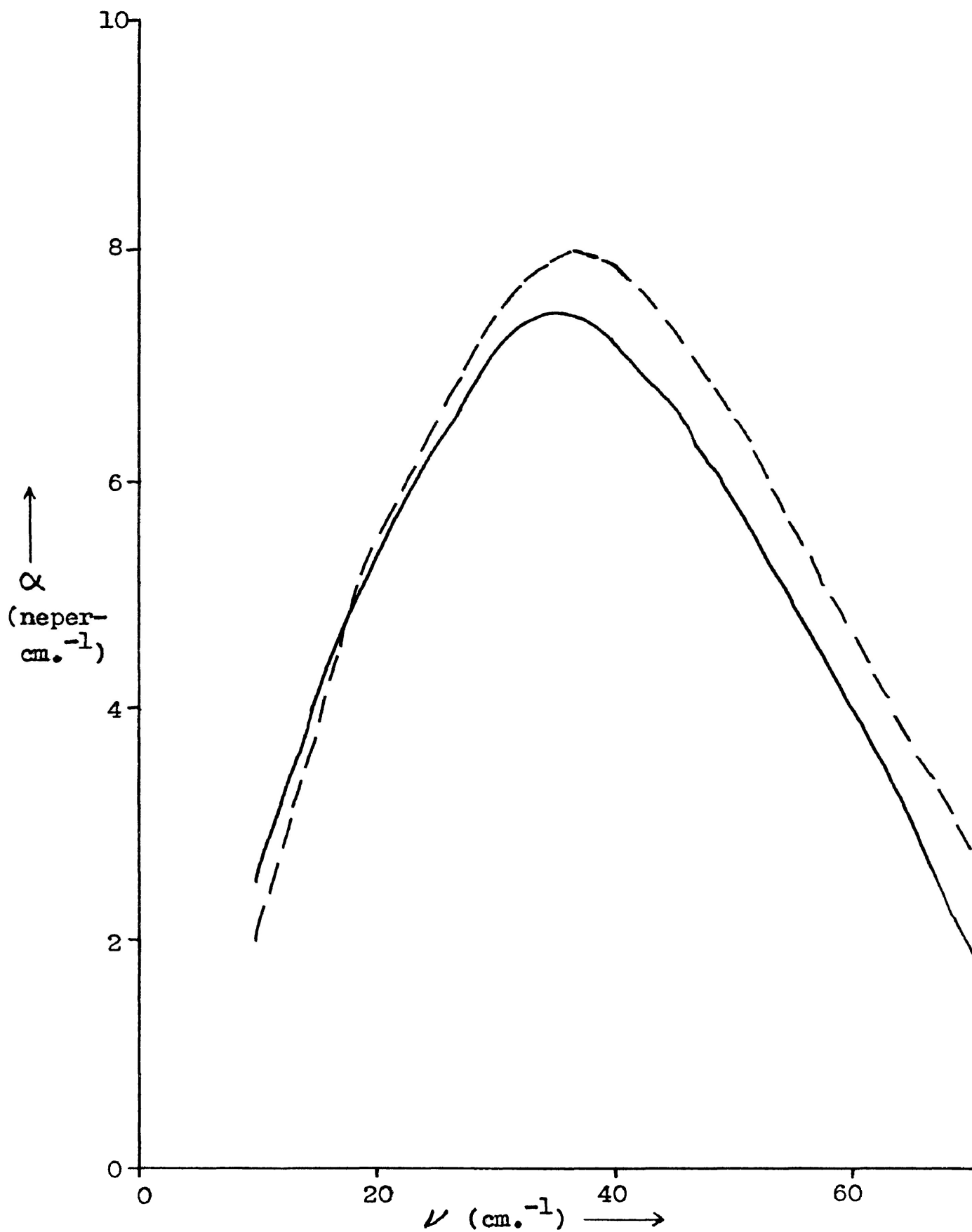


Figure III-3: Absorption Spectra of Bromoform

————— 37°C (310°K)
----- 12°C (285°K)

tabulated in Table III-3. Again, there was a small increase in

Table III-3: SPECTRAL DATA FOR BROMOFORM

Temperature <u>°C</u>	Physical <u>°K</u>	Physical <u>State</u>	$\alpha_{\max.}$ (neper- cm. ⁻¹)	$\nu(\alpha_{\max.})$ (cm. ⁻¹)	$\Delta\nu_{1/2}$ (cm. ⁻¹)	$\int \alpha(\nu) d\nu$ (neper- cm. ⁻²)
37	310	Liquid	7.5	35	50	355
12	285	Liquid	8.0	37	50	340

$\alpha_{\max.}$ and $\nu(\alpha_{\max.})$ as temperature was lowered. Comparing these spectra with those of chloroform, one notes that the absorption was less intense in the compound in which the more massive bromine atoms have replaced the chlorines. The peaks' locations on the frequency scale were slightly higher than in chloroform, although they were comparable to those of the latter at similar elevations of temperature over the melting point.

1,1,1-trichloroethane - CH_3-CCl_3

1,1,1-trichloroethane, or methyl chloroform, contains a methyl group, whose van der Waals radius is similar to that of chlorine ($-CH_3 = 2.0 \text{ \AA}$, $-Cl = 1.8 \text{ \AA}$)¹, in place of chloroform's hydrogen. The molecular shape is then virtually spherical, and one might reasonably expect that molecular rotations would be hindered little by steric factors. Such is indeed the case, for the first solid phase formed on cooling below the melting point of -33°C (240°K) exhibits dielectric properties characteristic of unimpeded molecular rotation.⁴⁹ At a temperature of -49°C (224°K), however, a phase transition occurs to a solid which exhibits no molecular rotation. This phase transition temperature is referred to as the lambda point.

Table III-4: SPECTRAL DATA FOR 1,1,1-trichloroethane

Temperature		Physical	$\alpha_{\text{max.}}$	ν	$\Delta\nu_{1/2}$	$\int \alpha(\nu) d\nu$
$^{\circ}\text{C}$	$^{\circ}\text{K}$	State	(neper- cm.^{-1})	($\alpha_{\text{max.}}$) (cm.^{-1})	(cm.^{-1})	(neper- cm.^{-2})
37	310	Liquid	36	25	70	2100
12	285	Liquid	38	35	70	2300
-31	242	Liquid	33	38	65	1900
-40	233	Rotator Solid	35	38	70	2000
-46	227	Rotator Solid	39	45	70	2200
-53	220	Non-Rot. Solid	65	59	~ 15 } (shoulder)	~ 1800
			47	46		
-73	200	Non-Rot. Solid	55	61	~ 10 } (shoulder)	~ 1100
			39	51		

Figs. III-4, III-5 and III-6 show the spectra for methyl chloroform from which were derived the data of Table III-4 above. The three liquid phase spectra are depicted in Fig. III-4; Fig. III-5 covers the transition from liquid to rotator solid phases; and in Fig. III-6, the two spectra obtained for the non-rotator solid phase are shown with three higher-temperature spectra for comparison. It is immediately apparent that the spectra of the rotator solid phase were very similar to those of the liquid phase, whereas in the previously-presented cases of chloroform, chloroform-d and bromoform, the solid-phase spectra differed markedly from those of the liquid. However, decreasing the temperature to below the lambda point in methyl chloroform did produce striking changes in the absorption peaks. The main peaks of the non-rotator solid phase were at higher

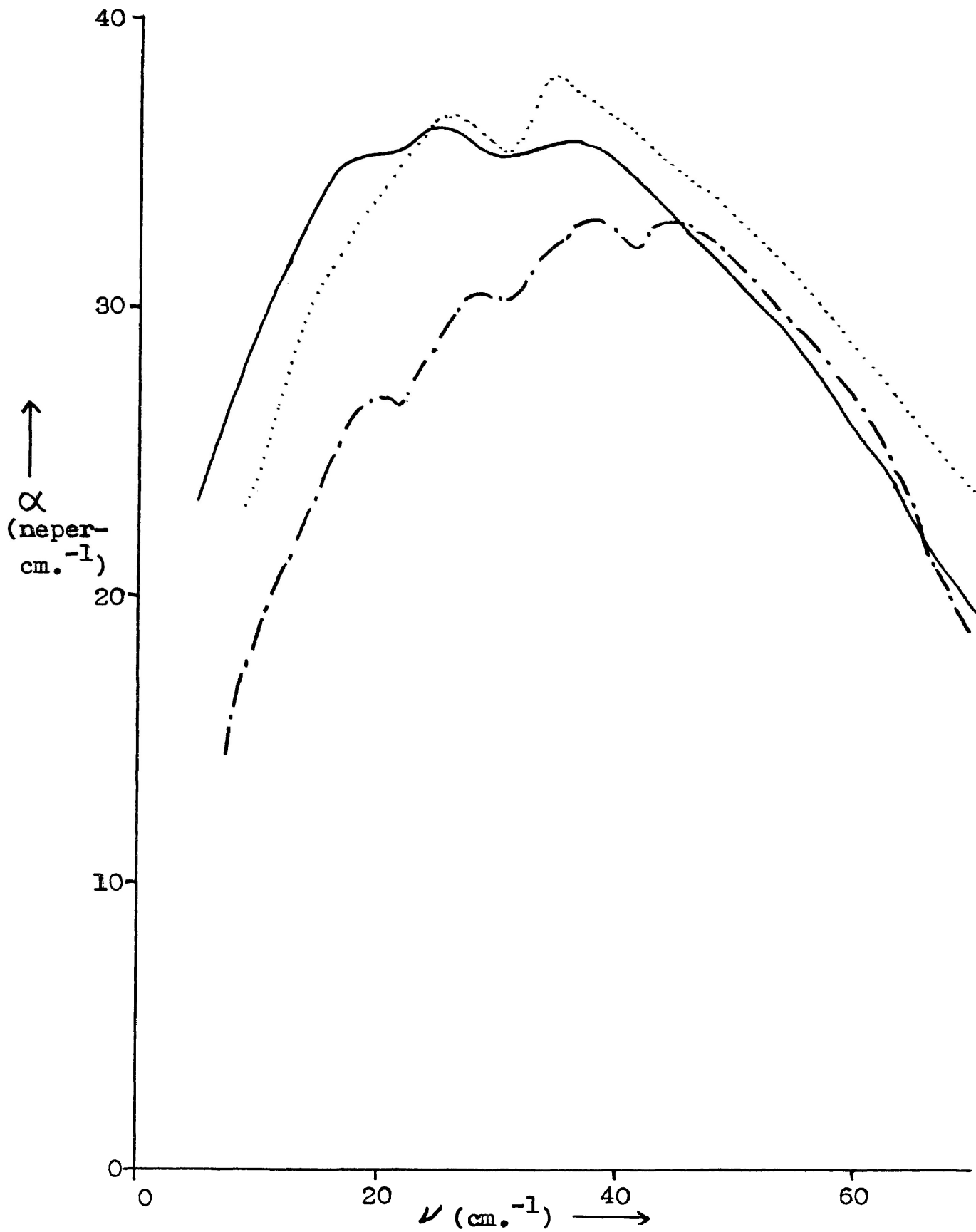


Figure III-4: Absorption Spectra of 1,1,1-trichloroethane

—————	37°C (310°K)	— · — · —	-31°C (242°K)
·····	12°C (285°K)		

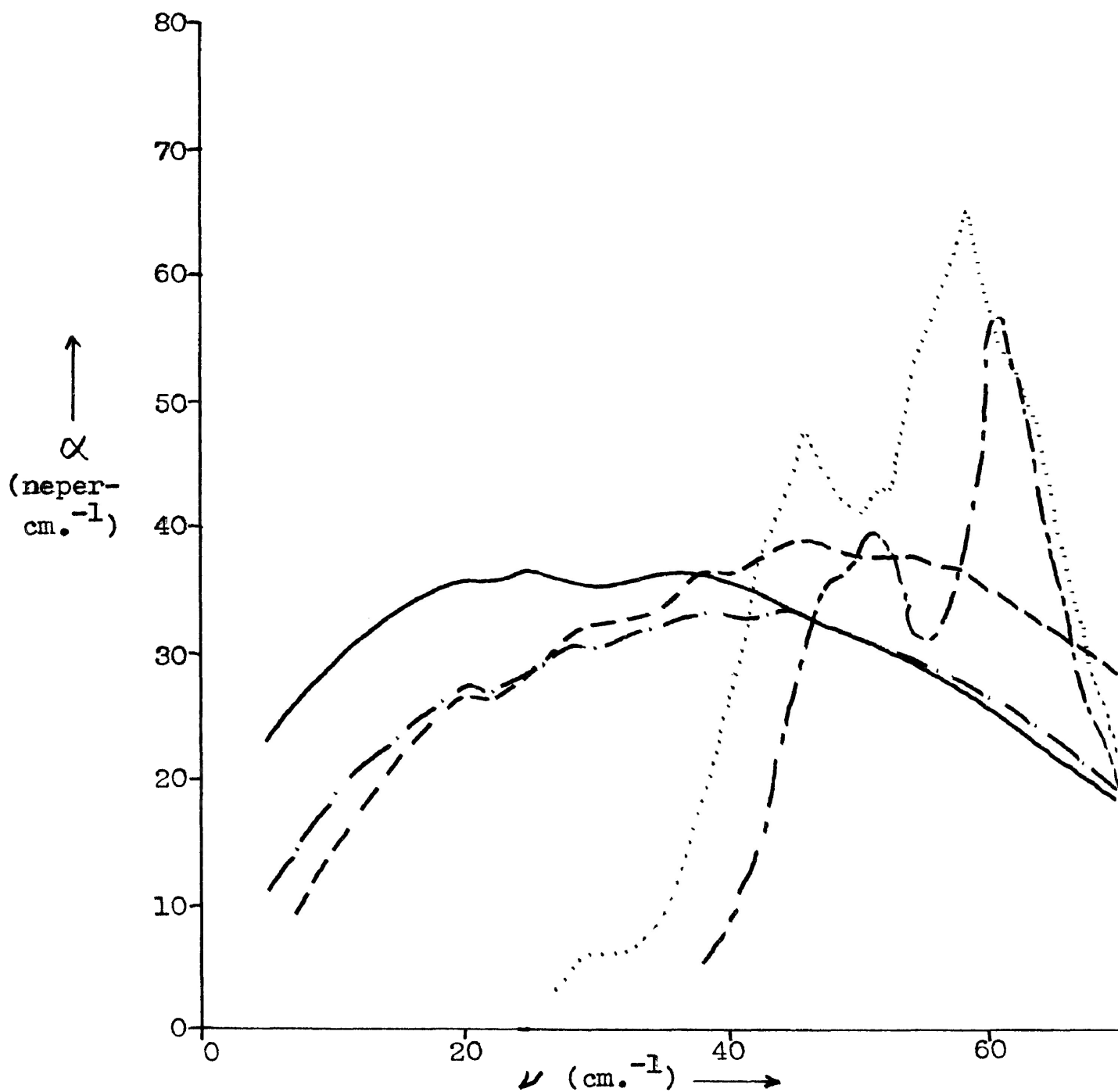


Figure III-6: Absorption Spectra of 1,1,1-trichloroethane

—————	37°C (310°K)	-53°C (220°K)
- - - - -	-31°C (242°K)	—————	-73°C (200°K)
- · - · -	-46°C (227°K)		

frequency, and their intensities were considerably enhanced over those of the other two phases. It is of interest, too, that the lower-frequency secondary peak near 50 wavenumbers in the non-rotator solid was located close to that of the rotator solid in terms of frequency. One may note, also, the considerable narrowing of the peaks on passing through the lambda point. These narrow peaks were difficult for the computer to integrate properly, for the program used assumed a simple polynomial function to describe the peaks to be integrated, and in these cases only a very rough approximation of a second-degree (i.e., quadratic) polynomial produced useable results. Hence the integrated intensities recorded in Table III-4 for the non-rotator solid phase were marked as only approximate values. The half-height widths of these peaks were also quoted as approximate values because the close proximity of the lower-frequency shoulder made estimation of this parameter difficult.

Within the liquid and rotator solid phases of methyl chloroform, the shift of peak frequency with temperature was as noted previously. However, the changes in α_{\max} and integrated intensity were rather small (10% and less) and failed to show the monotonic increases with decreasing temperature observed in chloroform and its analogues earlier. One must then examine the origins of the bands' frequency and intensity shifts with temperature. One might suggest that the entire band shifts as one unit to higher frequency and

absorption coefficient with decreasing temperature, but the data for absorption coefficient and integrated band intensity of methyl chloroform contradict this idea, unless one is willing to discard the assumption that such shifts must be monotonic. Alternatively, one could consider Hill's hypothesis³³ that the absorption bands occurring in the far-infrared region are composed of a large number of overlapping bands broadened by heavy damping, and add to this the idea that the relative contributions of the several component bands to the overall band envelope is temperature-dependent. In such a situation, the individual component bands' shifts might or might not be monotonic with frequency, but there would be no necessity in either case that the total band exhibit such behaviour.

α, α, α -trichlorotoluene - $C_6H_5-CCl_3$

This compound might be referred to as phenyl chloroform, to emphasize its position in the progression begun with chloroform and 1,1,1-trichloroethane (methyl chloroform). This terminology is not common, however, so it will not be used. α, α, α -trichlorotoluene has a melting point of -4.75°C (268°K). With the large C_6H_5 - group attached, the molecule's shape is certainly far from spherical, and Smyth's data⁴⁹ do not note any known rotator solid phase.

The spectra shown in Fig. III-7, with associated data tabulated in Table III-5, exhibit a temperature effect similar to that of chloroform. The liquid phase band was smooth and broad, whereas that of the

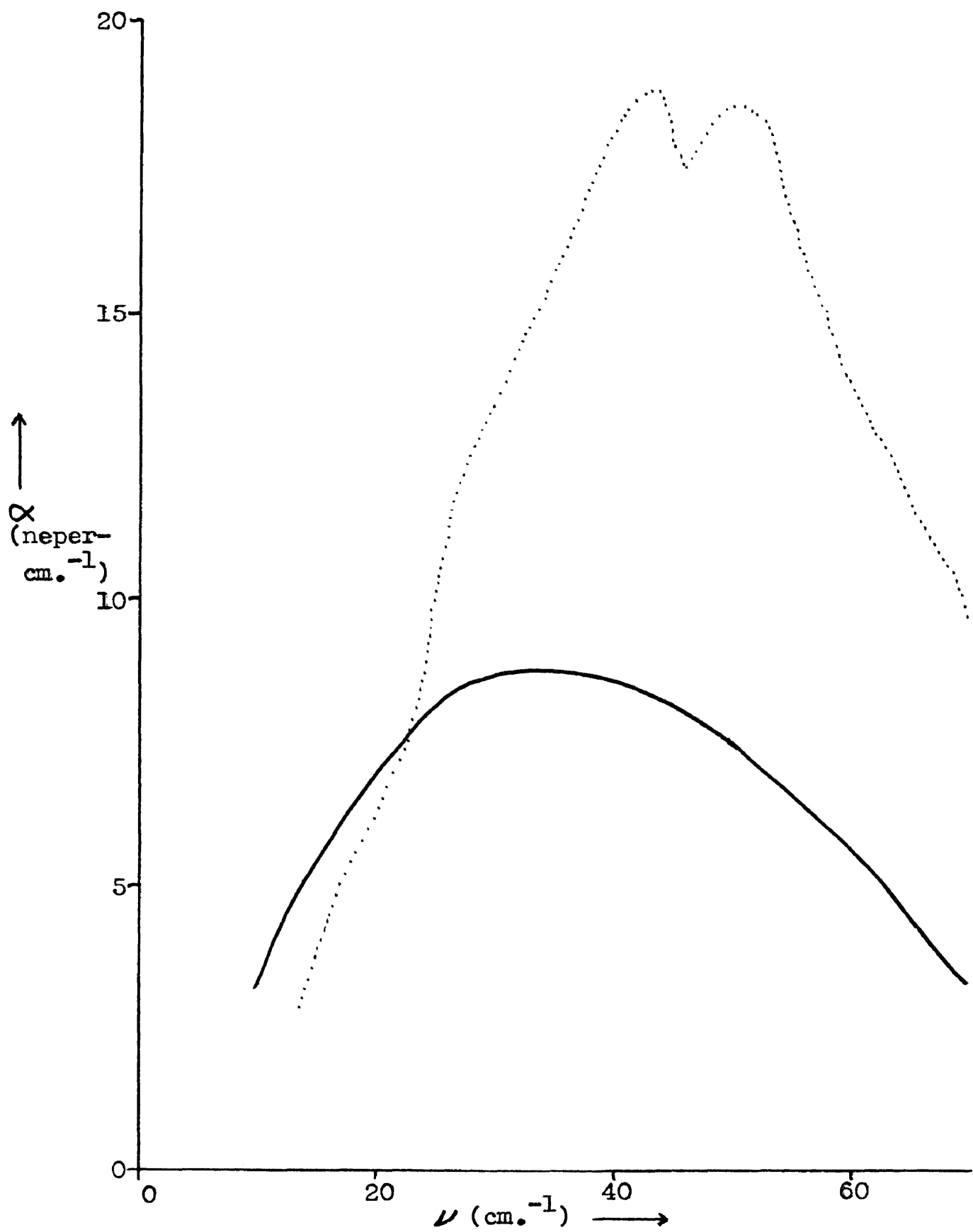


Figure III-7: Absorption Spectra of α, α, α -trichlorotoluene
 ————— 37°C (310°K) -10°C (263°K)

solid was much more intense and consisted of two overlapping peaks at higher frequency than in the liquid.

Table III-5: SPECTRAL DATA FOR α,α,α -trichlorotoluene

Temperature		Physical	$\alpha_{\text{max.}}$ (neper- cm. ⁻¹)	ν ($\alpha_{\text{max.}}$) (cm. ⁻¹)	$\Delta\nu_{\frac{1}{2}}$ (cm. ⁻¹)	$\int \alpha(\nu) d\nu$ (neper- cm. ⁻²)
<u>°C</u>	<u>°K</u>	<u>State</u>				
37	310	Liquid	8.6	32	55	450
-10	263	Liquid	19 19	43 51	(overlapping double band)	830

2,2-dichloropropane - $(\text{CH}_3)_2\text{CCl}_2$

Table III-6: SPECTRAL DATA FOR 2,2-dichloropropane

Temperature		Physical	$\alpha_{\text{max.}}$ (neper- cm. ⁻¹)	ν ($\alpha_{\text{max.}}$) (cm. ⁻¹)	$\Delta\nu_{\frac{1}{2}}$ (cm. ⁻¹)	$\int \alpha(\nu) d\nu$ (neper- cm. ⁻²)
<u>°C</u>	<u>°K</u>	<u>State</u>				
37	310	Liquid	43	30	50	2100
12	285	Liquid	49 46	27 48	55	2700
-32	241	Liquid	70	43	70	4500
-38	235	Rotator Solid	81	48	65	4800
-73	200	Rotator Solid	43 32	50 34	60 (shoulder)	2000
-88	185	Non-Rot. Solid	~120 ~100	57 66	10 8	----
-103	170	Non-Rot. Solid	~120 ~100	57 66	10 8	----

The spectra obtained for 2,2-dichloropropane are shown in Figs. III-8 and III-9, and the derived data tabulated in Table III-6 above. This material has a melting point of -34.6°C (238.5°K), and

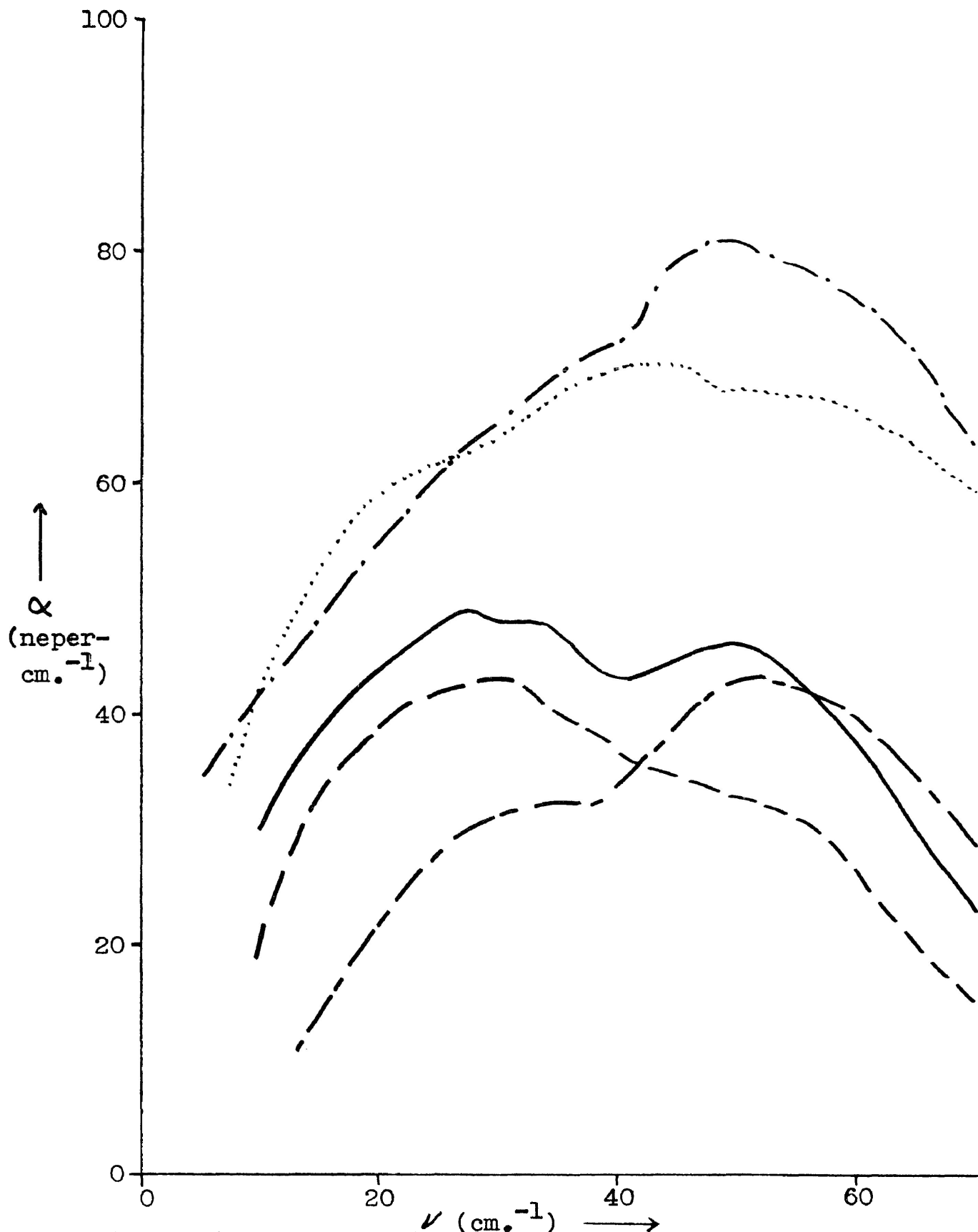


Figure III-8: Absorption Spectra of 2,2-dichloropropane

- | | | | |
|-------|---------------|-----------|---------------|
| ----- | 37°C (310°K) | - · - · - | -38°C (235°K) |
| ————— | 12°C (285°K) | ----- | -73°C (200°K) |
| | -32°C (241°K) | | |

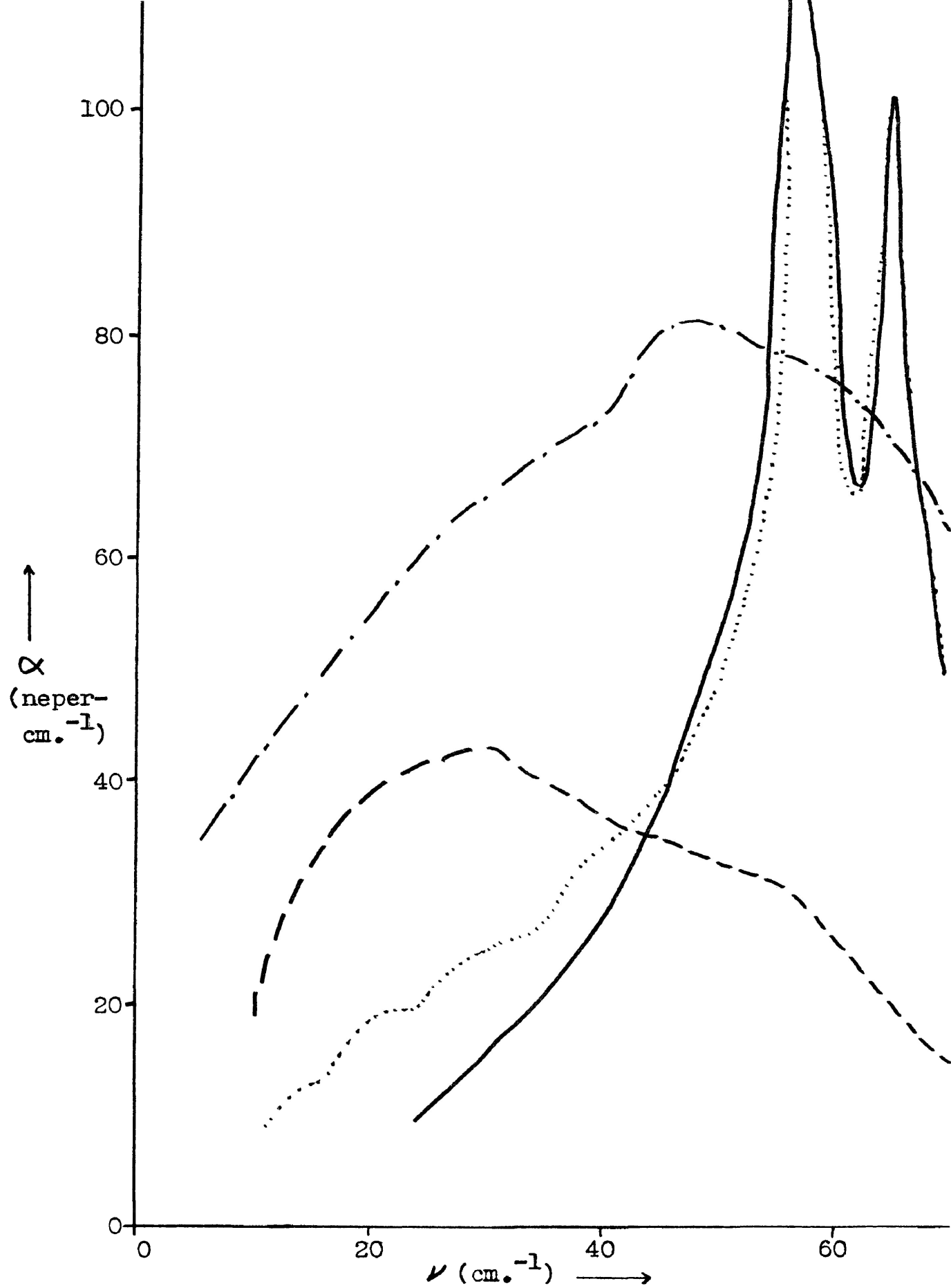


Figure III-9: Absorption Spectra of 2,2-dichloropropane

-----	37°C (310°K)	—————	-88°C (185°K)
-·-·-·-	-38°C (235°K)	·····	-103°C (170°K)

exhibits a lambda point at -85°C (188°K).⁴⁹ Fig. III-8, then, contains spectra for the liquid and rotator solid phases, while Fig. III-9 shows two spectra obtained for the non-rotator solid, with two higher-temperature spectra repeated from Fig. III-8 for comparison. The evident trends were similar to those in 1,1,1-trichloroethane. As temperature was lowered, both peak intensity and frequency increased with no severe changes in the smoothness of the envelopes throughout the liquid and rotator phases, with one exception: the peak intensity for the cold rotator solid at -73°C (200°K) was less than that of the other spectra. The phase transition into the non-rotator solid was accompanied by considerable intensity increase and band narrowing, and there were two distinct peaks at 57 and 66 wavenumbers.

The spectra in Fig. III-8 were particularly interesting. It seemed reasonable to view the bands as composed of two overlapping bands, one near 30 wavenumbers, and one near 50 wavenumbers. At 37°C , the lower-frequency band was dominant, while at 12°C , their intensities were nearly equal. On both sides of the melting point, the higher-frequency band had become more important. A further reduction of temperature within the rotator solid phase to -73°C reduced the intensity of the lower-frequency band appreciably, so that it became a shoulder on the higher-frequency band. Indeed, the spectra at $+37^{\circ}\text{C}$ and -73°C seemed almost to be reflections of each other across the 40 wavenumber line, just as their temperatures' digits were reversed.

The sharp peaks of the spectra of the non-rotator solid phase (see Fig. III-9) were so intense that their tops could not be estimated accurately and have been noted as approximate values in Table III-6. They were, however, extremely narrow by comparison with the bands of higher-temperature phases, so that reasonable estimates of peak width at half-height could be obtained. The new peak shapes were not amenable to integration by the computer program used, though, so that integrated absorption intensity measurements were not available. It will be noted that the lower-frequency sides of these peaks appeared to have a tail. This tail might be the beginning of the appearance of a new absorption band which would intensify with lower temperature, or they might originate equally well from a small amount of material of the rotator phase due to incomplete phase transition, since such transitions between two solid phases are sometimes slow.

It seemed noteworthy that the sharp peaks of the non-rotator solid, which were probably due to translational molecular vibrations, were located at frequencies not far removed from the positions of the cooled rotator-phase solid bands. One might suggest, then, that if the spectra of the warmer phases were indeed composed of two main bands, the higher-frequency of these (i.e., the band near 50 wavenumbers) was due to translational motions, and that the lower-frequency band near 30 wavenumbers, the intensity of which was reduced considerably by cooling, was linked to molecular rotational motions. Such a suggestion must be regarded, however, as tentative, in view of likely

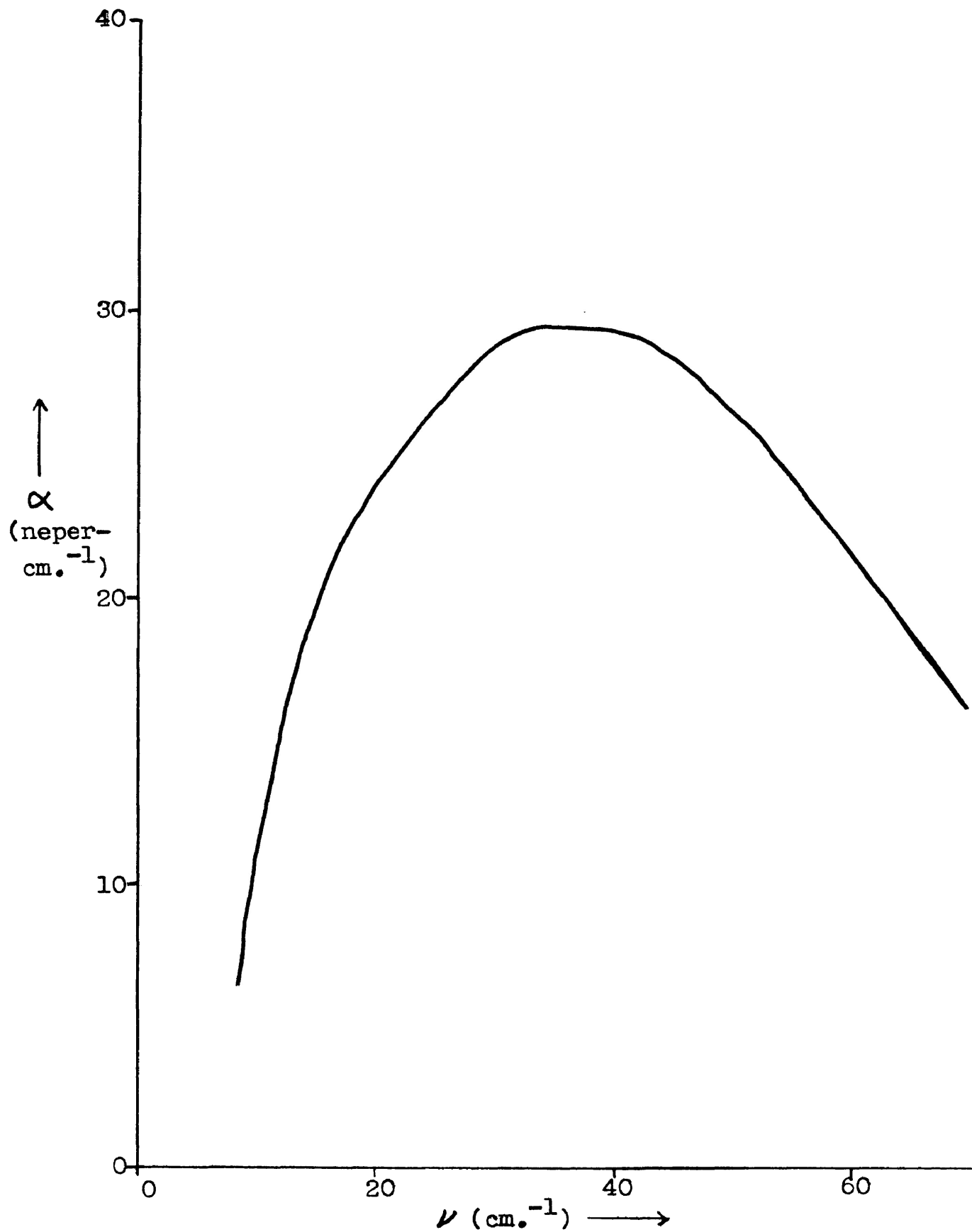


Figure III-10: Absorption Spectrum of 2,2-dibromopropane at 37°C (310°K)

differences in intermolecular distances between the two phases.

2,2-dibromopropane - $(CH_3)_2CBr_2$

Only one temperature was used for this material, the resulting spectrum of which is shown in Fig. III-10, from which the data of Table III-7 were derived.

Table III-7: SPECTRAL DATA FOR 2,2-dibromopropane

Temperature °C	Physical °K	State	$\alpha_{max.}$ (neper- cm. ⁻¹)	ν ($\alpha_{max.}$) (cm. ⁻¹)	$\Delta\nu_{1/2}$ (cm. ⁻¹)	$\int\alpha(\nu)d\nu$ (neper- cm. ⁻²)
37	310	Liquid	29	36	50	1600

Comparing this spectrum with those of 2,2-dichloropropane, one notes that the band intensity and integrated intensity here were lower, but that the band's location on the frequency scale shifted to higher value by six wavenumbers (at the same temperature of 37°C). Further, there was no evidence of two separate bands, although the high-frequency side did seem to be pulled out into a tail.

2-bromo-2-methylpropane (tert-Butyl Bromide) - $(CH_3)_3CBr$

Tertiary-butyl bromide has a melting point of -20°C (253°K), and Smyth⁴⁹ quotes two lambda points for this compound - below 41.5°C (231.6°K), a solid phase exists in which limited molecular rotation is possible, while below -64.4°C (208.7°K), a non-rotator solid exists. Spectra were recorded in the temperature range from 37°C down to -71°C to cover this set of phases. Fig. III-11 contains the spectra of the

liquid phase, Fig. III-12 extends the coverage to -68°C , and Fig. III-13 shows the spectrum obtained at -71°C , along with three higher-temperature spectra for comparison. The data derived from these spectra were tabulated in Table III-8.

Table III-8: SPECTRAL DATA FOR 2-bromo-2-methylpropane

Temperature $^{\circ}\text{C}$	Physical $^{\circ}\text{K}$	Physical <u>State</u>	$\alpha_{\text{max.}}$ (neper- cm.^{-1})	ν ($\alpha_{\text{max.}}$) (cm.^{-1})	$\Delta\nu_{1/2}$ (cm.^{-1})	$\int\alpha(\nu)d\nu$ (neper- cm.^{-2})
37	310	Liquid	34	19	40	1300
12	285	Liquid	39	25	45	1800
-18	255	Liquid	42	29	50	1900
-35	238	Rotator Solid	37	30	50	1600
-48	225	Limited- Rot. Solid	33	40	35	1100
-68	205	(see below)	18	38	30	550
-71	202	Non-Rot. Solid	~ 120 ~ 90	47 61 (shoulder)	~ 20	3500

It is apparent that the spectra of the liquid, rotator solid, and limited-rotation solid were all similarly broad and of comparable intensity, while that of the non-rotator solid at -71°C was distinctly different, as was the case previously where rotator solid phases were known to exist. An interesting point was that even the solid with some limit on rotation of the molecule gave a broad absorption band.

The spectrum recorded at -68°C seemed strange. At that temperature, the solid should have been in the non-rotator phase, being 3.6 degrees below the lambda point. The spectrum, however, appeared like

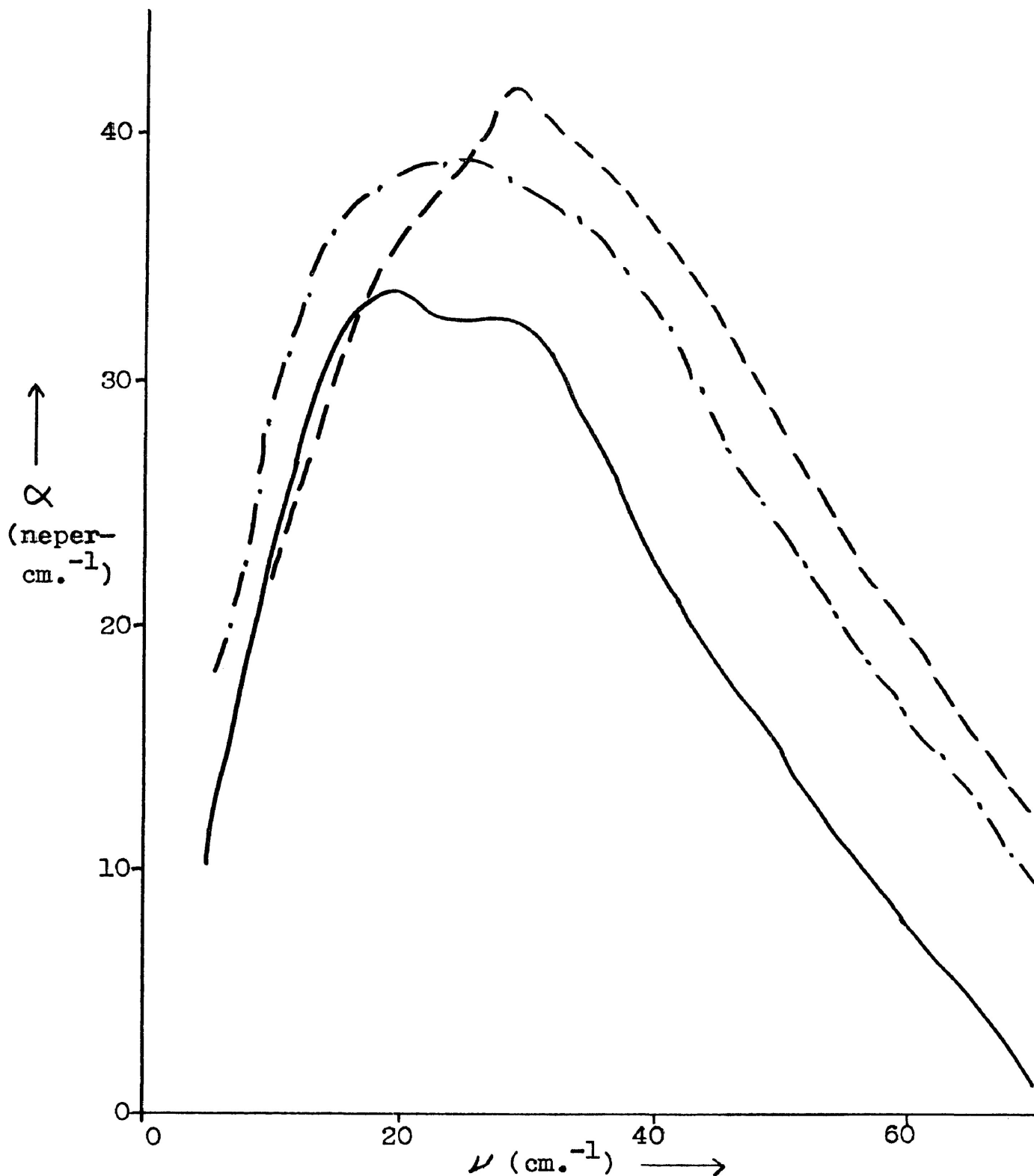


Figure III-11: Absorption Spectra of 2-bromo-2-methylpropane

—————	37°C (310°K)	-----	-18°C (255°K)
- · - · -	12°C (285°K)		

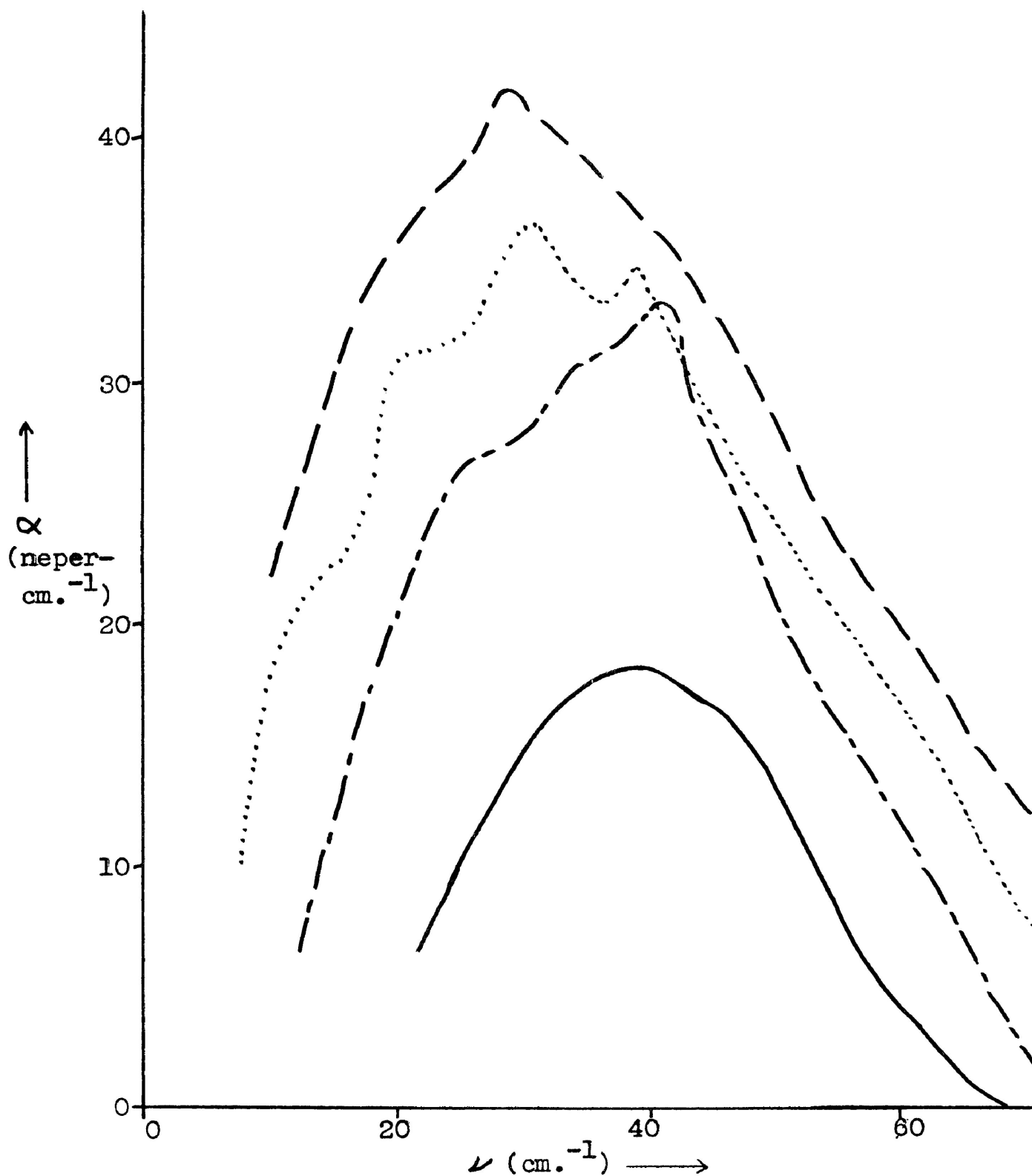


Figure III-12: Absorption Spectra of 2-bromo-2-methylpropane

-----	-18°C (255°K)	-----	-48°C (225°K)
.....	-35°C (238°K)	—————	-68°C (205°K)

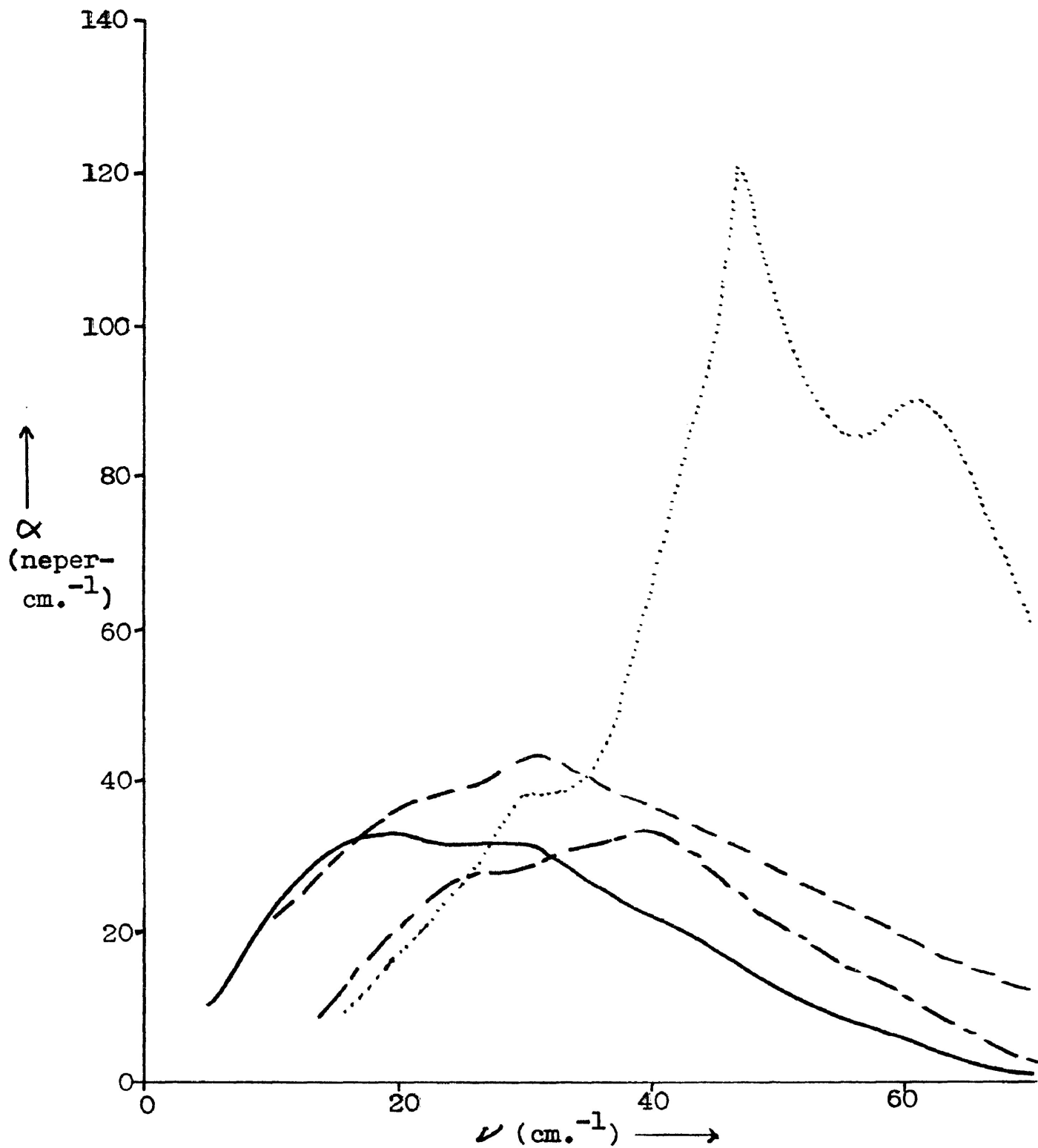


Figure III-13: Absorption Spectra of 2-bromo-2-methylpropane

—————	37°C (310°K)	— · — · —	-48°C (225°K)
- - - - -	-18°C (255°K)	·····	-71°C (202°K)

that of the limited-rotation phase, whereas the spectrum recorded just three degrees colder was distinctly different. It would seem likely that the expected phase transition had not occurred at the time the spectrum was recorded so that this was really the limited-rotation phase. Such a situation could have arisen due to supercooling or to poor temperature control. For these reasons, the spectrum recorded at -68°C has been graphed in Fig. III-12 with those of the rotator and limited-rotation phases.

Brot *et al.*⁵ have reported far-infrared absorption spectra for the liquid and three solid phases of tert-butyl chloride, with results comparable to the present work on the bromine analogue. The rotator and limited-rotation solid phases gave broad absorption features similar to that of the liquid, with the maximum intensities reduced from that of the liquid. In the non-rotator solid, the band was differentiated into two peaks of intensity approximately 30 neper-cm.⁻¹, located at 52 and 83 wavenumbers. In the spectrum of tert-butyl bromide at -71°C shown in Fig. III-13, the main peak was at 47 wavenumbers, with a distinct shoulder at 61 wavenumbers, and a hint of a possible low-frequency shoulder at 31 wavenumbers. However, the intensities of these peaks were considerably increased over those of the warmer phases, in contrast with the results for the chloride reported by Brot *et al.*

Durig *et al.*¹⁸ have also reported absorption spectra for tert-butyl chloride and bromide in a paper dealing with a series of similar "globular molecules" in their non-rotator solid phases. Their prime

concern was for the frequencies of the absorption peaks, so that their spectra gave no indication of the intensities of these peaks, beyond the qualitative observation that the absorptions in the bromide were noted to be less intense than those of the chloride. In the case of the tert-butyl chloride, they found that the peak located by Brot *et al.* near 52 wavenumbers (at a temperature of 160°K) was split into two peaks at 54.8 and 59.0 wavenumbers (at a temperature of 143°K). Their spectra of tert-butyl bromide, however, showed only one peak near the 50 wavenumber range (at 83°K), whereas the present work suggests that this peak, like that in the chloride, is composed of two peaks separated by approximately 14 wavenumbers at 202°K.

Durig *et al.* have assigned the lowest-frequency band in tert-butyl chloride to libration about the C-Cl bond in which the methyl groups of adjacent molecules in the crystalline cell move in the same direction. They assigned the next higher band to a librational motion about an axis perpendicular to the C-Cl axis. For the bromide, the experimental problem of obtaining sufficient absorptions, plus the lack of information on the structure of the solid crystals, prevented their being able to make assignments for the peaks observed, other than to state that the single band they observed near 50 wavenumbers must be due to librational motions. They were able to obtain Raman spectral data from which they assigned the two bands observed near 60 wavenumbers to translational motions. Since these bands were not infrared-active, their work suggests that in the tert-butyl halides

no absorption bands due to translational motions will be observed in the far-infrared region. Instead, the bands observed were assigned to librational motions. This must be borne in mind in dealing with other far-infrared absorptions, although obviously the symmetry species of the molecules and of the crystal structure are the prime determining factors in such assignments, and these will differ from one molecular species to another, and from one solid phase to another.

In liquid phase, and in rotator solid phases where applicable, there remain the broad absorption features for which one must account. Durig *et al.* would suggest that these are primarily due to motions similar to those observed in non-rotator solid phases, but that the bands are broad due to the rapidly fluctuating electric fields present in the vicinity of a particular molecule arising from molecular reorientation.

Carbon Tetrachloride - CCl_4

Carbon tetrachloride has a melting point of -23°C (250°K). Spectra were obtained over a range of temperatures down to -145°C and these are shown in Figs. III-14 and III-15. Fig. III-14 contains four spectra in the temperature range 37°C (310°K) to -45°C (228°K). In Fig. III-15, two spectra obtained at lower temperatures are shown with two spectra repeated from Fig. III-14 for comparison. The associated data are tabulated in Table III-9.

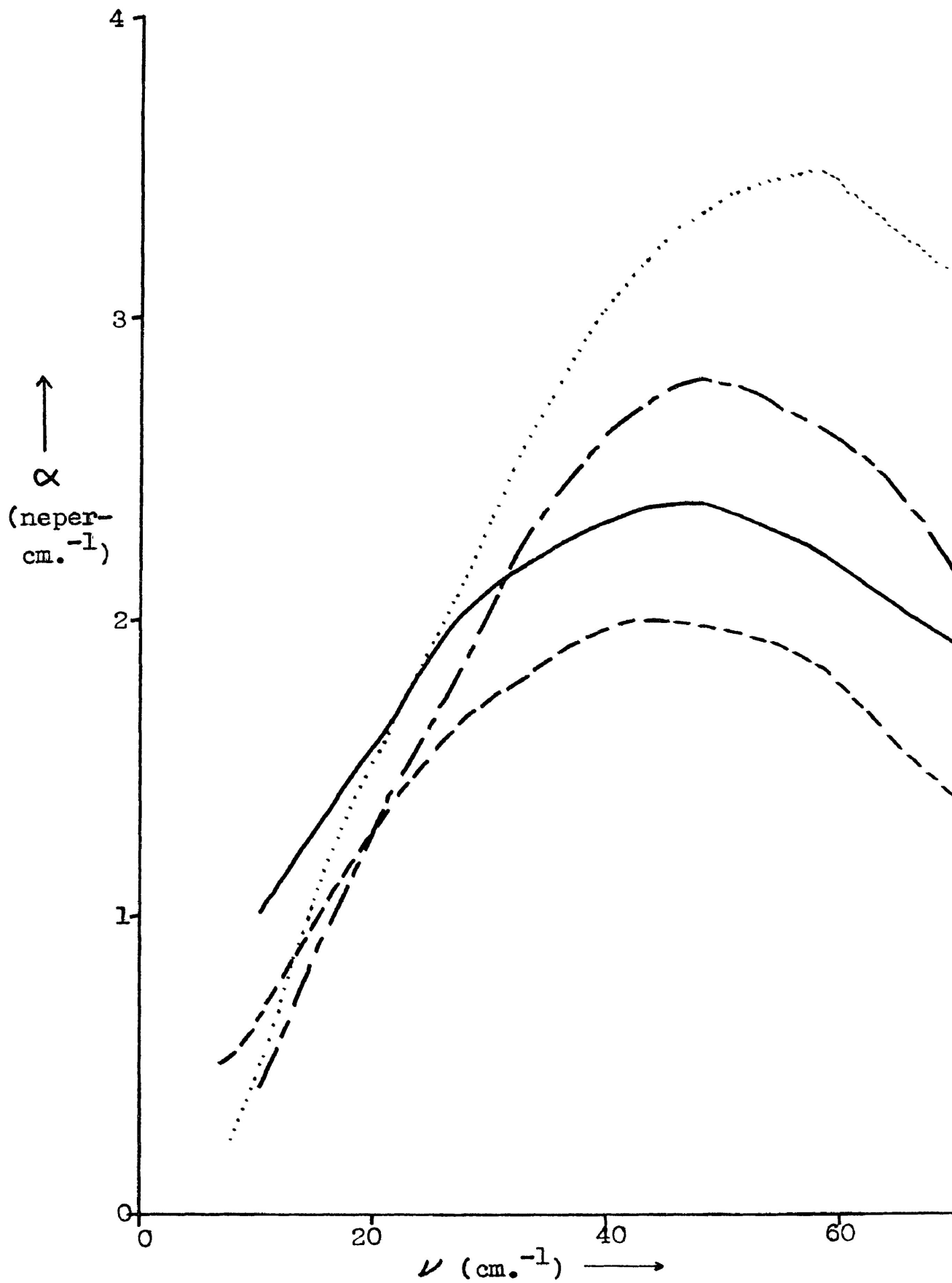


Figure III-14: Absorption Spectra of Carbon Tetrachloride

-----	37°C (310°K)	-----	-40°C (233°K)
————	-20°C (253°K)	-45°C (228°K)

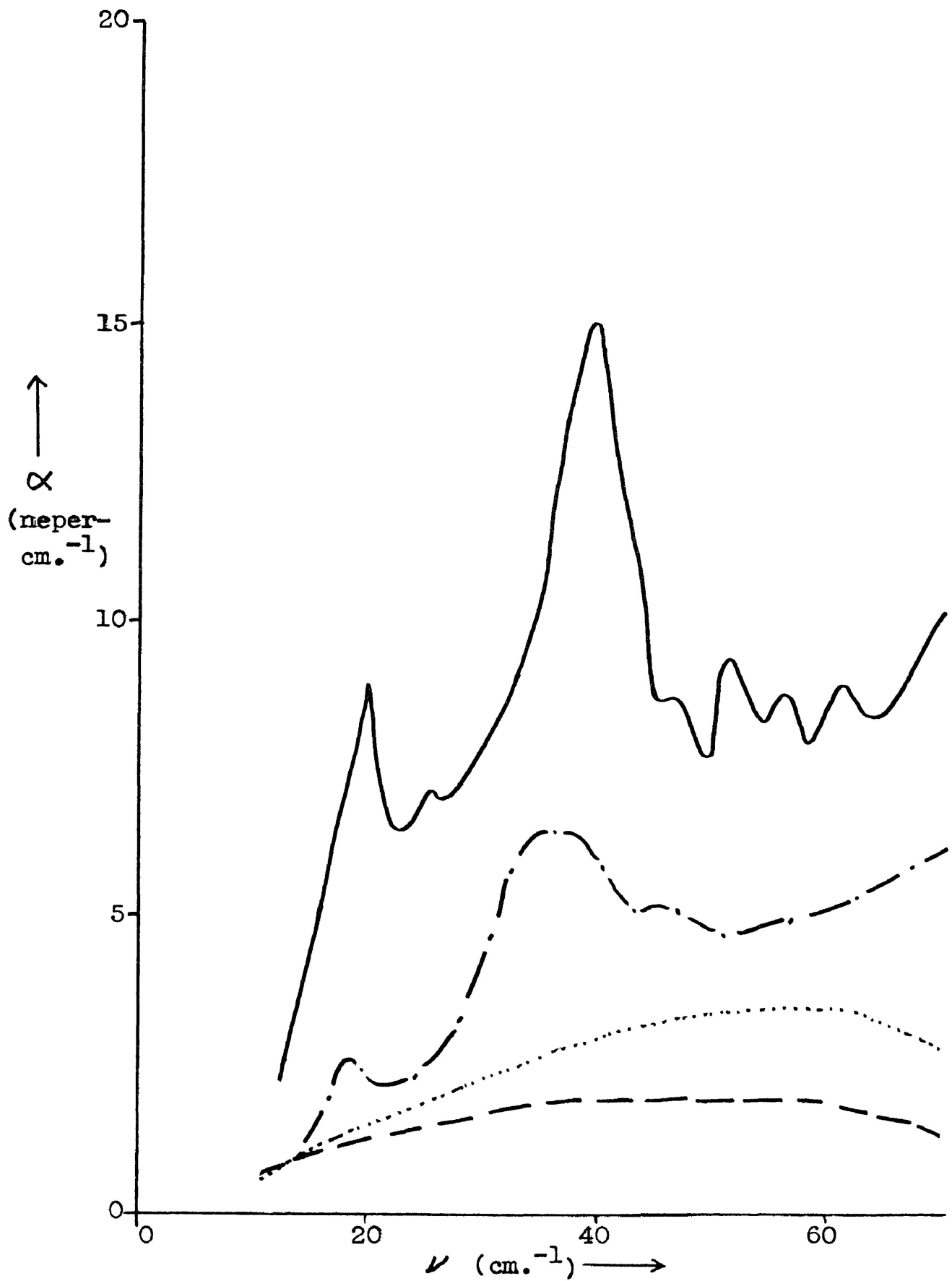


Figure III-15: Absorption Spectra of Carbon Tetrachloride
 - - - - - 37°C (310°K) - · - · - · -60°C (213°K)
 ······ -45°C (228°K) ————— -145°C (128°K)

Table III-9: SPECTRAL DATA FOR CARBON TETRACHLORIDE

Temperature		Physical	$\alpha_{\text{max.}}$	ν	$\Delta\nu_{\frac{1}{2}}$	$\int \alpha(\nu) d\nu$
$^{\circ}\text{C}$	$^{\circ}\text{K}$	State	(neper- cm. ⁻¹)	($\alpha_{\text{max.}}$) (cm. ⁻¹)	(cm. ⁻¹)	(neper- cm. ⁻²)
37	310	Liquid	2.0	44	60	115
-20	253	Liquid	2.4	46	75	140
-40	233	Solid	2.8	48	65	155
-45	228	Solid	3.5	57	70	190
-60	213	Solid	6.5	35	--	---
			2.6	18	(shoulder)	
-145	128	Solid	15.0	39	12	---
			9.0	19	(shoulder)	

It was apparent from the spectra that a trend was obtained here similar to what was evident previously. The smooth broad band of the liquid phase shifted to higher frequency and increased intensity as temperature was decreased. The spectrum of the very cold solid was distinctively differentiated into several very intense, narrow peaks. However, there is a major difference between the previously-mentioned compounds and carbon tetrachloride. All compounds dealt with previously in this work possess a permanent molecular electric dipole moment, whereas the entirely symmetric species CCl_4 does not. That being the case, it seemed at first thought rather surprising that the response of the system to temperature change should be the same for two so disparate situations. The only striking difference between the previous spectra and those of carbon tetrachloride was that in the latter, the absorption intensity was approximately an order of magnitude less than that of

the polar compounds.

The spectra of the liquid were in excellent agreement with those published by Garg *et al.*²⁴ and Chantry *et al.*¹¹, and with tabulated data given by Davies *et al.*¹⁵. The temperature used to obtain the absorption spectrum of the very cold solid (i.e., 128°K) was chosen specifically so that a check could be made with a spectrum reported previously by Chantry *et al.*¹¹. The result of the present work compared very well with this reference data, which showed four sharp peaks at 19, 38, 52 and 55 wavenumbers, with peak intensities of 6, 15, 10 and 10 neper-cm.⁻¹, respectively. In Fig. III-15, it may be seen that the present results show these four peaks at 19, 39, 51 and 56 wavenumbers, with peak intensities of 8.8, 15.0, 9.4 and 8.8 neper-cm.⁻¹, respectively. The one difference among these four lies in the intensity of the 19 wavenumber peak. In a preliminary trial at standard resolution of 2 wavenumbers, this peak's intensity was only 5 neper-cm.⁻¹. The spectrum shown in Fig. III-15 was obtained later with a resolution of 1 wavenumber, with the result that the 19 wavenumber peak's intensity was found to be considerably higher than previously suspected. This is in keeping with a common feature of absorption spectra that the observed intensity of a narrow peak may be erroneously low if the spectrum is recorded at reduced resolving power. Possibly this is the explanation for this difference between the present work and that of Chantry *et al.*

In addition to these four peaks, however, there appear to be

three other possible peaks in the spectrum of the cold solid, located at 25, 47 and 61 wavenumbers. The former two are rather obscured in the shoulders of the strong main peak, but the latter is easily discernible, rising from the strong absorption continuum which extends to higher frequency. (In their study of the far-infrared absorption spectra of solid methane and perdeuterated methane, Savoie and Fournier⁴⁸ suggest that this extended absorption feature may be due to librational motions, multi-phonon processes, or more likely, to light scattering by crystal lattice defects.)

Perhaps the most interesting aspect of these spectra of carbon tetrachloride was their appearance just below the melting point. The spectra of the solid at -40°C and -45°C were very similar to those of the liquid, while the spectrum recorded at -60°C was similar to that of the very much colder solid. In the compounds examined earlier in this work, such behaviour was associated with the existence of a rotator solid phase. Carbon tetrachloride is a spherical molecule, so one might reasonably expect molecular rotation in some solid phase. During the experimental work to obtain these spectra, it was noted that as the temperature of the CCl_4 sample was lowered the transmitted intensity, as indicated on the strip chart recorder, dropped off abruptly at a temperature of about -53°C . As discussed earlier, this had been found to correlate with abrupt changes of the absorption spectrum. Following this point, the spectra of CCl_4 at -45°C and -60°C

were recorded, and the correlation was seen to be maintained. The results indicated that, based on an extension of the trends observed with compounds known to have rotator solid phases, carbon tetrachloride might also exhibit a rotator solid phase. A search of the literature disclosed two papers which might support such a view. Higgins *et al.*³⁰ studied the molar volumes of what they call the "plastic crystal" phase of carbon tetrachloride as a function of temperature. Presumably their nomenclature indicated a solid phase in which there was considerable disorder of the crystal. Savoie and Fournier⁴⁸ studied the far-infrared absorption spectra of CH_4 and CD_4 in several phases of the solids. The spectra of these two compounds, and of carbon tetrafluoride, in phase I were composed of a single broad, featureless band very similar to those of the corresponding liquid phases. The authors state, without citing any particular reference, that numerous other studies have established that little hindrance to molecular rotation occurs in methane at the freezing point. Thus the spectrum of carbon tetrachloride in the solid phase near the freezing point exhibits features comparable to those obtained with methane, methane- d_4 and carbon tetrafluoride indicative of relatively unhindered molecular rotation, a process which, it is believed, does in fact occur at least for methane.

1,4-dioxane - $C_4H_8O_2$

1,4-dioxane has a melting point of 13°C (286°K). Far-infrared absorption spectra for this compound at individual temperatures have

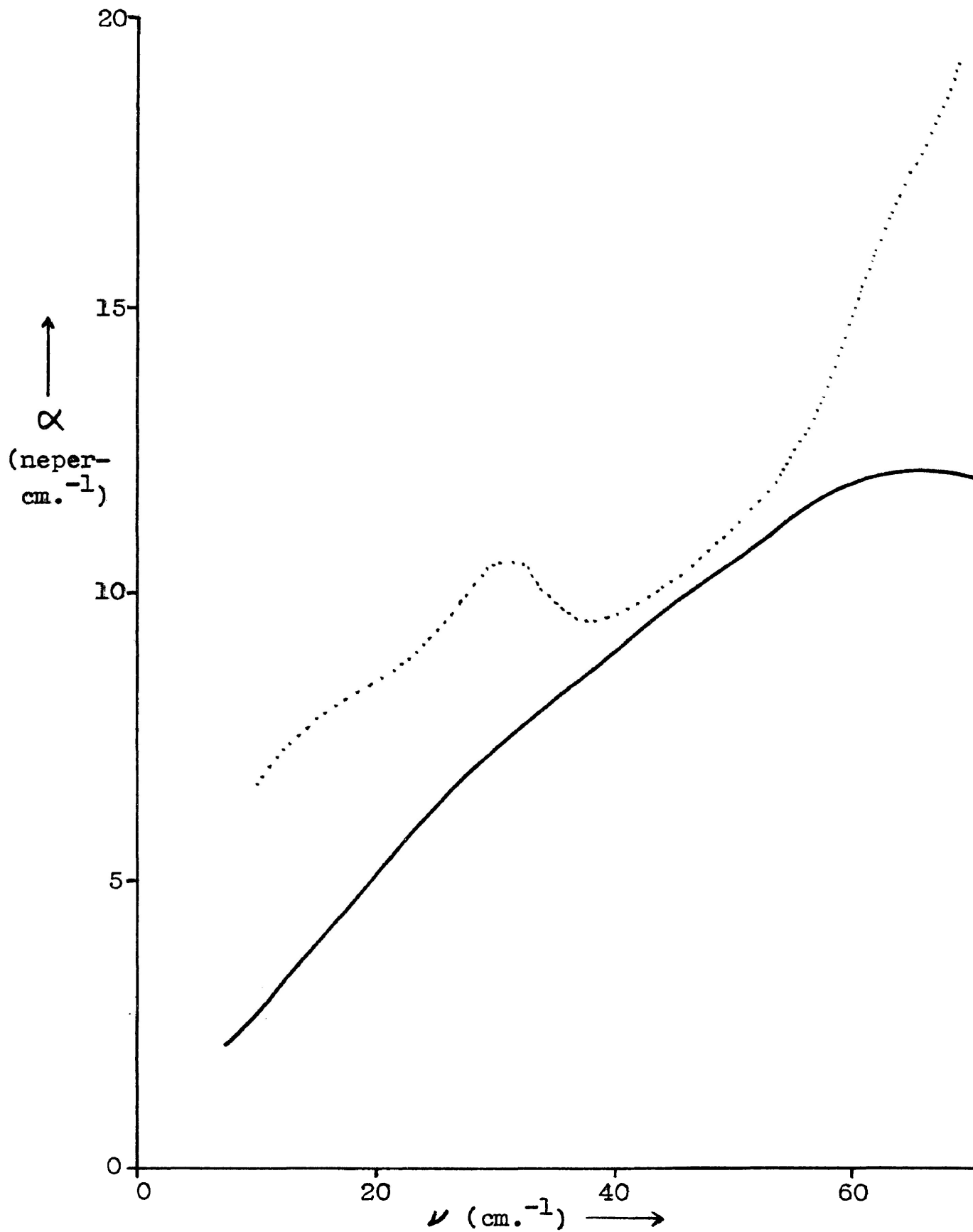


Figure III-16: Absorption Spectra of 1,4-dioxane

— 37°C (310°K) 5°C (278°K)

been reported previously (see, for example, Ref. 2), showing a broad band with maximum intensity occurring at 70 wavenumbers, which is just at the edge of the range of the equipment used for this work. Hence the band observed here and shown in Fig. III-16 could not be located accurately on the frequency axis, although it did appear to exhibit a maximum near 65 wavenumbers, when sample temperature was 37°C (310°K). The spectrum of the solid at 5°C (278°K) was of greater interest. The band intensity appeared to have increased appreciably, and a new peak centered at 31 wavenumbers on the shoulder of the main peak was noted. Bearing in mind the results of the previous work, one might speculate that this differentiation into narrower bands in the solid suggests that there is no molecular rotational freedom in the solid 1,4-dioxane, which seems reasonable in view of the fact that this molecule exists preferentially in the chair form, and is not planar.

Table III-10: SPECTRAL DATA FOR 1,4-dioxane

Temperature		Physical	$\alpha_{\text{max.}}$ (neper- cm. ⁻¹)	ν ($\alpha_{\text{max.}}$) (cm. ⁻¹)	$\Delta\nu_{1/2}$ (cm. ⁻¹)	$\int \alpha(\nu) d\nu$ (neper- cm. ⁻²)
<u>°C</u>	<u>°K</u>	<u>State</u>				
37	310	Liquid	12	~65	---	---
5	278	Solid	>20 11	>70 31	---	---
				(shoulder)		

General Discussion

The common trends seemed to be that, as temperature was lowered within the liquid phase, the absorption band's maximum intensity,

its location along the frequency axis, and its integrated absorption intensity all tended to increase. Where rotator phase solids existed, these trends were continued smoothly into that phase with no sharp discontinuity at the liquid's melting point. The phase transition to non-rotator from rotator solid phases, or where the latter was lacking, to non-rotator solid from liquid phases, was accompanied by sharp changes of the absorption band to one exhibiting much narrower and more intense bands than were present in the warmer phases.

The trend for band intensities to increase with decreased temperature was not always followed absolutely, for the 1,1,1-trichloroethane bands' intensities showed an initial decrease before rising again (see Figs. III-4 and III-5), while 2,2-dichloropropane (Fig. III-8) and 2-bromo-2-methylpropane (tertiary-butyl bromide) (Figs. III-11 and III-12) showed initial increases followed by decreases as temperature was lowered. The trend to increasing band frequency with decreasing temperature was maintained throughout, with the exception of carbon tetrachloride as it was changed from rotator to non-rotator solid phase.

Two trends previously established in the literature were demonstrated again. The non-polar materials, carbon tetrachloride and 1,4-dioxane, showed considerably less absorption intensity than polar materials, in agreement with the result of Chantry *et al.*¹¹ and of Davies *et al.*¹⁵. As shown by Jain and Walker,³⁷ for molecules with similar dipole moments replacing an atom within

the molecule with one of greater mass decreased the absorption intensity observed.

These effects on band frequency and intensity produced by changes of temperature, phase, molecular permanent dipole moment and constituent atom masses must be related to the mechanisms giving rise to the absorptions.

Before embarking on considerations of mechanism, it would be useful to consider two much simpler explanations for the intensity increases. It might be suggested that they are due merely to changes in sample thickness with temperature due to thermal expansion or contraction of the cell spacer. Such an idea could not account for the frequency shifts observed, and is in the wrong direction for the intensity shifts. If the cell spacer were to contract on being cooled, there would be less sample in the cell path, leading to decreased absorption, just the opposite of what was observed. Further, such a change should be the same for all compounds, which definitely was not the case.

Temperature would also affect the density of the material in the cell. Decreasing the temperature increases the specific gravity of the sample, thereby increasing the weight of material within the volume of the cell through which the interferometer beam passes. One would expect such a process to cause increased absorption intensity, which was observed. However, three materials also showed decreased absorption intensity over part of the temperature range. Further, one would not expect such specific gravity

changes to yield such large absorption changes as were observed in several situations. In addition to these qualitative considerations, one may remove from the data the portion dependent on merely the weight of material in the beam by use of the equation:

$$\sigma = \frac{\alpha M}{dN}$$

where σ is the absorption cross-section, in cm^2 ,

α is the absorption coefficient, in neper-cm^{-1} ,

M is the sample's molecular weight in grams,

d is the sample's density, in g./cm^3 , at the temperature at which the spectrum is recorded, and

N is Avogadro's number, 6.023×10^{23} .

A similar expression for the integrated absorption cross-section may be obtained by inserting $\int \alpha(\nu) d\nu$ in place of α . Data for the molar volume, V_m , of carbon tetrachloride in the "plastic crystal" phase were found in the literature in a paper by Higgins *et al.*³⁰ in the form of the relation:

$$V_m = 86.600 + 5.723 \times 10^{-2} \times (T-235) + 9.01 \times 10^{-4} \times (T-235)^2$$

where V_m is in ml./mole , and T is temperature in $^\circ\text{K}$. Similarly, Pugachevich *et al.*⁴⁵ give the following expression for the density of carbon tetrachloride in the liquid phase:

$$d = 1.6287 - 1.763 \times 10^{-3} \times t - 2.09 \times 10^{-6} \times t^2$$

where d is sample density, in g./cm^3 , and t is temperature in $^\circ\text{C}$. Using these data, Table III-11 was constructed.

Table III-11: DENSITY CORRECTIONS FOR CCl_4 ABSORPTIONS

Temperature		d	$\alpha_{\max.}$	$\int \alpha(\nu) d\nu$	$\sigma_{\max.}$	$\int \sigma(\nu) d\nu$
$^{\circ}C$	$^{\circ}K$	(g./cm. ³)	(neper- cm. ⁻¹)	(neper- cm. ⁻²)	(cm. ²)	(cm.)
37	310	1.5605	1.97	115	3.22×10^{-22}	188×10^{-22}
-20	253	1.6632	2.38	140	3.65×10^{-22}	215×10^{-22}
-40	233	1.7762	2.78	155	4.00×10^{-22}	223×10^{-22}

It may be seen from Table III-11 that, while the increases in intensity and integrated intensity are less when the data are converted to the density-independent data form, σ , the increases still exist. One may deduce that, in keeping with the qualitative reasoning outlined earlier, the mere weight of sample within the beam does not account entirely for the observed intensity increases, and it certainly could not account for intensity decreases over part of the temperature range. The intensity and frequency shifts of these bands must then originate in the changing structure of the samples at the molecular level as a function of temperature.

In the earlier presentation of the individual spectra, it was noted that those of 2,2-dichloropropane could be viewed as composed of two broad overlapping bands, the relative intensities of which were temperature-dependent. In that case, as temperature was decreased, the higher-frequency band seemed to increase in intensity prior to the decrease in the intensity of the lower-frequency band. A similar view might be taken of the spectra of 1,1,1-trichloroethane, except that the lower-frequency band would be seen as decreasing prior to increases in the higher-frequency band. In 2-bromo-2-

methyl-propane, the same viewpoint of two overlapping bands, the temperature dependence of which differ, might be taken. One might well extend this concept to say that in all of the spectra within the liquid and rotator solid phases (where the latter exist), both the frequency shifts to higher values and the intensity changes with decreasing temperature are due to decreasing intensity of lower-frequency bands and increasing intensity of higher-frequency bands. Hill³³ has suggested that the broad nature of the absorption bands observed in the far-infrared region may be due to the overlap of several bands, each of which is broadened by appreciable damping. She does not deal with temperature effects in this preliminary proposal, but it does not seem unreasonable to postulate that, whatever the mechanism is which would account for the existence of the bands and for their broadening, the mechanism might be temperature-dependent. Hill^{32,33} has proposed that the absorptions arise from rotational oscillatory motion of the entire molecule within small potential wells created by cages of neighbouring molecules, and that the damping of the oscillations arises from non-rigidity of such cages, allowing transfer of energy from the central molecule to the cage constituents. In the first of these papers, however, she asserts that for such a mechanism to be operative, the potential energy barriers to molecular rotation must be greater than kT , the available thermal energy, and that such a condition could not be met by compounds which exhibit rotator solid phases because the existence of these solid-phase molecular rotations

indicates that in the solid, and therefore presumably in the liquid, the available thermal energy exceeds the barrier. This particular speculation has since been shown to be in error, by the present work and by the results of Savoie and Fournier⁴⁸ and of Brot *et al.*⁵. These same latter data, however, confirm the strong effects of molecular rotational motion on the absorption spectra.

Whiffen's early work on non-polar materials⁵³ led him to suggest that the absorptions arise from the existence of small molecular dipole moments produced in these species by distortions of the molecule due to bimolecular collisions. In his view, these distortions would be further altered by subsequent collisions which occurred before the molecule had had sufficient time to reorient itself by rotation to align itself with the applied electric field. Chantry *et al.*¹¹ postulated that the suggested small molecular dipole might arise not from bimolecular collisions, but from the inductive effects of neighbouring molecules which formed a temporary cage or, in their terminology, a "liquid lattice". The thermal motions of these neighbouring molecules would produce a fluctuating inductive effect on the central molecule, causing its induced dipole to oscillate. They pointed out, as had Hildebrand,³¹ that the use of a point dipole approximation to represent a molecule's effect on its neighbours is not justifiable when, as is the case in liquids, the intermolecular distances are of the order of the molecular diameter. Hildebrand concluded "that the forces between polyatomic molecules are chiefly those between their neighbouring parts".

Rosenburg and Birnbaum⁴⁶ have reported a pressure-induced far-infrared absorption for gaseous carbon tetrafluoride. They found, in the range below 250 wavenumbers, two absorption peaks. The one near 200 wavenumbers was ascribed to a difference band from higher-frequency vibrational levels which should occur at 197 wavenumbers, because its intensity was proportional to the gas density. A lower-frequency band, however, was found to be composed of two contributions. One was linearly dependent on density, and was suggested to arise from another difference band, while the intensity of the second contribution was proportional to the square of the gas density, and was ascribed to transient dipole moments induced by molecular octupolar fields and/or bond angle distortions during bimolecular collisions.

Savoie and Fournier⁴⁸ found that the phase II solid of methane and that of methane-d₄ each gave two sharp absorption peaks with isotopic frequency ratios dependent on the square root of the molecular mass, similar to what might be expected of translational modes. However, they point out that the frequency of the peak in the liquid phase, near 200 wavenumbers, suggested strongly that the absorptions in this phase are predominantly of rotational origin, for comparing them with frequencies observed for carbon tetrahalides showed that the frequencies were dependent on the square root of the molecular moment of inertia, and not on the square root of the molecular mass. It would seem, then, that it is hazardous to suggest that the absorption mechanism dominant in one phase of a material is also of

prime importance in its other phases.

Kroon and van der Elsken³⁹ have studied the influences of methyl and phenyl substituents, solvent, and temperature on the absorption spectra of dilute solutions of several strongly polar compounds. As temperature was decreased, the band maxima shifted to higher frequency, but the integrated absorption cross-section was unchanged. Their data on a 4% solution of acetonitrile (CH_3-CN) in n-heptane were presented as absorption cross-section, σ , vs. frequency. These results are in sharp contrast with those of the present work, in which shifts of absorption intensity have been found with temperature which exceed the changes in sample density. Jain and Walker³⁷ have found similar shifts of absorption intensity with samples of halogen-substituted benzene derivatives, also recorded in pure liquid phase.

On the basis of the observed effects on band intensity of molecular dipole moment and substituent group masses, Jain and Walker³⁷ have found that, for pure liquid samples of a number of compounds, the maximum value of the absorption coefficient, α , is linearly dependent on the ratio μ^2/I , where μ is the molecular dipole moment, and I is its mean moment of inertia for rotations. They noted that Gordon's formula for the integrated band intensity of an absorption arising from purely rotational motion contains this same factor. In their work, they were unable to obtain integrated band intensities, and thus used the band's maximum intensity as a reasonable correlate of the integrated intensity.

Four of the compounds used in the present work were used by Jain and Walker. Since the integrated intensities were now available, an opportunity was afforded to compare results. In Table III-12 are contained the appropriate data for this purpose. In view of the strong effects of temperature on the absorption intensity found here, the values for integrated absorption intensity given in this table were obtained by interpolation of the present data to yield an estimate of the value at 20°C, the sample temperature in the work of Jain and Walker.

Table III-12: DIPOLE MOMENTS, ROTATIONAL MOMENTS OF INERTIA AND INTEGRATED ABSORPTION INTENSITY FOR FOUR COMPOUNDS AT 20°C.

C O M P O U N D	$CHCl_3$	$CHBr_3$	CH_3CCl_3	$(CH_3)_3CBr$
Dipole Moment (Debyes)	1.11	1.0	1.66	2.23
$10^{40} \times$ Average Moment of Inertia (g.-cm ² .)	254	660	345	412
$10^{-37} \times \mu^2/I$	4.87	1.51	7.97	12.03
$\int \alpha(\nu) d\nu$ (neper-cm. ⁻²)	1100	350	2200	1600

Fig. III-17 is a graph of $\int \alpha(\nu) d\nu$ vs. μ^2/I for these four compounds. It is apparent that the point for tertiary-butyl bromide is far from the graph line, which was not the case when Jain and Walker used the absorption coefficient in place of the integrated absorption intensity. This suggested that it might be informative to construct a graph of $\int \alpha(\nu) d\nu$ vs. α_{max} . to determine whether in fact α_{max} . is a good indicator of the integrated intensity. For these purposes, the data of the present work were collected in Table III-13. The resultant

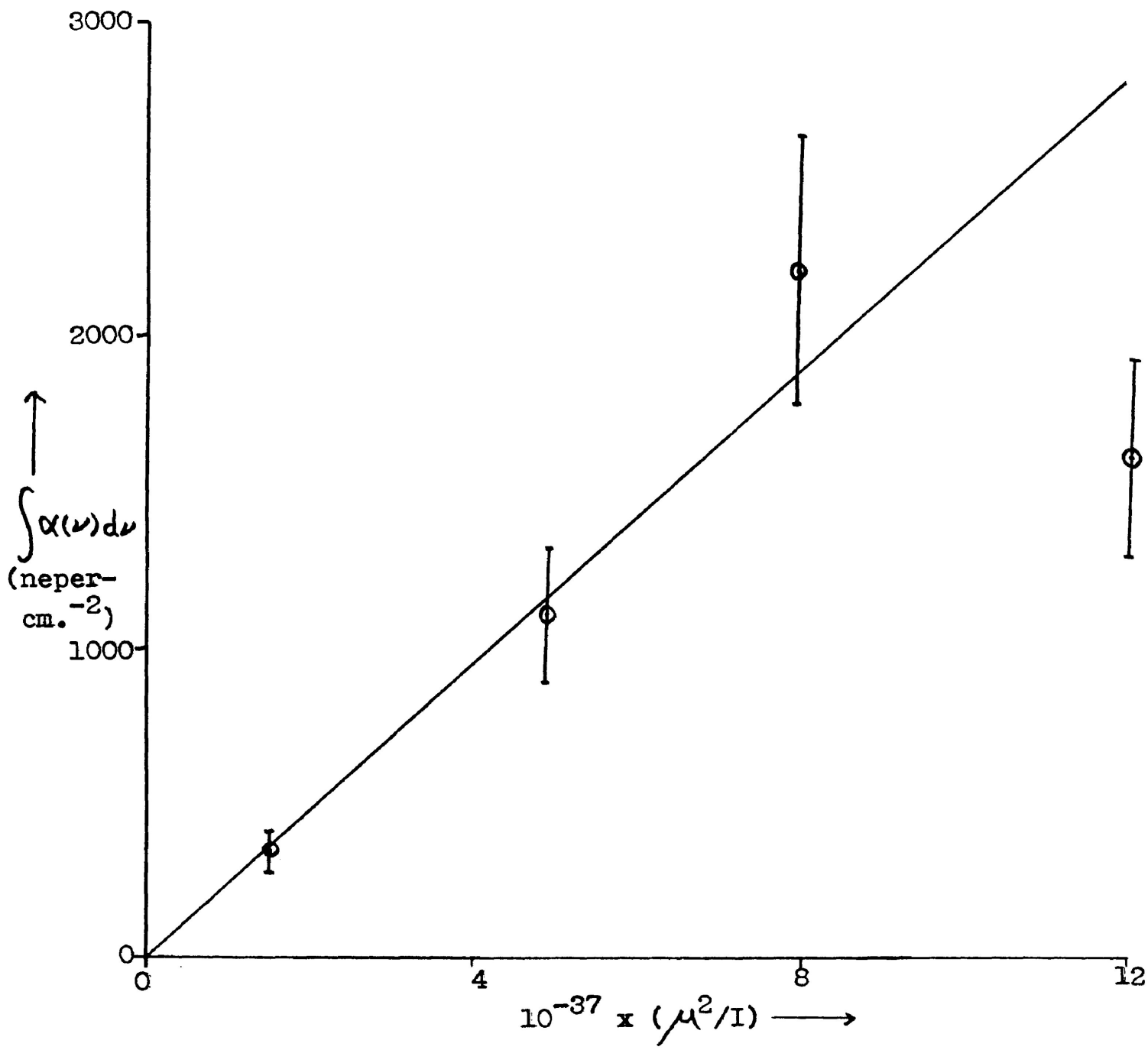


Figure III-17: Relationship between $\int \alpha(\nu) d\nu$ at 20°C and (μ^2/I)

graph is shown in Fig. III-18, in which it was apparent that there was a good correlation between the two parameters for most materials investigated, but that several points lay far from the line. This means, of course, that one cannot

Table III-13: CORRELATION OF MAXIMUM ABSORPTION INTENSITY WITH INTEGRATED ABSORPTION INTENSITY

C O M P O U N D	$\alpha_{\max.}$ (neper-cm. ⁻¹)	$\int \alpha(\nu) d\nu$ (neper-cm. ⁻²)
Chloroform	18	1250
	17	1100
	29	1600
	37	2100
Chloroform-d	10	470
	18	850
	17	900
Bromoform	7.5	355
	8.0	340
1,1,1-trichloroethane	36	2100
	38	2300
	33	1900
	35	2000
	39	2200
2,2-dichloropropane	43	2100
	49	2700
	43	2000
2-bromo-2-methylpropane	34	1300
	39	1800
	42	1900
	37	1600
	33	1100
	18	550
Carbon tetrachloride	2.0	115
	2.4	140
	2.8	155
	3.5	190

rely entirely on $\alpha_{\max.}$ as a measure of $\int \alpha(\nu) d\nu$. The

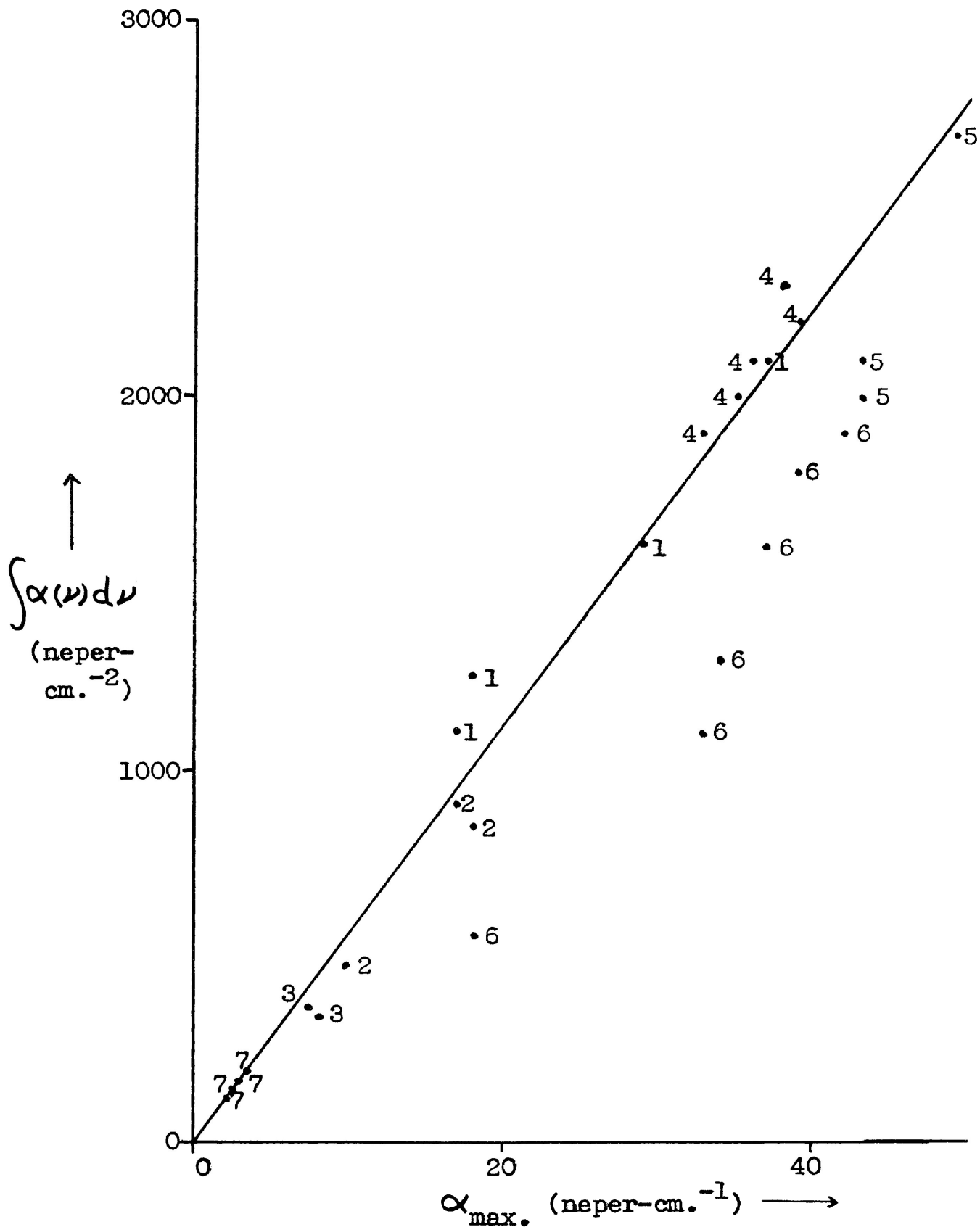


Figure III-18: Correlation of integrated absorption intensity with maximum absorption intensity

- | | |
|-------------------------|------------------------|
| 1 Chloroform | 5 2,2-dichloropropane |
| 2 Chloroform-d | 6 tert-butyl bromide |
| 3 Bromoform | 7 Carbon Tetrachloride |
| 4 1,1,1-trichloroethane | |

points for 2,2-dichloropropane and tertiary-butyl bromide were particularly far from the line. The spectra of the former were so different from those of other materials that they stimulated the concept of two very distinct overlapping bands centred 20 wavenumbers apart. The latter showed bands with their absorption maxima occurring at lower frequency than other materials, giving rise to a general band shape with a sharp drop from the peak at low frequency, and a much more gentle slope on the high-frequency side. In other words, the band shapes for these two materials were markedly different from those of the others investigated, so that it does not seem unreasonable that the relationship between peak height and peak area was different for these compounds.

Aside from the assumed correlation between peak maximum intensity and integrated intensity, the linear relationship of α_{\max} with (μ^2/I) of Jain and Walker would have trouble in the area of temperature. Given the strong effect of temperature observed in the present investigation, one must decide at what temperature to derive intensity information for such a graph. One might pick one arbitrary temperature and make all measurements there, but it would seem likely that the absorption mechanism is dependent on the structure of the liquid at the microscopic level (which is temperature-dependent). With such a view it would be desirable to refer all measurements to some arbitrarily-chosen liquid structure, rather than to a temperature which is the same for all liquids. However,

how should one choose the structure? One would require first detailed knowledge of liquid structure as a function of temperature, pressure and composition, but this is just the information lacking at present, the information which far-infrared absorption spectroscopy may help to provide.

Hill³² suggested in her earlier development of a mathematical expression for the frequency of far-infrared absorption that the phenomenon was due to absorption of energy from the electromagnetic field to enable molecular species to overcome a potential energy barrier, of the order of the thermal energy kT , produced by a temporary molecular cage, and thereby to rotate through a relatively small angle. She asserted, however, that such a potential energy barrier was not sufficient to hinder the rotation of certain classes of molecules which exhibited rotator-phase solids, and therefore must have been exceeded by the thermal energy possessed by these molecules. But surely not all molecules in a system which exhibits molecular rotation will possess the minimum energy required to overcome this barrier. A distribution of molecular energies must exist, perhaps similar to a Boltzmann distribution, in which a significant proportion of the molecules are unable to rotate, while only those with energy exceeding the barrier may rotate. This concept is similar to that of an activation energy for rotation.

The source and magnitude of the potential energy barrier must be identified. Hill has suggested that it is of the order of kT

or larger and that it arises somehow from a molecular cage structure. At room temperature, kT is approximately equal to 40×10^{-15} ergs, whereas the energy associated with a frequency of 40 wavenumbers (near the centre of the band under investigation here) is approximately 8×10^{-15} ergs, or about 20% of the average thermal energy kT . It might seem reasonable to say, then, that the average barrier height is approximately equal to kT , but the barrier heights at the microscopic level will also fall into a distribution, for the structure of the molecular cages will not be constant from one site to the next. Hence, although a particular molecule might be a member of a statistical assemblage of species whose average energy is kT , and might reside in a molecular cage which is also a member of another assemblage of structures providing an average barrier to rotation of the order of kT , there is no way that one can assign a definite energy to the molecule and a definite energy barrier to the cage in which it is found. There will be, however, some difference between the energy possessed by the molecule and that required for it to rotate. This energy might be acquired by subsequent collisions with other molecules, or from an applied electromagnetic field. In the latter case, the frequency absorbed might reflect the difference between possessed and required energies. The concentration per unit volume of cages and entrapped molecules which, in combination, give rise to this energy difference would be determined by the two relevant distribution functions, and would in turn determine the magnitude of the absorption of energy from the electro-

magnetic field applied.

Both the frequency and intensity of absorption would be dependent upon a statistical distribution of energies and energy barriers, and not on an average value of each. What, then, would happen if the temperature of the system were changed? If we assume for the moment that the distribution function for the energies possessed by molecules is akin to that of Boltzmann, then a decrease of temperature would mean that more molecules would be found to have the lower energies. Further, if the potential energy barriers created by the molecular cages were dependent on intermolecular distances, the distribution of barriers would be shifted to higher values on decreasing the temperature. The result would be that the energy separations would increase, leading to the absorption of higher-frequency radiation, and that the total number of absorbing species might also increase due to increased population of the lower energy levels, leading to increased total absorption intensity.

A change of sample density, and therefore of intermolecular distance, accomplished by a change of pressure, would have a somewhat different result. Increasing pressure might shift the distribution of energy barriers to higher values, but it should not affect the kinetic energy possessed by the molecules, so that a pressure change which altered intermolecular distance would be expected to produce less drastic changes in the absorption band than would a change of temperature which accomplished the same alteration of intermolecular distance, but altered the molecular kinetic energy simultaneously.

All of the foregoing arguments deal with the system as if only one simple rotational mode of molecular motion were possible, governed by two distributions. It would seem much more likely, however, that there would be several axes of rotation, plus molecular translations and intramolecular librational motions. Each such mode of motion could be expected to be under the influence of the two distributions associated with them - that is, for each mode of motion, there would be associated a distribution of kinetic energies and a distribution of energy barriers to motion in that mode. Such a situation would surely lead to overlap of absorption bands in this region if the average energy differences involved were of the same order of magnitude. Durig *et al.*¹⁸ have assigned the sharp peaks observed in non-rotator solid phases of tert-butyl halides to librational motions. Savoie and Fournier⁴⁸ assigned the broad absorption features of methane and methane-d₄ to molecular rotational motions, and the sharp peaks for these same materials in non-rotator solid phases to translational motions in the lattice. It would seem, then, that absorption of far-infrared radiation is possible due to all three of these modes of motion. This must surely imply a particularly complex absorption band shape in which the absorption intensity at a particular frequency would be the algebraic sum of the intensities of each of several overlapping bands, while each of these latter intensities would be determined by the integration of the product of two probability distributions (possibly exponential functions, as is the Boltzmann distribution) over a range of energies.

A mathematical formulation of this approach would be very difficult with no prior knowledge of the number and kind of absorption modes or of the form of the several distribution functions involved. This rather detracts from the usefulness of these concepts to those who prefer to have analytical mathematical formulations, but some consolation may be obtained from the fact that, to this experimenter's knowledge, the only attempt to formulate a mathematical model to date was that of Hill³² in 1963, and the expressions obtained from that work have been found since then to give answers which do not correlate with experimental results (see, for example, Ref.13). The ideas under discussion presently, however, do provide at least a qualitative account of the observed shifts of far-infrared absorption bands with temperature, and provide some suggestions about what might be expected were the samples to be subjected to changes of pressure at constant temperature.

There has not been any mention yet in this discussion of the origin of the barriers to molecular motion beyond the ideas that they must depend on intermolecular distances and that they arise from a cage of molecules surrounding the absorbing species. This cage, of course, is a very transitory thing, which will fluctuate rapidly in time, both in size and in the relative orientations of the component molecules. The simplest means of intermolecular interaction giving rise to energy barriers is dipole-dipole interaction, in this case between the cage constituents and the trapped

molecule. As has been pointed out by Chantry *et al.*¹¹ one cannot, in this situation, treat these molecular dipoles as point dipoles. Hildebrand³¹ stated that the principle forces of interaction between polyatomic molecules in condensed phases must be those between their neighbouring parts. Davies *et al.*¹³ suggested that the main contribution to local interactions was from repulsive forces. Perhaps it would be more appropriate then to view the cage not as a relatively simple array of point molecular dipoles, but as a much more complicated array of interatomic dipoles arising from the electronic charge density distributions within the molecules. Thus even molecules which did not possess a permanent molecular dipole moment could interact through this mechanism with their nearest neighbours. There has been some work which misses this concept. For example, Bulkin⁶ has dismissed the idea of a cage or "liquid lattice" on the grounds that the absorptions present in dilute solutions of polar solutes were unchanged from those of the pure solute, which he interprets as indicating that dipole interaction is not involved, since the solvent molecules lack a permanent molecular dipole for interaction. In the present concept, however, net molecular dipoles are not required; all that is necessary is a set of interatomic dipoles which may or may not add vectorially to a non-zero molecular dipole moment.

One should expect, further, that the interactions of neighbouring molecules might produce distortions of the electronic charge

distributions in each molecule, giving rise to short-lived induced molecular dipole moments. Since the absorption of energy from the electromagnetic field applied requires a change of magnitude and/or direction of a molecular dipole moment, this process of induced dipole moments could account for the existence of absorptions even by non-polar materials such as carbon tetrachloride. Such an induced dipole would be very small, which might account for the considerable decrease in absorption intensity on passing from polar to non-polar molecules.

Pardoe⁴⁴ has calculated the magnitudes of the dipole moments to be expected from two sources - bending of a bond angle, and distortion of the molecular charge distribution induced by neighbouring molecules. He concluded that neither mechanism alone could account for the apparent molecular dipole moments derived from experimental data using the Kramers-Krönig relationship, but that a combination of the two could give rise to such a dipole moment. Data on the absorption coefficient of binary mixtures of non-polar materials at arbitrarily-chosen frequencies as a function of concentration were found to be consistent with a theoretical model which assumed a contribution from a bimolecular collisional process. This was interpreted as lending support to the concept that molecular distortion resulting from collisions is the source of the apparent dipole moments in molecules which lack permanent molecular dipole moments. However, Pardoe's data for the effect of temperature on the absorption spectra of non-polar materials showed a shift of the peak to

lower frequency with decreased temperature, opposite to what has been noted in the present work. This effect was suggested to be inconsistent with the postulate of bimolecular collisions, since the frequency of such collisions is thought to increase with decreased temperature.

Whiffen⁵³ suggested that the observed absorptions of carbon tetrachloride could be accounted for by a dipole moment of 0.1 *D* created by distortion of a *Cl-C-Cl* bond angle of about 6°, but that the absorptions of benzene would require a particularly favourable orientation of neighbours. To this experimenter, there does not seem to be the requirement of bond angle distortion. Only a distortion of electronic charge distribution by the inductive effects of very close parts of neighbouring molecules is necessary, although bond angle distortion might contribute in some cases.

CHAPTER IV

Conclusions and Suggestions for Further Work

Conclusions and Suggestions for Further Work

The effects of temperature on the far-infrared absorption spectra of several polar and non-polar compounds have been observed in the region of 10 to 70 wavenumbers. In general, decreasing temperature brought about increases in the frequency of maximum absorption, the intensity of maximum absorption, and the integrated absorption intensity of the band. The spectra of rotator-phase solids were very similar to those of the respective liquids, whereas the spectra of non-rotator solid phases were considerably different, being composed of several very much narrower and more intense bands than those of the liquid phases.

These effects have been considered with reference to the postulates that the absorptions in liquid and rotator phases are composed of several overlapping bands, each of which corresponds to a particular mode of molecular motion which is influenced by two probability distributions, one related to the energy possessed by a particular molecule, and one related to the energy barrier to molecular motion. The latter barrier was viewed as arising from the interactions of molecules within a temporary cage structure, the interactions being those of the electronic charge distributions of very close parts of neighbouring molecules. Such interactions could also give rise to short-lived induced molecular dipole moments which contribute to a molecule's ability to interact with the applied electromagnetic field and thereby absorb the energy required to over-

come the barrier to molecular motion.

Further studies of the effects of temperature would be useful, particularly at higher temperatures than were possible in the present investigation. Temperatures near the boiling points of various compounds might well produce interesting effects on the spectra.

The effects of pressure changes on the spectra should be studied, since the present approach would suggest that they would differ somewhat from the effects due to temperature.

Appendix I following contains an outline of a proposal for a modification to the single-beam interferometer which is aimed at gaining the advantage of sampling-time absorption intensity ratioing inherent in double-beam spectrometers while retaining the sensitivity of a single-beam system. Appendix II contains a suggestion for an instrument which might detect certain phase changes.

Appendices

Appendix I

Most far-infrared instruments in use now are single-beam interferometers. The use of the interferometric technique, of phase-locked high-gain signal amplifiers, and of the single-beam mode are dictated by the low output of the source and the low sensitivity of the detectors available, of which the most commonly used is the pneumatic Golay cell.

It would be advantageous to have a double-beam instrument so that the intensities of the beams transmitted by the sample-filled cell and by a reference absorber (either an identical cell unfilled or one filled with a solvent blank) could be measured and ratioed at the same time. By using a single-beam system, one obtains these intensity measurements at times which may be separated by anywhere from 30 minutes to 4 hours, depending on what adjustments of the system (e.g., sample temperature) must be made. Such long times between sampling place very stringent conditions on the stability of the source, detector and amplifier.

In a double-beam instrument, however, each beam receives slightly less than half of the source's output energy, a loss which cannot be tolerated in the far-infrared region. Further, the beams fall on separate detectors, which must be accurately matched if reliable data are to be obtained. It would be useful to have an instrument which combines the advantages of immediate or sample-time ratioing of two beams with the sensitivity of a single-beam system.

Low⁴², in a review of instrumentation, outlines an interferometer available from Digilab Inc., subsidiary of Block Engineering, Inc., as model FTS-14. The system combines an interferometer with a small dedicated digital computer which handles machine operation, data acquisition, and data processing by Fourier transform to yield the spectrum. This system operates in a double-beam mode in a novel way. There are a pair of mirrors which, on command from the computer, may be flipped to direct the beam through either of two optical paths in which sample and reference are placed. Thus at any particular time the system is a single-beam one, but it gathers data alternately from two single beams with little time separation between them. This system, however, is rather expensive, partly due to the incorporation of the computer and partly due to several other features. Low quotes a price of (U.S.)\$65,000.

It has occurred to this experimenter that a simpler system of beam switching could be adapted to interferometers which lack a dedicated digital computer and depend on external installations for Fourier transform processing of the interferogram. One could use a periodically rotating slotted wheel with the front surface reflective to far-infrared radiation. This wheel would either pass the beam through its slots to one path, or reflect the beam to another path. Fig. A-1(a) shows an example of such a wheel. This component could be driven by the same system that provided beam chopping if their phase relationship were maintained constant. In Fig. A-1(b), a sketch is shown of a chopper wheel which could be used with the

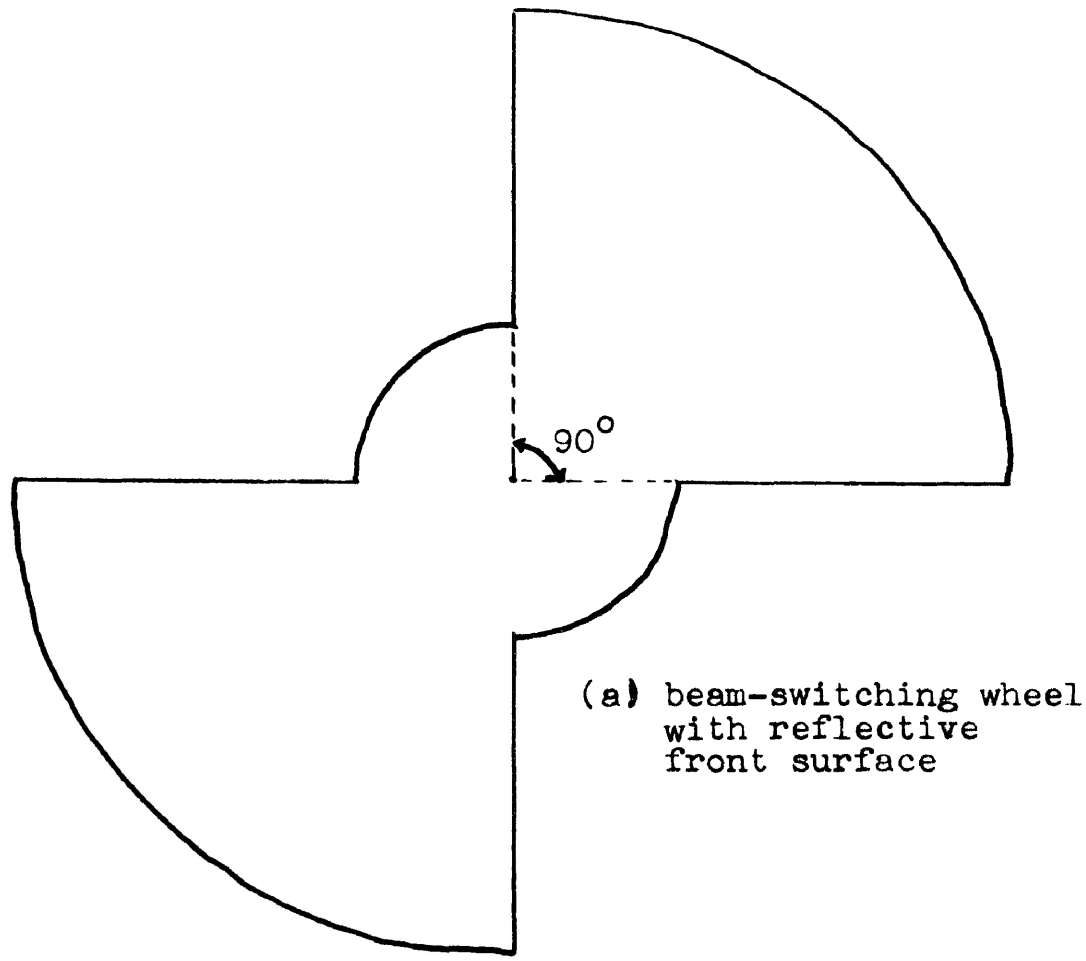
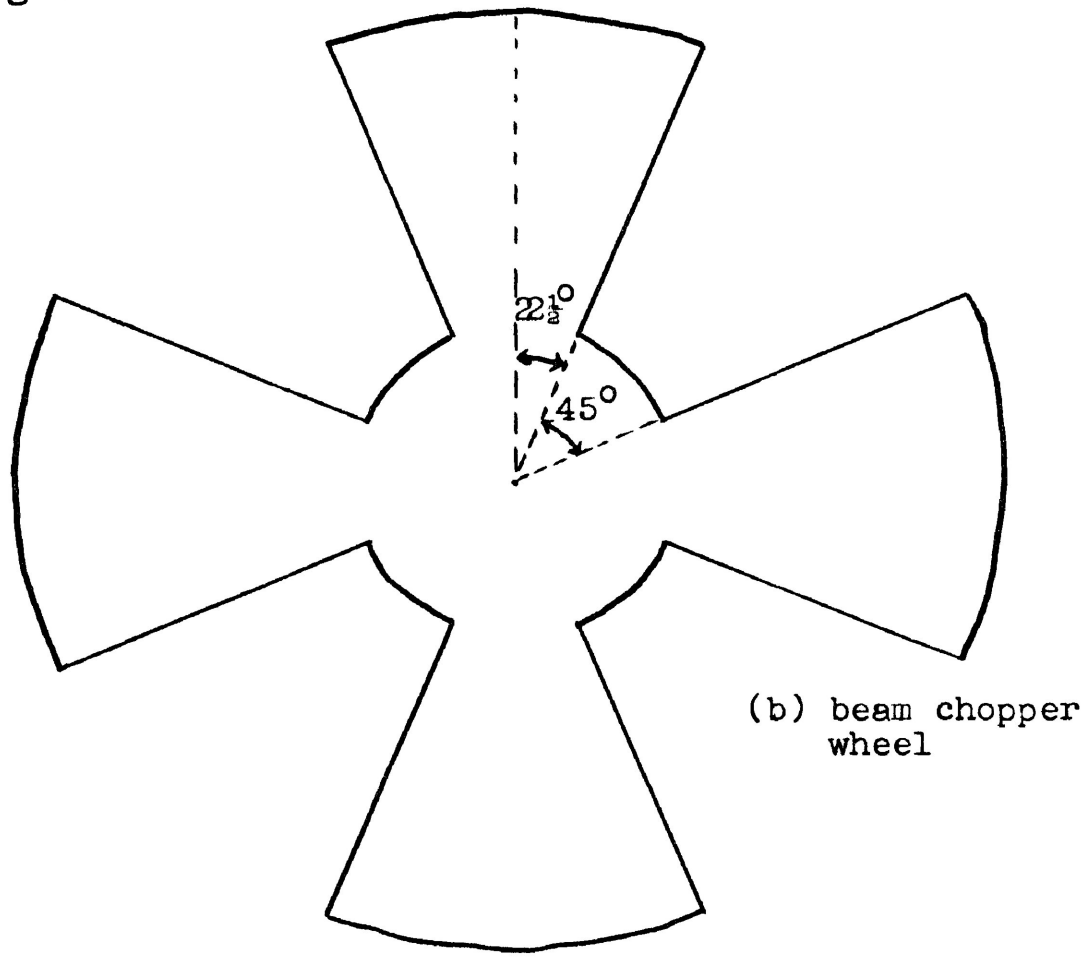


Figure A-1: The two beam-interrupting wheels



beam switcher of Fig. A-1(a). Note that it is suggested that a suitable phase relationship would be that the leading and trailing edges of the cut-out portions of the beam-switching wheel should coincide with the middles of the blanking portions of the beam chopper wheel. The sequence of signals produced by this system for one revolution of the pair of wheels would then be: off, beam 1, off, beam 2, off, beam 1, off, beam 2 .

Having created two alternating beams, one must then recombine them at the detector. For a similar problem in a full double-beam grating spectrophotometer, Helms *et al.*²⁹ have used a pair of mirrors mounted one atop the other to direct the two beams to the same detector. This arrangement does not produce two exactly coaxial beams, but their arrangement was such that the acceptance angle of the Golay cell allowed both beams to be fully captured by this detector. Such an arrangement might well be adapted to the present proposal, with the additional help of a conical light pipe, or light cone, to direct the two beams into the detector.

In Fig. A-2 a suggested arrangement of the optical components of the system is shown. M_1 is the rotating beam-switcher, and M_4 and M_7 are the two mirrors which direct the two beams to the detector via a light cone, LC . In this diagram, the two beams resulting from the beam-switcher have been shown as dashed lines to indicate the relationship of one beam "on" and one beam "off" at a particular instant.

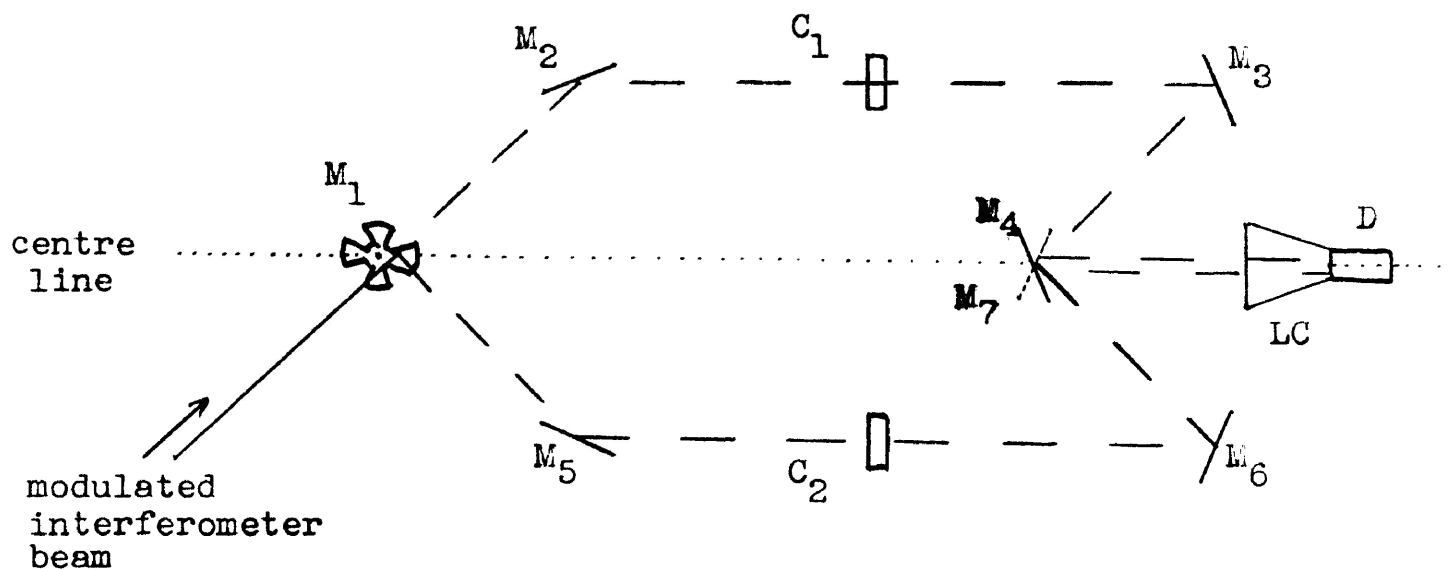


Figure A-2: Arrangement of optical components

- M_1 = rotating beam-switching wheel
- M_2, M_3 = mirrors for beam #1
- M_5, M_6 = mirrors for beam #2
- M_4 = mirror for beam #1 (below M_7)
- M_7 = mirror for beam #2 (above M_4)
- C_1 = cell position in beam #1
- C_2 = cell position in beam #2
- LC = light cone
- D = Golay (or other) detector

The sequence of output signals from the detector would be that of the beams incident upon it as outlined above. The system electronics would then be required to sort out these two signal trains. For this purpose a sort of dual-channel phase-locked amplifier would be required which separated the two sets of signals according to information concerning the position of the beam-switching mirror which could be provided by a suitable transducer. After amplification each signal could be demodulated separately using the same reference signal as supplied by a transducer on the beam chopper wheel. A simple digital logic "flip-flop" type of circuit could be used to direct the detector signal to either of the two amplifier channels. The sequence of signals appearing at the inputs of the two channels after this sorting procedure would then be as follows:

<u>CHANNEL #1</u>	<u>CHANNEL #2</u>
beam "on"	no signal
beam "off"	no signal
no signal	beam "on"
no signal	beam "off"

The demodulated outputs of the two channels could be fed in sequence to an analog-to-digital converter which could punch out the final data on paper tape (or any other suitable form) for presentation to a computer. On the paper tape would be a record of beam transmitted intensities which contained alternately information for beam #1 and beam #2. This final data conversion and output system's choice of which channel to work on at a particular time could also

be governed by the beam-switching mirror's motion.

Perhaps the largest problem in developing such a system would be the amplifier. The response time of a Golay cell is such that it is impractical to attempt to modulate the incident beam at frequencies exceeding 20 hertz. Thus the beam switching could not be done any faster than 10 hertz. This 10 hertz signal would be the input to the two channels of the amplifier, which would have to be designed to have a band width of several hertz, so that the amplifier band width would become an appreciable fraction of the frequency to which the amplifier was tuned. Further, since the incident signal would be modulated essentially by two sources (at 10 and 20 hertz), an appreciable fraction of the total signal intensity would occur at higher-frequency harmonics of their sum frequency, and be lost to an amplifier tuned only to the 10 hertz signal. These problems of amplifier design would require careful study, for they would have to be solveable for the system proposed to be practical.

Appendix II

As outlined in the details of the experimental methods, it was noted that the intensity of radiation transmitted by the sample, as indicated on the strip chart recorder, altered drastically when the sample passed from a rotator to a non-rotator phase during cooling. If this is, in fact, a general feature of most materials, this fact could be put to use in the design of an instrument for the detection of such phase changes. In such an instrument the complex interferometer modulator would not be necessary. It would require the source, chopper, beam filters, phase-locked amplifier, Golay detector, sample temperature indicator-controller, and strip chart recorder. The instrument could then measure, in essence, the integrated transmitted intensity in the far-infrared region as a function of sample temperature. Abrupt changes in this transmitted intensity might indicate changes in the rotational freedom possessed by molecules, thereby detecting a phase change and identifying the associated changes at the molecular level.

(Ref. - 1)

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