

THE INFRARED SPECTRUM OF SOLID METHANOL

by

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I. INTRODUCTION

Though it has been widely recognized that the Debye theory of atomic specific heats¹ has its shortcomings^{2,3,4}, the Debye curve, nevertheless, gives the best agreement between experiment and theory for most elements⁵. In extending this theory to molecular lattices, the classification of the degrees of freedom of the molecule and its atoms complicates the problem. Lord⁶ has derived an expression for the specific heats of molecular crystals which, though useful for many substances, has its inadequacies when applied to others: it is often insufficient for low temperatures, and requires a knowledge of either the rarely accessible expansion data for molecular lattices or their low frequency internal vibrations.

For methyl alcohol neither of these is known at present, but it is possible from theoretical considerations to calculate a value of 660 cm^{-1} for its lowest internal frequency (the others are known), which is due to the motion of the hydroxyl hydrogen perpendicular to the C-O axis. Lawson and Randall⁷, however, found this frequency at 270 cm^{-1} in the vapor spectrum. The difference between these two figures may be qualitatively accounted for, but it seems advisable to take the spectrum of solid methanol in the region from $250\text{-}900 \text{ cm}^{-1}$ so as to obtain the exact magnitude of this frequency which can then be used in the correlation of Lord's equations with experimental observations.

II. THEORETICAL DISCUSSION

In his attempt to interpret the heat capacities of molecular lattices, Lord⁶ found the thermodynamic expression,

$$C_p - C_v = \alpha^2 VT/\beta \quad (1)$$

for the conversion of experimentally determined C_p , the specific heat capacity of the lattice at constant pressure, to C_v , the specific heat capacity of the lattice at constant volume, at any Kelvin temperature, T , may not be used since the values of α , the coefficient of thermal expansion, β , the coefficient of compressibility, and V , the molar volume, all of which are functions of temperature, though often known for atomic lattices, are rarely available for molecular solids.

From a consideration of the equation of state for solids⁹,

$$\alpha = \frac{\beta}{V} k \sum_{j=1}^{j=3N} \frac{x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} \frac{d \ln \theta_j}{d \ln V}$$

where

$$x_j = \frac{\theta_j}{T} = \frac{h\nu_j}{kT}$$

and by breaking up C_v into an extramolecular part, C_{v_L} , and an intramolecular part, C_{v_I} , he derived an alternate expression for $C_p - C_v$:

$$C_p - C_v = (a C_{v_L} + b C_{v_I})^2 T \quad (2)$$

where $a = \frac{d \ln \theta_l}{d \ln V}$ and $b = \frac{d \ln \theta_i}{d \ln V}$ are constants essentially independent of temperature.

In the same paper Lord⁶ developed a method for determining Cv_L and Cv_I by extending to molecular crystals the Debye equation for atomic lattices^{1,10},

$$Cv = 3R \left[\frac{3}{x_{\max}^3} \int_0^{x_{\max}} \frac{x^4 e^x}{(e^x - 1)^2} dx \right] = 3RD(\theta/T) \quad (3)$$

where $D(\theta/T)$ is known as the Debye specific heat function. In order to accomplish this it was proposed that the N atoms of the lattice be grouped into N/S molecules of S atoms each in which case the $3N$ degrees of freedom may be classified into $(3S - 6) N/S$ intramolecular and $6N/S$ extramolecular degrees. The following assumptions were then made:

(1) The frequencies associated with the $(3S - 6) N/S$ degrees of freedom are N/S - fold degenerate.

(2) These N/S - fold degenerate frequencies have approximately the same values as the $3S - 6$ frequencies of the S atomic molecule in the gas phase. Thus the Cv_I can be determined by the Einstein equation for specific heat capacity^{6,11}:

$$Cv_I = \sum_{i=1}^{i=3S-6} Cv_i$$

$$Cv_i = R \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} = E(x_i)$$

where $E(x_1)$ is known as the Einstein specific heat function for one degree of freedom, and

$$x_1 = \frac{h\nu_1}{kT} \cdot C = 1.44 \frac{\nu_1}{T} \quad (4)$$

for values of ν_1 in cm^{-1} .

(3) The $6N/S$ extramolecular degrees of freedom may be classified as $3N/S$ degrees corresponding to translation of the molecules and $3N/S$ corresponding to rotation.

(4) The frequencies associated with both the $3N/S$ translational and the $3N/S$ rotational degrees follow a Debye distribution. Thus from equation (3)

$$Cv_L = Cv_{Lt} + Cv_{Lr} = 3RD_t(\theta_t/T) + 3RD_r(\theta_r/T) \quad (5)$$

(5) Since θ_t and θ_r cannot be determined independently a kind of mean value θ may be substituted for both of them in equation (5); thus

$$Cv_L = 6RD(\theta/T) \quad (6)$$

In many cases this last assumption has shown to be valid only for values of $T > 0.3$ or 0.4θ . In such cases for values of $T < 0.3$ or 0.4θ , θ_T has values lower than θ .

From equation (6) and a further simplification of equation (2) it is possible to compute the approximate magnitude of ν_1 of the lowest frequency internal vibration. Equation (2) is solved for Cv_L :

$$Cv_L = \frac{-(2abCv_I + 1) + \sqrt{1 + 4abCv_I T + 4a^2 T Cp}}{2a^2 T} \quad (7)$$

and it is noted from a glance at Sherman's and Ewell's tables¹² of Cv_i as a function of x_i and a consideration of expression (4) that where $x_i > 10$ at temperatures below

$$T = 1.44 \frac{v_i}{x_i} = 0.144 v_i$$

Cv_i may be considered negligible in comparison to Cp and Cv_L . Thus equation (7) becomes

$$Cv_L = Cv = \frac{-1 + \sqrt{1 + 4a^2 T Cp}}{2a^2 T} \quad (8)$$

as long as $T < 0.144 v_i$.

Using the empirical relationship given for a by Nernst and Lindemann¹³:

$$a = \sqrt{\frac{0.0214}{T_m}}$$

where T_m is the melting point in °K, Cv_L may be calculated from experimental values of Cp at T and a knowledge of the melting point of the particular substance in question. From these values of Cv_L and Beattie's tables¹⁴ for values of θ/T as a function of Cv_L , θ may be determined by equation (6).

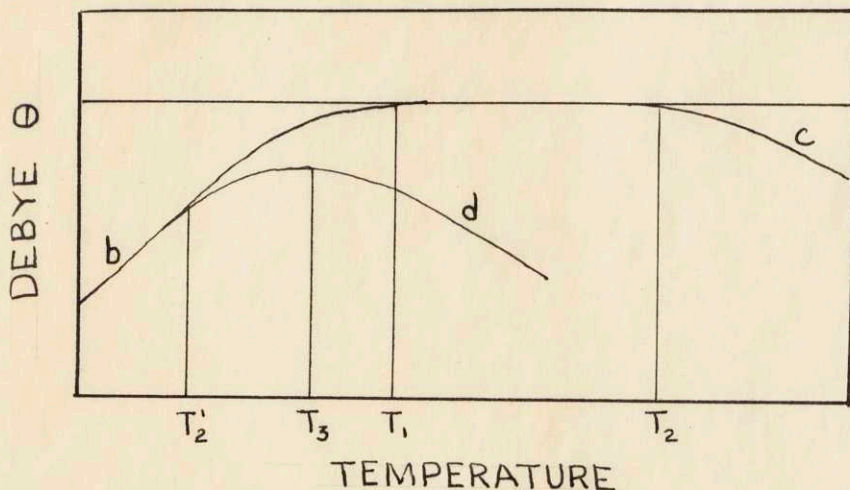


Figure 1

The difference between the theoretical value of Θ and those calculated from equations (8) and (6) may be shown graphically as in Figure 1 where the line a represents the theoretical value of Θ which is constant for all temperatures, and b is a curve of the calculated values of Θ at low temperatures where equation (6) no longer holds. Curve c represents the first case of calculated values of Θ when $T > 0.144 v_1$ (equation (8) becomes void): where $T_2 = 0.144 v_1$ is larger than T_1 , the temperature at which equation (6) becomes valid. In such a case the lowest internal frequency may be qualitatively determined from the relationship:

$$v_1 = 7T_2 \quad (9)$$

Curve \underline{d} represents the second case when $T > 0.144 v_1$: where $T' = 0.144 v_1$ is less than T_1 . In this case only an apparent value for the lowest internal frequency can be qualitatively determined from T_3 , the temperature at which the slope of \underline{d} becomes negative. This calculated v_1 will be of higher magnitude than the actual v_1 and in rare cases may even be higher than the real values of the two lowest internal frequencies.

From the specific heat data of solid methanol by Kelley¹⁵ the Debye θ was determined over a temperature range of 20 -150°K using a melting point of 175.2°K¹⁵ in computing the value of the constant \underline{a} . The results of these calculations are reproduced in Table 1 and plotted as a function of temperature in Figure 2.

v_1 calculated from equation (9) by taking $T_2 = 95^\circ\text{K}$ is approximately 660 cm^{-1} , but it is difficult to determine from this graph whether this is a real or only an apparent value of the lowest internal frequency of methanol. The several approximately equal magnitudes of θ for 75 -95°K causing a flat in that region indicates that 660 cm^{-1} might be the real value of v_1 . The short length of this flat region, however, renders the data inconclusive. It is impossible, moreover, to discount lower frequencies since the use of a second parameter, \underline{b} , in computing θ by means of equations (7) and (6) allows a θ which is constant over a large temperature range at $T > 100^\circ\text{K}$ to be calculated for v_1 as low as 250 cm^{-1} .

TABLE 1

| $T(^{\circ}\text{K})$ | $C_p(\text{cal/mol})^{15}$ | $\theta(\text{calc})$ | $T(^{\circ}\text{K})$ | $C_p(\text{cal/mol})^{15}$ | $\theta(\text{calc})$ |
|-----------------------|----------------------------|-----------------------|-----------------------|----------------------------|-----------------------|
| 21.6 | 1.51 | 177 | 81.5 | 9.00 | 229 |
| 34.3 | 3.44 | 198 | 85.5 | 9.30 | 228 |
| 43.9 | 4.84 | 216 | 89.3 | 9.69 | 227 |
| 56.0 | 6.43 | 221 | 93.2 | 9.94 | 229 |
| 59.5 | 6.85 | 220 | 97.2 | 10.23 | 225 |
| 63.3 | 7.25 | 219 | 111.1 | 11.23 | 216 |
| 70.0 | 8.00 | 225 | 121.4 | 11.75 | 219 |
| 74.0 | 8.39 | 226 | 133.7 | 12.64 | 191 |
| 77.6 | 8.74 | 228 | 147.9 | 12.97 | 205 |

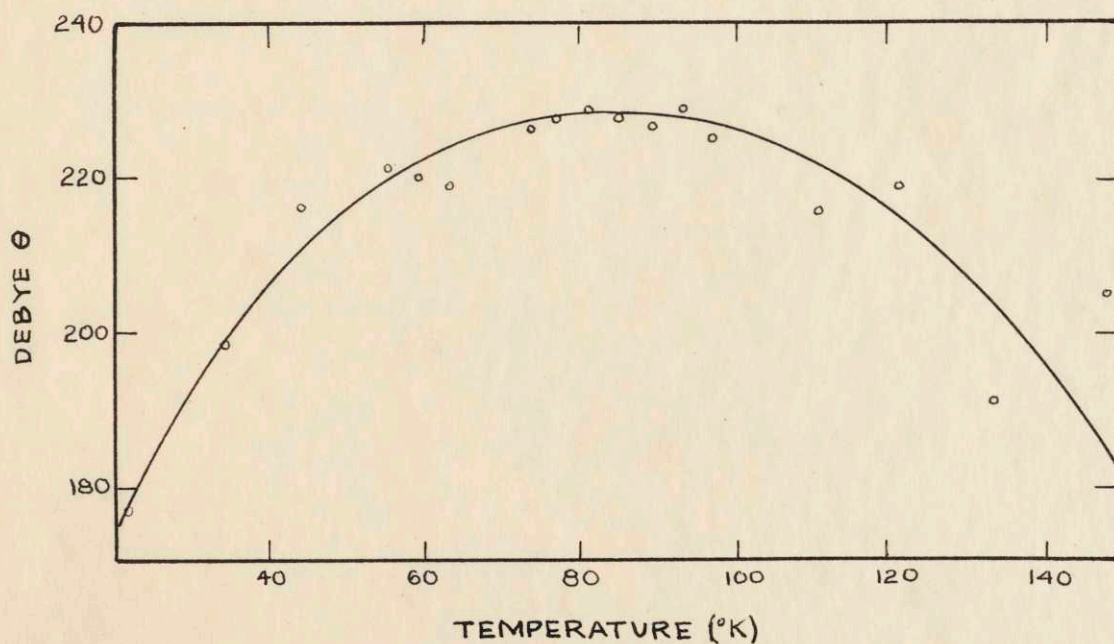


Figure 2

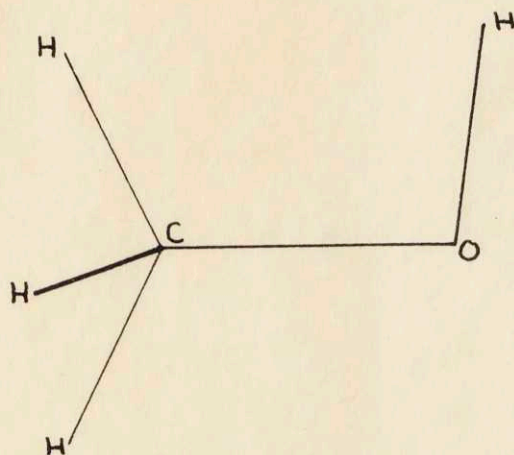


Figure 3

Borden and Barker¹⁶, on taking the infrared spectra of methanol vapor, discovered a broad region of absorption consisting of many bands between 860 cm^{-1} and 380 cm^{-1} (the low frequency limit of their experiments), and predicted that the region of most intense absorption would occur at 360 cm^{-1} . Lawson and Randall⁷, however, took the spectrum further into the infrared and found the wide absorption region culminated in a band of strong intensity at 270 cm^{-1} .

On the basis of Figure 3, assumed to be the structure of methanol, this low frequency absorption has been analyzed by Borden and Barker in their paper and also in an article by Koehler and Dennison⁸. The following material is a summary of their analyses.

It was proposed that the molecule approximates a symmetric top rotator, the slight asymmetry being due to the relatively light hydroxyl hydrogen (hereafter denoted by H),

with the moment of inertia about the principal A axis, the C-O axis, broken into two parts: I_{A1} , the moment of inertia of the OH bar, and I_{A2} , the moment of inertia of the methyl group.

For this picture of the methanol molecule one might expect an internal rotation of the OH bar with respect to the methyl pyramid. It is useful to consider the methyl group as being stationary, since the rotation of an isolated $-CH_3$ about the A_2 axis produces no change in dipole moment and hence is inactive in the infrared, and consider all the internal energy causing the rotation as concentrated in the OH bar. For such a case the selection rules for the pure rotational spectrum will be

$$\Delta J = 0, \pm 1 \quad \Delta K = \pm 1 \quad \Delta K_1 = \pm 1 \quad \Delta K_2 = 0$$

where K_1 and K_2 are quantum numbers referring to the hydroxyl and methyl groups respectively, and J and K are the quantum numbers referring to the whole molecule.

Herzberg¹⁷ derived a formula for the Q branch of the pure internal rotation spectrum where $\Delta J = 0$:

$$v = A_1 - B \mp 2BK \pm 2A_1K_1 \quad (10)$$

where $A_1 = \frac{h}{8\pi^2 c I_{A1}}$ and B is the constant associated with the degenerate moment of inertia around the axis perpendicular to the A axis. The upper signs hold for positive ΔK and ΔK_1 and the lower, for negative ΔK and ΔK_1 . Since $A_1 \gg B$,

equation (10) represents a series of bands of spacing $2A_1$. Borden and Barker assigned the $600-800\text{ cm}^{-1}$ bands which were spaced at approximately 40 cm^{-1} as these pure rotational bands and calculated from their spacing an O-H distance of about 0.92 \AA .

Below 600 cm^{-1} however, the spacing of the bands decreases, while their intensity increases. This may be explained by considering the hindering effect of the methyl hydrogens on the rotation of the OH bar. An energy level diagram of this effect is shown schematically in Figure 4, which is a plot of the internal potential energy as a function of the angle of rotation of the OH bar with respect to the methyl group. The large splitting of the level $n = 1$ and higher levels is caused by passage through the potential barrier and accounts for the complicated spacing of the bands in the region of $270-600\text{ cm}^{-1}$.

The intense absorption at 270 cm^{-1} may be accounted for by identifying that frequency with the fundamental transition from $n = 0$ to $n = 1$, which corresponds to a perpendicular vibration of the H.

If one is to assume that this one of the 3S-6 frequencies of methanol has approximately the same value in the solid as in the vapor phase, then the author's calculation of 660 cm^{-1} for the lowest internal frequency of the molecule is only an apparent value.

From considerations of this oscillation in the liquid and solid states, however, a reasonable shift to higher fre-

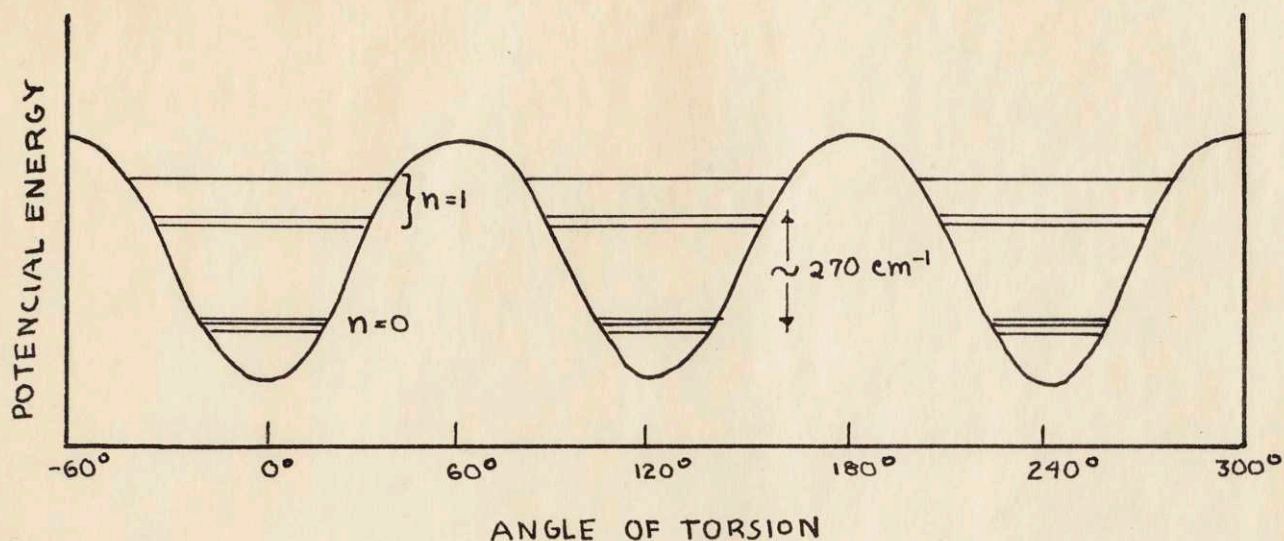


Figure 4

quencies may be expected. Errara, Gaspart, and Sack¹⁸ from investigations of the O-H stretching frequency in the vapor, liquid, and dilute solutions in inert solvents concluded that intermolecular H-O association explains the shift of that vibrational frequency from 3682 cm^{-1} in the vapor to 3400 cm^{-1} in the liquid. This shift to lower frequencies is probably due to the weakening of the intramolecular O-H bonding. But for the perpendicular torsional oscillation intermolecular association might be expected to increase the force acting on a displaced H thereby increasing the frequency of the vibration.

The following effects appear simultaneously on liquification: (1) the height of the potential barrier will be increased to infinity resulting in the disappearance of the rotational bands; (2) the number of minima per 360° will be increased many times; (3) the fundamental frequency for the

transition from $n = 0$ to $n = 1$ should shift from 270 cm^{-1} to a higher value, but the random orientation of the molecules in the liquid phase makes these changes indiscrete. These effects should manifest themselves in the appearance of a broad band with its center at a value higher than 270 cm^{-1} .

On solidification the formation of a definite lattice structure should result in the sharpening of the broad band in the liquid spectrum and its center should be at the same frequency as that of the liquid.

III EXPERIMENTAL ARRANGEMENT AND PROCEDURE

Low Temperature Apparatus

The low temperature apparatus used to take the spectrum of solid methanol is shown full size in Figure 5. It consisted of a cold finger in thermal contact with a copper cell-holder which was suspended in an evacuated system. The path of the energy through the instrument may be represented for the right hand drawing of the figure by a line parallel to the horizontal dimension of the paper.

The apparatus was cooled by introducing at N liquid nitrogen which then rests in the copper well, E. A threaded brass sleeve, G, was soldered onto E so that the copper cell-holder, C and B, which was screwed onto G, could be easily removed. The walls of the well, E, were too thin to thread. Copper was chosen for the cell-holder, C and B, because of its high thermal conductivity. Previously, a brass cell-holder of similar dimensions was tried, but this took two to three hours to cool to temperatures about 180°K and would then get no colder.

The cell, A, was made of two KBr plates separated by a thin silver spacer which was almagamated in order to get a tight seal. It was filled by placing the spacer on one of the KBr plates, adding a few drops of methanol to be tested, and sliding the second plate into place in such a manner as to rid of air bubbles the space intended for the methyl alcohol. The KBr plates had first been ground on fine emery paper, then

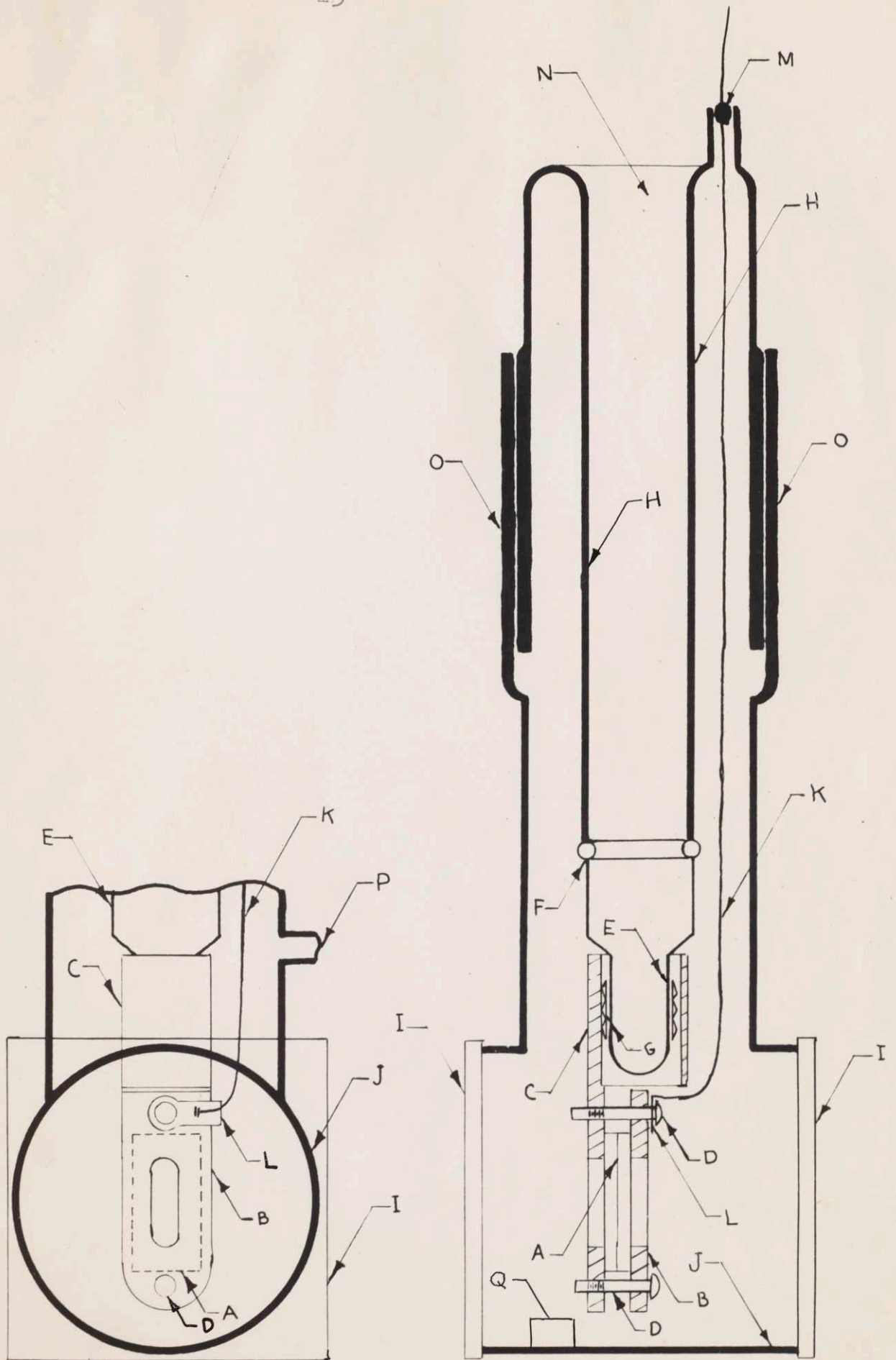


Figure 5

polished on a pitch lap with buffing powder as an abrasive. They often, but not always cracked at temperatures around 125°K. By rough observation it was noted that the methanol seemed to solidify into one crystal which took advantage of all the space provided for it. The cell was clamped into place by tightening the screws, D, connecting the two copper cell-holder plates, B and C, which were amalgamated to make good thermal contact with the salt plates.

The cylindrical pyrex column, H, was connected to that part of the apparatus already described by joining it onto the nonex ring, F, which was part of the General Electric copper to glass joint, E to F. A ring seal connected H to the male part of a 50/50 ground glass joint, the female part of which was joined to the pyrex tube, J. Stopcock grease, when used to seal the ground glass joints at O, flowed when a vacuum was applied to the system. This caused the joints to make too good a contact with each other over so large an area that too great a force had to be applied to separate the joints. A non-flowing seal, Apiezon black wax, therefore, was used. In order to seal and separate the joints successfully, they had to be heated to the melting point of the wax for each operation.

Two KBr plates, I, polished in the same manner as those used for the cell, were sealed to the pyrex tube, J, with glyptal. The KBr windows restricted the use of the apparatus to wave lengths lower than 35 μ .

A constantin-copper thermocouple, K, introduced into the instrument through the Apiezon black wax seal at the outlet, M, was soldered to a lug, L, which made thermal contact with one of the screws, D, and the copper plate, B. Though more accurate knowledge of the temperature of the methanol might have been obtained by connecting the thermocouple directly to the KBr cell plate, A, the difference between the temperature of the copper cell-holder, B, and the sample was probably not more than 10 or 20°. This figure was ascertained by running the spectrometer at a constant wave length of approximately 15μ while cooling the methanol, and noting that a sharp discontinuity appeared in the transmission curve, which was attributed to the phase transition of methyl alcohol at 175.2°K, when the thermocouple read a value corresponding to about 160°K.

It was desirable to evacuate the system, by applying a vacuum through a stopcock connected to P, to prevent condensation of moisture on the KBr plates, A and I, and to cool the cell to lower temperatures than might otherwise be permissible. With a vacuum in the apparatus no water vapor would be present to condense on the cell plates, A, and now the only possible mechanisms of cooling down the KBr windows, I, were by loss of heat by conduction along the walls of the instrument, or by radiation. The apparatus was found to be vacuum tight but all precautions taken to prevent loss of sample from the cell were of no avail since the vapor pressure of methanol is very high at room temperature. By placing a small cup of P_2O_5 , Q, in the system before sealing the ground glass joint, however,

and closing off the apparatus to the air for an hour before running a curve, the air inside the instrument had sufficiently dried so that no moisture condensed on the inner cell windows, A, on cooling down to a temperature near the freezing point of methyl alcohol. Here the vapor pressure of the methanol is so low that a vacuum could be applied in order to cool the system to lower temperatures without loss of sample. Some moisture condensed on the outside KBr windows, I, before the system was evacuated. These were wiped, but more water vapor condensed, though more slowly, even after a vacuum had been applied. The windows were wiped, therefore, whenever it was suspected that the condensed moisture was cutting down the transmission of energy.

When liquid air was continuously present in the well, E, it took less than one-half hour to cool the apparatus in the above manner to a thermocouple reading corresponding to 110°K .

It is conceivable that the low temperature cells devised by Conn, Lee, and Sutherland¹⁹ and Avery and Morrison²⁰ might have been used for these experiments. But the complexity of the optical paths needed for these instruments restricts their applicability. In addition to this disadvantage, Avery's and Morrison's apparatus was limited to use with solids only. Since the mirror on the bottom of their cell was not flat, liquids could not be distributed to an even thickness but would flow to the middle. It, therefore, seemed advisable to design and construct an apparatus for the more general case when the optical path is direct, and to one that would take the spectrum of both solids and liquids at low temperatures.

Other Equipment

The cell used to take the spectrum of methanol vapor was a modification of the type built by White²¹. Thallium-bromo-iodide windows on this cell allows the spectrum to be taken out as far into the infrared as 45μ with a thallium-bromo-iodide prism.

A Perkin-Elmer infrared spectrometer was employed which was modified to permit an alternate optical system to be used with the gas cell. The approximate resolution of the instrument for the various prisms used is given in Table 2.

TABLE 2

| <u>Prism</u> | <u>Resolution</u> | <u>Region</u> |
|--------------|-----------------------|-----------------------|
| NaCl | 2.5 cm^{-1} | 750 cm^{-1} |
| KBr | 5 | 600 |
| KRS-5 | 10 | 350 |

A General Motor's amplifier and a Brown potentiometer were employed in transmitting the thermocouple signal to an energy transmission curve. The source was a globar

The sample used was Mallinckrodt C.P. acetone free methyl alcohol which had a minimum assay of 99.5 and a boiling point range of $64-67.5^{\circ}\text{K}$. No further purification was attempted.

Experimental Curves

The author desired to get a complete spectrum of the vapor, liquid, and solid phases in the region $950\text{-}250\text{ cm}^{-1}$. The outer KBr windows on the low temperature apparatus, however, set a practical lower limit at 300 cm^{-1} for spectra taken in that instrument. Because there was no indication of sharp bands above 750 cm^{-1} in the liquid and solid spectra taken with the KBr prism, it seemed unnecessary to run these two phases with the NaCl prism.

Table 3 gives a complete summary of the curves taken. They are numbered according to their designation in Figure 6 and not in the order which they were run.

TABLE 3

| <u>Curve</u> | <u>Phase</u> | <u>Path length</u> | <u>Pressure</u> | <u>Prism</u> | <u>Region</u> |
|--------------|--------------|--------------------|-----------------|--------------|---------------------------------|
| (1) | Vapor | 160 cm | 60 mm | NaCl | $960\text{-}650\text{ cm}^{-1}$ |
| (2) | Vapor | 160 cm | 60 | KBr | 710-385 |
| (3) | Vapor | 160 cm | 30 | KBr | 470-385 |
| (4) | Liquid | 0.01 mm | - | KBr | 970-385 |
| (5) | Solid | 0.01 mm | - | KBr | 970-610 |
| (6) | Solid | 0.025 mm | - | KBr | 970-385 |

It was unfortunate that the thermocouple of the spectrometer burned out in the middle of curve (5) before the sample had been run with the thallium-bromo-iodide prism. If it is replaced before completion of this report, methanol spectra will

be taken in that region and the results presented in an appendix.

Curve (4) and Curve (5) were different phases of the same sample; the former, run in the dried atmosphere at room temperature, and the latter at 110°K after cooling down and then evacuating.

Radiation curves to represent 100% transmission were taken in the evacuated gas cell, and in the low temperature apparatus with a single KBr plate in the cell-holder and the system evacuated. In addition a spectrum of the inner salt plates to be used in the low temperature cell was taken and no absorption due to impurities noted. In this manner any irregularities in the transmission curve due to absorption by substances in the path of the energy would remain fixed.

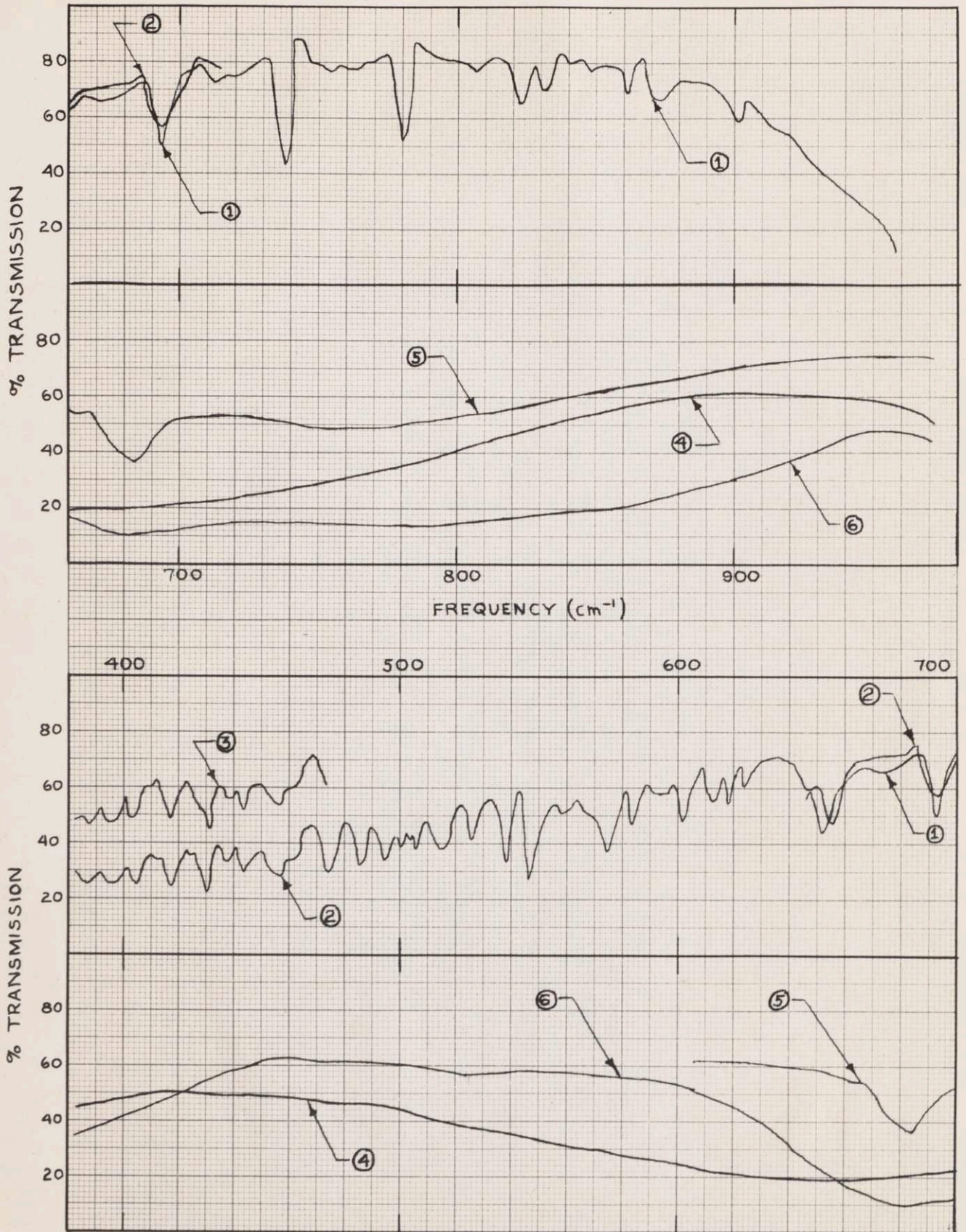


Figure 6

RESULTS

The curves taken are summarized in Figure 6 where per-cent transmission is plotted as a function of the frequency in wave numbers.

The most intense lines in the region of absorption in the vapor are compared to those obtained by Borden and Barker¹⁶ in Table 4. The agreement between the two sets of values is in general within reasonable error. The presence of water in the author's sample may account for some of the discrepancies observed between the two sets of data. The line at 526 cm^{-1} may be due to the strong rotational band of water vapor²² at that frequency, and the shift from 452 to 457 cm^{-1} may be caused by the strong absorption band in the H_2O rotational spectrum at 458 cm^{-1} . It is unlikely, however, that the strong band found in the methanol sample at 430 cm^{-1} may be attributed to the relatively weak absorption band of water vapor at 432 cm^{-1} .

The line at 902 cm^{-1} might be due to a higher rotational transition than was observed by Borden and Barker since it is about 40 cm^{-1} above the 860 cm^{-1} band. Possibly this line in their spectrum was washed out by the strong vibrational band at 1034 cm^{-1} . The absorption at 873 and 833 cm^{-1} cannot be accounted for by the author, but the fact that they are separated by 40 cm^{-1} may have some significance.

The appearance of the liquid spectrum (4) substantially agrees with that predicted. The rotational lines disappeared and the vibrational frequency, at 270 cm^{-1} in the

TABLE 4

| Salter | Borden and Barker ¹⁶ | Salter | Borden and Barker ¹⁶ |
|----------------------|---|----------------------|---|
| 902 cm ⁻¹ | - | 515 cm ⁻¹ | $\left\{ \begin{array}{l} 517 \text{ cm}^{-1} \\ 515 \end{array} \right.$ |
| 873 | - | | |
| 861 | 860 cm ⁻¹ | 506 | 506 |
| 833 | - | 500 | 501 |
| 822 | 821 | 494 | 495 |
| 780 | $\left\{ \begin{array}{l} 780 \\ 778 \end{array} \right.$ | 486 | $\left\{ \begin{array}{l} 486 \\ 484 \end{array} \right.$ |
| 738 | | 737 | |
| 693 | 695 | | $\left\{ \begin{array}{l} 464 \\ 462 \\ 460 \end{array} \right.$ |
| 654 | (650) | 463 | |
| 624 | 624 | | |
| 618 | 618 | 457 | 452 |
| 612 | 611 | 444 | 444 |
| 602 | 600 | 448 | 440 |
| 583 | 583 | 430 | - |
| 574 | 575 | 417 | 416 |
| 546 | 549 | 404 | 401 |
| 538 | $\left\{ \begin{array}{l} 541 \\ 540 \end{array} \right.$ | 396 | 392 |
| | | | 386 |
| 526 | - | | |

vapor, was broader and shifted to a higher value in the liquid. The center of this wide band was about 650 cm^{-1} . The sharpening of the 650 cm^{-1} band in the solid spectrum (5) also agrees with theory. That its center had shifted to 684 cm^{-1} may be accounted for by the fact that the most popular arrangement of molecules in the liquid is not necessarily the same as the configuration of the crystalline solid.

Two unusual features appeared in the spectrum (6) of the thicker sample of solid methanol. The first is the large amount of absorption on the high frequency side of the 684 cm^{-1} band. This is not consistent with the spectrum of the thinner sample which appeared symmetrical on either side of the band. The author finds it difficult, indeed, to adequately account for this absorption. The second feature is the drop in transmission observed at the low frequency end of the spectrum. It is possible that this absorption may be explained by assigning the fundamental frequency of the torsion oscillation in methanol to a band at 342 cm^{-1} in which case the observed band at 684 cm^{-1} would be a first overtone of this fundamental. The trend, though slighter, also seems to be present in the liquid spectrum. It now appears extremely unfortunate that the instrument went out of order before the methyl alcohol spectra were taken in the low frequency region with the thallium-bromo-iodide prism to substantiate this last hypothesis.

In comparing the intensities of the spectra (1) and (2) to (4) and (5) one should note that the number of molecules

in the path of the energy is ten times as great in the former as in the latter. This, however, has no effect on the author's interpretation of the data. Parts of the vapor spectrum were also run at 15 mm pressure, and, while the intensity of the bands decreased, they, nevertheless were still observable. The ratio of the number of molecules of methanol in the path of the energy in (3) to those in (6) is 2:1.

If the 684 cm^{-1} band is the fundamental frequency, then the 660 cm^{-1} frequency calculated from theory represents the real value of the lowest internal frequency within reasonable error. Then the Debye θ in Figure 2 reaches its constant value of 228 before decreasing again. Taking a known C_p at a temperature above T_1 (Figure 1) and solving equation (2) for \underline{b} , one may compute the magnitude of \underline{b} . For $\nu_i = 684 \text{ cm}^{-1}$ and $\theta = 228$, $b = 0.205$. C_p at various temperatures may be calculated from these values and equations (6) and (2) and compared to the experimental C_p^{15} . This is done in Table 5. where column 3 is the calculated C_p for the 684 cm^{-1} band.

If, however, there is a strong band at 342 cm^{-1} , it must be the low frequency fundamental, and the theoretical value of 660 cm^{-1} is only the apparent ν_i . Utilizing the C_{v_i} from this 342 cm^{-1} band, the observed specific heat data and equations (8) and (6), one may determine a Debye θ which increases over the low temperature region until it reaches a value of about 241 at 100°K and remained approximately constant to the transition temperature, 157°K . For this frequency, therefore, $\theta = 241$ and the product of bC_{v_i} must be negligible

TABLE 5

| T(°K) | Cp _{exp} (Cal/mol) ¹⁵ | $v_i = 684$ | $v_i = 342$ |
|-------|---|------------------------------|------------------------------|
| | | $\theta = 228, b = 0.205$ | $\theta = 241, b = 0$ |
| | | Cp _{Calc} (Cal/mol) | Cp _{Calc} (Cal/mol) |
| 21.6 | 1.51 | 0.78 | 0.68 |
| 43.9 | 4.84 | 4.21 | 3.79 |
| 59.5 | 6.85 | 6.51 | 6.11 |
| 70.0 | 8.00 | 7.84 | 7.52 |
| 77.6 | 8.74 | 8.61 | 8.32 |
| 89.3 | 9.69 | 9.63 | 9.38 |
| 97.2 | 10.23 | 10.23 | 10.13 |
| 111.1 | 11.23 | 11.16 | 11.18 |
| 118.0 | 11.64 | 11.59 | 11.70 |
| 125.4 | 12.18 | 12.07 | 12.12 |
| 129.4 | 12.28 | 12.29 | 12.32 |
| 133.7 | 12.64 | 12.67 | 12.60 |
| 147.9 | 12.97 | 13.68 | 13.30 |
| 152.3 | 13.69 | 14.21 | 13.52 |

in comparison

to $a \cdot Cv_L$ since no decrease in calculated θ was observed at high temperatures (150°K). The calculated Cp taking $v_i = 342$, $\theta = 241$ and $b = 0$ is given in column 4 of Table 5.

There is good agreement in each case between calculated and experimental Cp above T_L and below the transition temperature at which point the Einstein and Debye theories no longer give

a complete picture of the specific heat capacity. Because of this agreement for both frequencies, assignment of the fundamental frequency cannot be made from these considerations.

V. FUTURE WORK

As soon as the thermocouple in the Perkin-Elmer spectrometer has been replaced, the author hopes to run the spectrum of solid methanol in the region $400-250\text{ cm}^{-1}$ to ascertain whether or not an absorption band is present around 342 cm^{-1} .

It might also be profitable to study the spectrum of methanol vapor at different pressures, and methanol liquid as solute in varying concentrations in a non-polar solvent over the region $900-250\text{ cm}^{-1}$. In the case of the vapor, at very low pressures weak rotational lines should be observed culminating in a stronger band at 270 cm^{-1} . On increasing the pressure the intensity of these bands should increase until it reaches a maximum. At still higher pressures intermolecular association may be expected to take place resulting in a decrease in the intensity of the rotational levels and the appearance of a broad background of absorption with its center at 650 cm^{-1} . In the case of the liquid the opposite effect should take place. As the concentration of liquid methyl alcohol in a non-polar solvent decreases the breaking up of the intermolecular forces should result in the slow disappearance of the broad band at 650 cm^{-1} and the introduction of a comparatively sharp band at 270 cm^{-1} .

Other molecules for whom the specific heat data is known, but the lowest internal frequency is not might be studied by comparing the value for ν_1 obtained by

$$\nu_1 = 7T_2$$

with the spectrum of the crystalline solid.

SUMMARY

1. From theoretical considerations an upper limit of approximately 660 cm^{-1} has been set for the lowest internal frequency of solid methyl alcohol.
2. This frequency appears at 270 cm^{-1} in the vapor, but one can predict that this would shift to higher frequencies in the liquid and solid spectra.
3. A band at 684 cm^{-1} was found in the solid spectrum, and at 380 cm^{-1} , the lower frequency limit of the spectra taken, there was a trend toward another absorption band possibly at 342 cm^{-1} in which case the 684 cm^{-1} band would be the first overtone. The author was unable to prove conclusively the frequency of the fundamental in the solid.
4. The Debye θ of solid methyl alcohol was calculated for each possible value of the lowest internal frequency:

$$\nu_1 = 684 \text{ cm}^{-1}, \quad \theta = 228$$

$$\nu_1 = 342 \text{ cm}^{-1}, \quad \theta = 241$$

5. An apparatus for taking the infrared spectra of liquid and solids at temperatures as low as 100°K was designed and constructed.

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