PART I. STUDIES OF SOME ABSORPTION SPECTRA IN THE PHOTOGRAPHIC INFRA-RED.

PART II. STUDIES OF THE HYDROGEN BOND.

PART III. THE RAMAN SPECTRA OF $CCl_2F-CClF_2$ AND $CClF_2-CClF_2$.

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PART I. STUDIES OF SOME ABSORPTION SPECTRA IN THE PHOTOGRAPHIC INFRA-RED.

ABSTRACT

Absorption of formaldehyde and difluoro-methane under low dispersion in the photographic infra-red region is described, and approximate vibrational assignments made. An attempt was made to study some of the bands of difluoro-methane under high dispersion, but does not yield much information. The C-H band of formic acid monomer photographed under high dispersion is discussed. It has the same rotational structure as the O-H bands. The small moment of inertia is calculated for the third C-H vibrational state, and the band origin located.

STUDIES OF SOME ABSORPTION SPECTRA IN THE PHOTOGRAPHIC INFRA-RED.

1. Formaldehyde.

The spectrum of formaldehyde vapor has heretofore never been photographed in the infra-red region. It was the purpose of this investigation to do this, and it was further hoped that the third harmonic C-H bands might be obtained and photographed under high dispersion, thus possibly yielding data of interest regarding molecular constants in the excited state. The third harmonic bands lie at too long a wave length to accomplish this, however, as will be described below.

The infra-red spectrum in the fundamental region and some of the ultra-violet spectrum have been obtained under high dispersion[1] and analyzed. The fundamental C-H stretching frequencies are at 2875 cm.$^{-1}$ for the perpendicular vibration and 2780 cm.$^{-1}$ for the parallel. These are markedly low as compared with C-H frequencies in other molecules, but if the anharmonicity constant were normal, it was thought that the third harmonics might lie in the photographically attainable region.

Experimental Procedure.

The main concern in working with formaldehyde vapor is the prevention of polymerization to solid products on the walls and windows of the absorption tube. By having the walls very clean and the for-

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(1) Infra-red: Ebers and Nielsen, J. Chem. Phys., 6, 311 (1938).
Ultra-violet: Dieke and Kistiakowsky, Phys. Rev., 45, 4 (1934).

maldehyde very pure, it is possible to keep the material for several hours without polymerizing. The procedure followed in preparing pure formaldehyde was that of Spence and Wild[2]. The absorption tube and preparation apparatus were well cleaned with cleaning solution before use, and baked out to remove oxygen. The preparation system was sealed directly to the absorption tube, and no stopcocks were used. This treatment did prevent polymerization in the main part of the system, but where the vapor came into contact with mercury, as in the manometer and liquid air trap to the mercury pump, polymerization occurred. This was not rapid enough to cause any trouble, however.

The pressure was regulated by the temperature of a cold acetone bath on the trap containing liquid formaldehyde. During the exposure it was kept at fifty centimeters. The absorption tube was ten feet long. A Bausch and Lomb Littrow glass prism spectrograph having a dispersion of 70 Å. per mm. in this region was used, with a slit of .1 mm., and Eastman 1 Z plates hypersensitized with ammonia solution. The source was a 500 watt tungsten projection lamp. The wave-length calibration was obtained from Na, K, Ca, and Ba arc lines, from the salts on a carbon arc. A background exposure using the empty absorption tube was taken alongside the absorption exposure.

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(2) Spence and Wild, J. Chem. Soc., 338 (1935).

Results.

There was no absorption found in the third harmonic region strong enough to be seen, although the plate was darkened to about 11,900 Å., the limit of its sensitivity. Two weak higher harmonic bands were observed, at 10,355 Å. and 9590 Å. (9654 cm.$^{-1}$ and 10,425 cm.$^{-1}$, respectively). The latter of these had a doublet structure. Neither of these was attempted with high dispersion; because of their weakness, a much longer absorption path would be required.

Discussion.

The doublet nature of the 10,425 cm.$^{-1}$ band is indicative of a parallel-type band; this band is also in the correct region for a fourth harmonic C-H stretching vibration band. Hence, it may be either the $4\nu_{\parallel}$ or the $2\nu_{\parallel} + 2\nu_{\perp}$ overtones. Assuming it is $4\nu_{\parallel}$, one calculates an anharmonicity constant $\omega_e x_e$ of 58 cm.$^{-1}$, which is abnormally high compared with C-H vibrations of other molecules, where it is 35 cm.$^{-1}$ on the average. This together with the low fundamental frequencies explains why the third harmonic falls at such a long wave length that it could not be found with the photographic technique; it would occur at 12,500 Å. Indeed, the absorption curves from 1 to 5 μ published by Patty and Nielsen[3] show a band

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(3) Patty and Nielsen, Phys. Rev., 39, 957 (1932).

at 1.25 μ, which is therefore one of the third harmonic C-H stretching vibrations.

The 9654 cm.$^{-1}$ band is undoubtedly a combination of a third harmonic C-H stretching vibration with one of the 1500-1700 cm.$^{-1}$ frequencies.

2. Difluoro-methane.

This molecule was investigated to determine its general absorption in the photographic region, and particularly to obtain the fine structure of the third harmonic C-H bands, since the moments of inertia are sufficiently small so that this might be accomplished. It was not found possible to do this, however, because of the overlapping of a strong atmospheric water absorption band.

Experimental Procedure and Results.

A small cylinder of difluoro-methane was obtained through the courtesy of Dr. A. F. Benning of the DuPont de Nemours Company. The boiling point was given as -51.7°, and the sample was substantially pure. The sample was held in a trap in a dry ice-acetone bath, and the absorption tube was filled by warming the trap until a suitable pressure was obtained.

A low dispersion photograph was taken, with the gas at a pressure of fifty centimeters in a six meter absorption tube. The low dispersion spectrograph, photographic materials and wave length calibration were as described previously. Several bands were observed, whose wave lengths and probable assignments are given in Table I.

The four third harmonic bands were fairly strong; the two low frequency ones of these are in the low sensitivity region of the plate, however. The 11,410 Å. band had an envelope of the perpendicular type, while the 11,250 Å. band had one of the parallel type, with a well-defined doublet structure. Figure 1 shows the appearance of these envelopes, as idealized from a microphotometer trace and visual inspection. The combination and fourth harmonic bands were extremely weak.

Table I. Bands of CH_2F_2 in the photographic infra-red region.

λ(Å.)	ν(cm.$^{-1}$)	Assignment
11,790	8,480	Third harmonics of C-H stretching
11,620	8,610	
11,410	8,760	
11,250	8,890	
10,350	9,660	Combinations of above with 1000-1300 cm.$^{-1}$ frequencies.
10,200	9,800	
10,080	9,920	
9,740	10,270	
8,970	11,140	Fourth harmonics of C-H stretching
8,890	11,240	

Several attempts were made to obtain high dispersion photographs of the 11,410 Å. band. A six meter absorption tube was first used, with a 32-32 candle power headlight lamp as source. The spectrometer used was the twenty-one foot grating spectrometer, having a dispersion of about 2 Å. per mm. in this region. The slit width was .2 mm. Hypersensitized Eastman 1Z plates were employed. Third

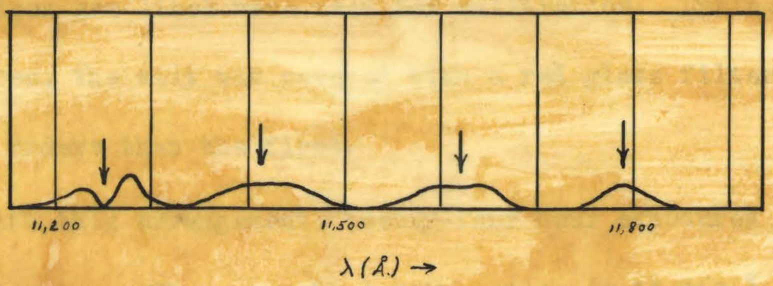

Figure 1. Bands of CH_2F_2, 11,000 Å. to 12,00 Å. Envelopes of two low frequency bands are not known.

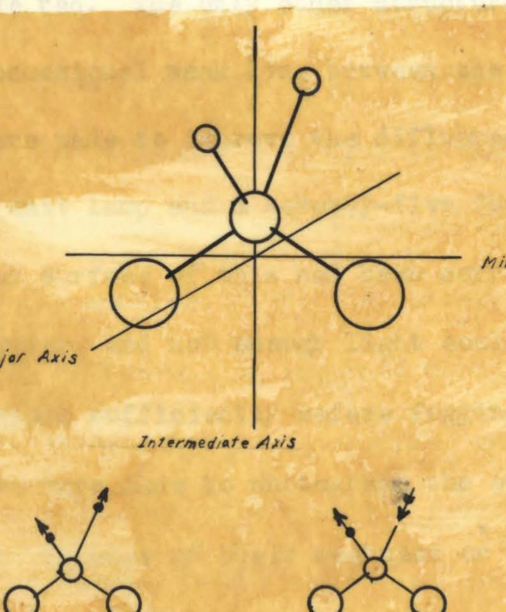

Figure 2. Axes of inertia and CH stretching vibrations for CH_2F_2.

order iron arc lines were used for calibration. During absorption exposures, the slit was covered with a red glass filter to cut out higher orders than the first.

With this arrangement, twenty-four hour exposures gave fairly good pictures. The water band with origin at 11,360 Å. overlies this whole region, however. The structure of the difluoro-methane bands stands out so little from the background that the water lines precluded any further analysis. There was a strong sharp Q branch observed, whose sharp edge lay at 11,247.7 Å., just at the center of the band measured in low dispersion, and which converged rather unusually to the red. The only other structure that could be detected was an occasional weak line between the water lines.

Efforts were made to improve the difluoro-methane absorption by using a 500 watt lamp and a seventy-five foot steel absorption tube. The inner surface of this had been corroded by previous use with acids, however, and not enough light could be gotten through to expose the plate sufficiently before fogging occurred.

No attempts were made to photograph the other bands under high dispersion, because of their weakness or unfavorable situation.

Discussion.

If one accepts the assignments of the four bands in the 11,000 Å. region as the four third harmonics of the symmetric and antisymmetric C-H stretching vibrations ν_s and ν_a, then two of the bands,

$3\nu_s$ and $\nu_s + 2\nu_a$, will arise from electric moment changes along the intermediate axis of inertia, and the other two, $2\nu_s + \nu_a$ and $3\nu_a$, will have electric moment changes along the axis of greatest inertia (see fig. 2). The former two (intermediate moment) should have no Q branch, while the latter two (greatest moment) should[4]. From this criterion we would make the following frequency assignments, on the basis of the presence of a Q branch in the 11,250 Å. band:

$3\nu_a$	11,250 Å.
$2\nu_a + \nu_s$	11,410 Å.
$\nu_a + 2\nu_s$	11,620 Å.
$3\nu_s$	11,790 Å.

This agrees with the rule that an antisymmetric frequency is higher than the corresponding symmetric one. Another argument for this assignment is that the Q branch converges to the red, and the intensity distribution of the P and R branches indicates a similar convergence for them. Thus the moments of inertia decrease in the upper state. For a symmetrical vibration, an increase would surely be expected.

Looking at the molecule as an almost - symmetrical spindle rotator, both of the types of vibrations involved here are perpendicular to the pseudo-symmetry axis, and so should appear in

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(4) See in this connection the envelopes given by Badger and Zumwalt, J. Chem. Phys., 6, 711 (1938).

general like perpendicular - type bands[5]. This is not true for the 11,250 Å. band, however; it has the parallel - type envelope. There is really no anomaly here, however; it is very probably a breakdown of the approximation of considering the molecule to be a symmetric top.

The interpretation of the four 10,000 Å. bands as combinations follows from the Raman frequencies of the liquid[6]; there are four frequencies there between 1000 and 1300 cm.$^{-1}$ which might be involved in such a combination.

3. Formic Acid.

A partial analysis has been made of the rotational fine structure of the third and fourth harmonic O-H bands of formic acid monomer[7]. In this work, the third harmonic C-H band was similarly investigated under high dispersion. It was originally hoped in studying this band that it would be possible to find the intensity of the ${}^{Q}Q$ branch relative to its intensity in the O-H bands. In the C-H vibration, the change of electric moment is almost parallel to the intermediate axis of inertia, and the ${}^{Q}Q$ branch should be small. The O-H bands, on the other hand, involve a change of electric moment

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(5) The moments of inertia calculated from a likely model are 92, 81 and $16 \cdot 10^{-40}$ g. cm.^{2}

(6) Glockler and Leader, J. Chem. Phys., 7, 382 (1939).

(7) Bauer and Badger, J. Chem. Phys., 5, 852 (1937).
Thompson, J. Chem. Phys., 7, 453 (1939).

with components along both intermediate and minor axes of inertia, and consequently have a noticeable ^QQ branch. Because of background unevenness it was impossible to decide to what extent a ^QQ branch was present in the C-H band, but it surely was not very prominent.

Thompson[7] had reported this band at 11,700 Å., from low dispersion photographs. This was confirmed, and the rotational analysis described below shows it to belong to the monomer, so it is undoubtedly the third harmonic C-H stretching vibration.

Experimental Procedure and Results.

The formic acid used was Baker and Adamson's reagent grade. Distillation from a sodium formate -concentrated sulfuric acid mixture[8] in a one-foot column further removed water. The fraction used came over at 100.4 - 101.4° (uncorr.). The distillation system was protected from moisture by a P_2O_5 tube. The formic acid was then transferred to a trap on the absorption tube under conditions which excluded water.

The absorption tube was of glass, ten feet long, surrounded with a heating coil of iron wire, and asbestos wrapped. During exposures the tube was kept at 110 - 120°, and the trap containing the acid at

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(8) Hamel, Chem. Zent., (I), 1701 (1905).

95 - 105°. This gave about one atmosphere of pressure (normal boiling point is 101.8°). Under these conditions, the formic acid monomer pressure is about 400 mm.[9].

A 500 watt tungsten projection lamp was the light source. The twenty-one foot grating spectrometer was used, with slit at .2 mm., and other experimental details as described previously.

Because the band occurs in a very insensitive wave length region of the plate, it was found that plates fogged before being sufficiently exposed. Recourse was had to the use of a plano - convex cylindric lens which had been obtained and mounted for this purpose by Professor Badger. This has a focus of 25 cm., an aperture of 4.5 cm., and is six inches long, enough to cover the region of interest. The image is compressed vertically by a factor of three or more by this lens, allowing correspondingly shorter exposure periods.

The lens was placed with the plane side towards the grating. It was adjusted perpendicular to the beam from grating to plate by interposing a small mirror between the grating and lens, and setting the lens so that the light reflected from the plane surface came back toward the grating. The cylindric axis of the lens was adjusted parallel to the plane of dispersion by tilting until the yellow mercury arc lines as viewed from the plate position were vertical. The

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(9) Coolidge, J. Am. Chem. Soc., <u>50</u>, 2166 (1928).

focus of the grating is not greatly changed by the introduction of the lens. The focus was adjusted by trial, the grating carriage being moved until a focus plate of iron lines showed sharp focus. When finally adjusted, the iron lines were vertical, and self-reversal could be clearly seen. The lines were slightly broadened, the result of an aberration introduced by the cylindric lens[10]. The aberration is negligible compared to the slit width used here.

Since the cylindric lens made it impossible to place an iron arc reference spectrum alongside the absorption spectrum, calibration was effected in the following way. Some sharp atmospheric water lines which were off to one side and had not gone through the lens were used as references, and absorption maxima of the formic acid band measured relative to these on the comparator. A plate was taken of atmospheric absorption, using the cylindric lens, and an iron arc superposed on this. The arc lines that had gone through the lens and lay in the same region as the formic acid band were also measured relative to the same water lines, and the calibration thus accomplished.

Several formic acid plates were taken with the cylindric lens, of which two were sufficiently good to show some band structure,

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(10) Bowen, Astrophys. J., 88 (2), 113 (1938).

namely, several ${}^{P}Q$ and ${}^{R}Q$ branch maxima. The exposure times required were about 13 hours. Unfortunately, the backgrounds were extremely irregular, which made it difficult to measure the maxima accurately and impossible to tell about the presence or absence of a ${}^{Q}Q$ branch. Figure 3 shows the microphotometer trace of the band, obtained by superposing the two plates exactly and running them through the microphotometer. This removes some of the background irregularity and grain.

Discussion.

The formic acid monomer is almost a symmetrical top molecule, the two largest moments of inertia being nearly equal and much greater than the small. Thus the levels might be fitted by the expression:

$$\frac{W}{hc} = \delta J(J+1) + (\gamma - \delta)K^2 \quad , K \leq J$$

$$\delta = \frac{h}{8\pi^2 c} \cdot \frac{1}{2}\left(\frac{1}{A} + \frac{1}{B}\right)$$

$$\gamma = \frac{h}{8\pi^2 c} \cdot \frac{1}{C}$$

where A and B are the large moments of inertia and C the small one. This expression was found by Bauer and Badger[7] to fit the O-H bands very well, for $K > 3$. The ${}^{R}Q$, ${}^{Q}Q$, and ${}^{P}Q$ branch maxima are the transitions $\Delta K = +1$ with $\Delta J = 0$, $\Delta K = 0$ with $\Delta J = 0$, and $\Delta K = -1$ with $\Delta J = 0$ respectively.

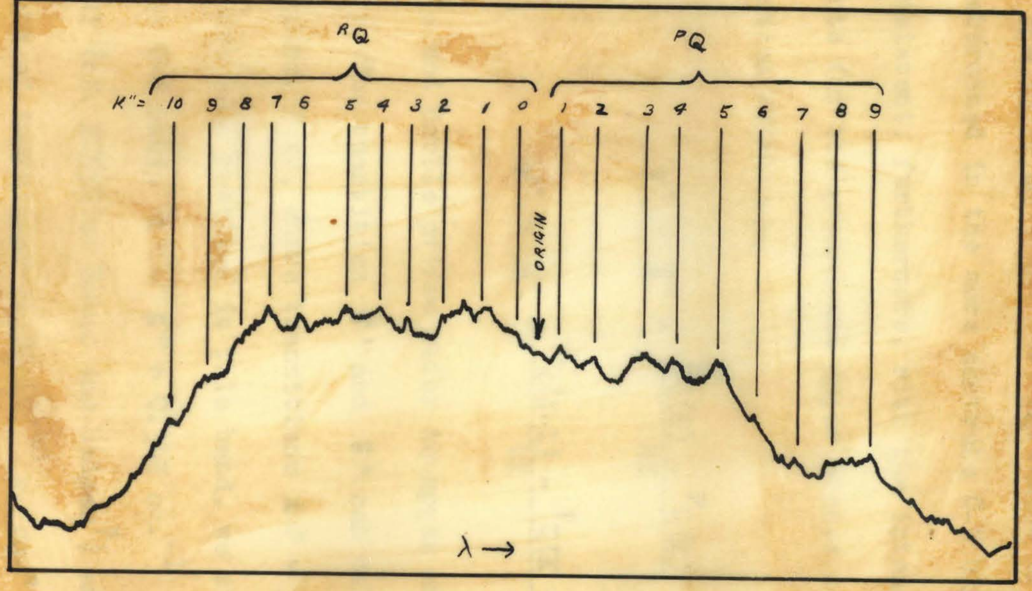

Figure 3. Microphotometer trace of HCOOH band at 11,700 Å.

Since a ${}^{Q}Q$ branch could not be picked out, there would be ambiguity in the numbering of the maxima according to K values in the lower state. The assignment of K was therefore made by choosing that numbering which gave the best agreement of $\gamma - \delta$ for the ground state as determined in the more accurate O-H band analyses. This is most consistent, furthermore, with the intensity distribution. The constants for the ground and upper states are calculated from the combination relations,

$$\gamma' - \delta' = \frac{{}^{R}Q(K) - {}^{P}Q(K)}{4K}$$

$$\gamma'' - \delta'' = \frac{{}^{R}Q(K-1) - {}^{P}Q(K+1)}{4K},$$

where single and double primes refer to upper and lower states respectively. The quantities δ' and δ'' can only be evaluated from P or R branches, i.e., where transitions $\Delta J = \pm 1$ occur. Since these have not been resolved in this band, we can again use the fact that for the O-H band, $\delta' = \delta'' = 0.348$ cm.$^{-1}$ Then we obtain $\gamma'' = 2.541$ (cf. 2.559 of Bauer and Badger[7]) and $\gamma' = 2.509$, giving small moments of inertia of $11.02 \cdot 10^{-40}$ g. cm.^{2} and $(11.16 \pm 10) \cdot 10^{-40}$ g. cm.^{2} is the ground and third C-H vibrational states respectively. The band origin is at 8507.7 cm.$^{-1}$

Table II. Frequencies and combinations of maxima in formic acid band at 8507.7 cm.$^{-1}$

K	^{R}Q	^{P}Q	$\frac{^{R}Q(K) - {}^{P}Q(K)}{4K}$	$\frac{^{R}Q(K-1) - {}^{P}Q(K+1)}{4K}$
0	8509.98			
1	8513.67	8504.81	2.215	2.170
2	8518.29	8501.30	2.124	2.256
3	8522.72	8495.62	2.258	2.202
4	8525.89	8491.87	2.126	2.219
5	8529.77	8487.22	2.128	2.165
6	8535.06	8482.59	2.186	2.177
7	8538.66	8477.53	2.183	2.214
8	8542,48	8473.07	2.169	2.188
9	8546.80	8468.63	2.171	
10	8550.04			

avg. $\gamma' - \delta$ for $K > 3$ = 2.161 ; avg. dev. .022

avg. $\gamma'' - \delta$ for $K > 3$ = 2.193 ; avg. dev. .019

The values are believed to be better than the average deviations indicate, since the deviations are less for the more accurately measureable higher K maxima.

PART II. STUDIES OF THE HYDROGEN BOND.

Abstract

Experiments on the freezing point depression of solutions of ethyl alcohol in carbon tetrachloride are described, and the association data derived therefrom are compared with spectroscopic measurements by others. It is concluded that the narrow O-H band in dilute solutions is due to monomers only. The O-H frequencies in the polymer are discussed. Monomer-dimer equilibrium constants for ethyl alcohol, benzyl alcohol, and phenol are compared. Widths of association bands of hydroxyl compounds are discussed, and the temperature effect on the frequency of association bands described. An elementary theory is given to explain these features of the association bands.

STUDIES OF THE HYDROGEN BOND

Although the phenomenon of hydrogen bonding has been recognized for several years and the spectroscopic study of it has brought forth a large number of papers, there are several questions concerning it about which little is known. The work described below is an attempt to further elucidate the questions of internal and free energy of hydrogen bond formation, and the interpretation of some of the spectroscopic details.

1. Freezing Point Depression of Solutions of Ethyl Alcohol in Carbon Tetrachloride.

Much work has been done on the study of hydrogen bonding by physical means (freezing point depression, distribution coefficients, etc.). It has generally been done with complicated molecules, however, and almost invariably in solvents such as benzene, where there is a large interaction with the solvent. This makes interpretation difficult if one is interested in hydrogen bonds themselves.

It was undertaken by Professor R. M. Badger and myself to measure the freezing point depression of solutions of ethyl alcohol in carbon tetrachloride, since here the results should be much less ambiguous.

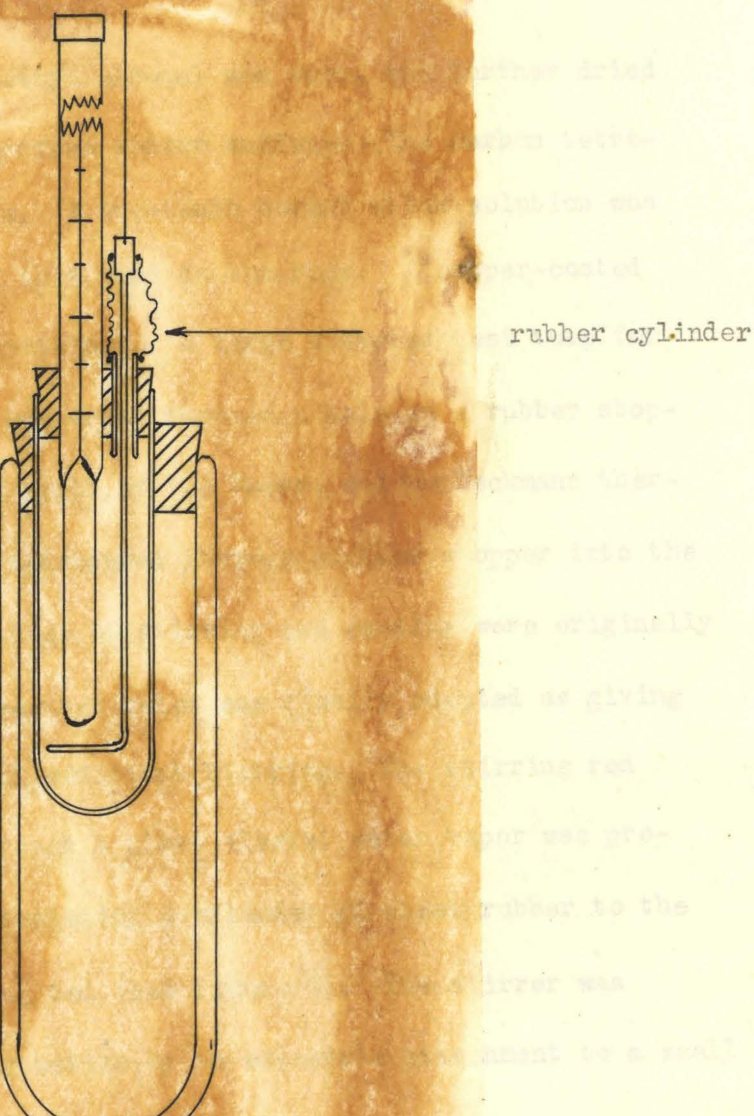

Figure 4. Freezing point apparatus.

Experimental Procedure.

Commercial absolute ethyl alcohol was used, and further dried for several days over anhydrous sodium sulfate. The carbon tetrachloride was reagent grade. A one-tenth normal stock solution was made up, and dilutions of this used in the runs. A copper-coated Dewar flask was used as container. A large diameter test tube for holding the solution was supported through a hole in a rubber stopper which fitted over the mouth of the Dewar, and the Beckmann thermometer and stirring rod introduced through another stopper into the test tube. Different methods of stirring and cooling were originally tried. The technique described below was finally adopted as giving a good rate of cooling and efficient stirring. The stirring rod entered the apparatus through a glass sleeve; water vapor was prevented from entering by fastening a cylinder of sheet rubber to the sleeve and to the stirring rod (see figure 4). The stirrer was driven in a reciprocating motion by an eccentric attachment to a small motor.

In making a run, the solution was cooled almost to the freezing point, and the Dewar separately cooled with cold acetone from a dry ice bath. The Dewar was emptied, and the tube containing the solution and thermometer placed in it. This resulted in a cooling rate which was sufficiently slow to give a good cooling curve. The temperature was read after 15 sec. intervals, using a telescope and reading to .001 degree. Cooling curves were constructed from the readings, and the freezing point read from these. Supercooling of about one-tenth degree was observed in nearly every case.

Results.

The results are given in Table III. Those on pure carbon tetrachloride and the dilute solutions are more discordant than the concentrated solutions, probably because the stirrer stuck due to the formation of larger crystals in the former case. The freezing point values are averages of from two to four good runs. The errors are estimated from the deviations.

The value of the freezing point lowering constant for non-associating molecules is taken from other sources[11], since it cannot be obtained with any certainty here by extrapolation. This quantity divided by the observed lowering per unit concentration gives the polymerization number, n, i.e., the average number of C_2H_5OH groups per molecule. Figure 5 shows the experimental values of n plotted against the formal concentration Q, with the estimated limits of error, and a smooth curve drawn through to represent the dependence.

Discussion.

It is readily shown that the limiting slope $\frac{dn}{dQ}$ is equal to the equilibrium constant of the reaction,

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(11) Beckmann and Wähtig, Z. Anorg. u allgem. Chem., 67, 17 (1910).

Table III. Freezing point depression measurements on solutions of ethyl alcohol in carbon tetrachloride.

formal conc. Q	freezing point** T	ΔT	$\frac{\Delta T}{Q}$	$n = \frac{KQ^*}{\Delta T}$
0	3.760±.012	0	(18.7)*	1.00
.0103	3.607±.014	.153±.026	14.8	1.26
.0258	3.425±.010	.335±.022	13.0	1.44
.0517	3.292±.004	.468±.016	9.05	2.03
.1033	3.028±.001	.732±.013	7.08	2.64

* Value for K, the lowering constant for non-associating molecules, from reference 11.

**Freezing point on the arbitrary scale of the Beckmann thermometer; the true freezing point of pure carbon tetrachloride is -22.9°C.

Table IV. Some of the association equilibrium constants for C_2H_5OH in CCl_4, as calculated by Lassettre's method.

	-23°	+20° E = 6000cal.	+20° E = 7000 cal.
K_2	29.5	4.99	3.72
K_3	1,006	28.8	16.00
K_4	37,000	178.7	74.0

Figure 5. Polymerization number vs. concentration, ethyl alcohol in CCl_4 at -23°, experimental values and assumed curve.

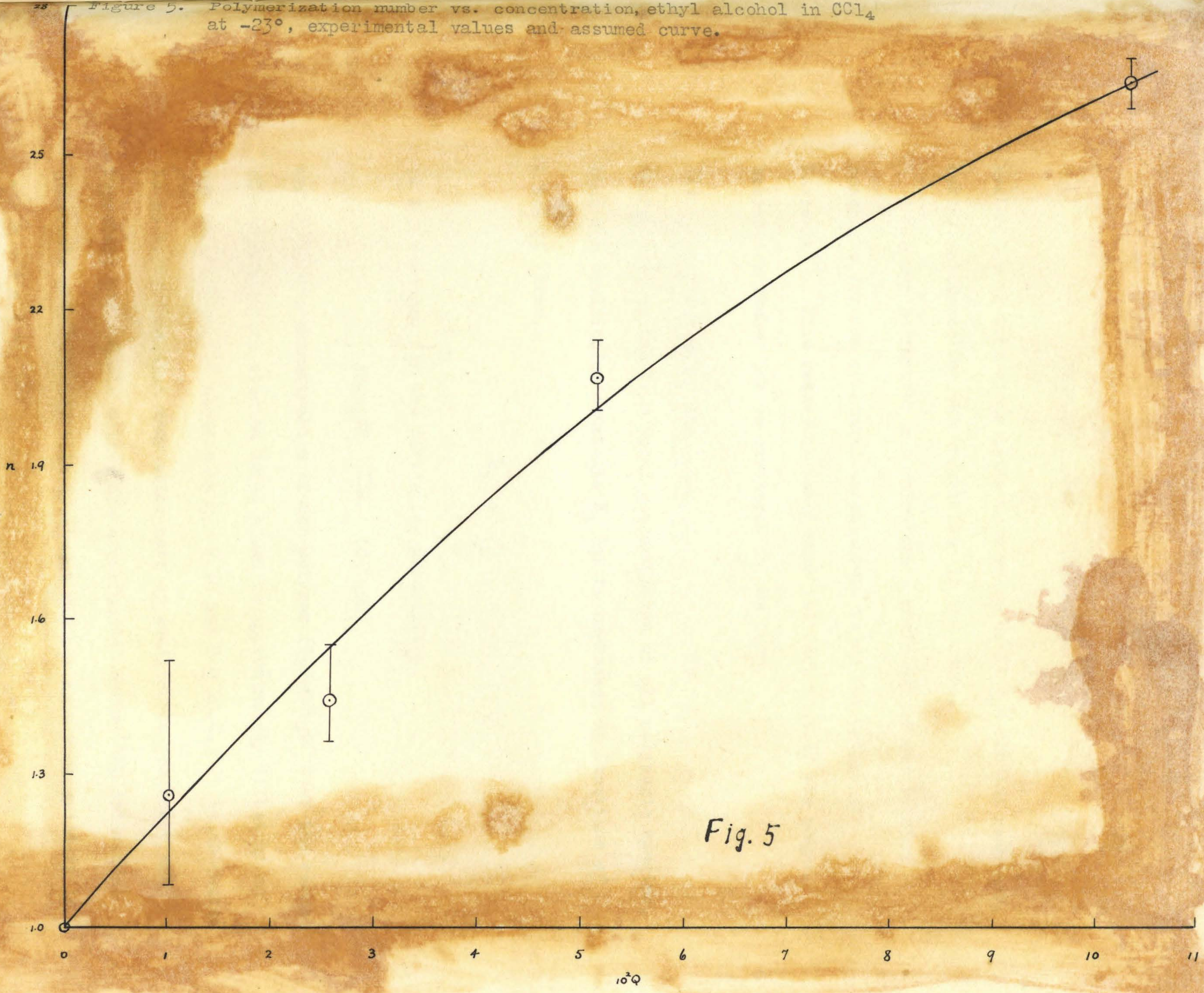

Fig. 5

$$2C_2H_5OH \rightleftarrows (C_2H_5OH)_2.$$

Evaluation of this slope leads to a value of 23 ± 4 for the constant, making allowance for the uncertainty in the curve.

One can go further and calculate a whole set of equilibrium constants for the continued association, using the method of Lassettre[12]. This method is based upon the fact that if the polymerization number can be expressed in the form,

(1) $n = 1 + \alpha Q + \beta N$,

where $N(=\frac{Q}{n})$ is the true total concentration of all polymeric species, then the equilibrium constants K_ℓ can be expressed as functions of α and β. Here,

$$K_\ell = \frac{C_\ell}{C_1^\ell}$$

is the constant for the particular association,

$$\ell C_2H_5OH \rightleftarrows (C_2H_5OH)_\ell ,$$

and C_ℓ is the concentration of the polymer $(C_2H_5OH)_\ell$. Over the range of concentrations studied here, n can be approximately fitted by an expression like (1) above with $\alpha = 9.10$ and $\beta = 20.4$. It is of course to be recognized that many other sets of equilibrium constants will represent the data to within the experimental error; the individual constants obtained from this treatment may not have much validity in

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(12) Lassettre, Chem. Rev., 20, 281 (1937).

themselves, but taken all together they very likely give a fair representation of the process of continued association.

Unfortunately the results of the freezing point measurements can not be directly compared with data obtained from other types of measurement made at room temperature. A correction of the equilibrium constants to room temperature has consequently been made as follows. We make the very reasonable assumptions that the association is completely due to hydrogen bond formation, and that the hydrogen bond energy is constant, irrespective of polymer size. However, we do not have a precise value for this energy. Estimates have been made from the heats of vaporization and sublimation of liquid ethyl alcohol, giving about 6800 calories per mole[13]. In solution in an inert solvent, we might expect about the same. Hydroxyl groups are capable of forming weak hydrogen bonds with carbon tetrachloride molecules, however, so in this solvent the energy should be reduced. Another estimate of the energy in solution can be obtained from the spectroscopic transmission curves published by Errera, Gaspart and Sack[14]. Curves are given for ethyl alcohol solutions in carbon tetrachloride at 20° and at 55°C. By finding a concentration at one temperature which has the same absorption curve as another concen-

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(13) Badger and Bauer, J. Chem. Phys., 5, 851 (1937).
Pauling, "Nature of the Chemical Bond," Cornell University Press (1939), p. 284.

(14) Errera, Gaspart and Sack, J. Chem. Phys., 8, 63 (1940).

tration at the other temperature, the ratio of equilibrium constants, and hence the energy, is approximately given by the ratio of these concentrations. The energy calculated in this way is between 6000 and 7000 calories. In Table IV are given some of the association constants as calculated from Lassettre's method, at -23° and also as corrected to +20°, assuming energy (heat content) values of 6000 and 7000 calories per mole. From these constants, curves have been calculated giving the monomer concentration versus formal concentration at +20° for each energy, and also true total concentration, N, versus formal concentration for each energy value. These curves are used later in the interpretation of spectroscopic results.

The estimation of the monomer-dimer constant from the limiting slope is valid, and makes no assumptions about the rest of the constants. The Lassettre treatment gives a somewhat different value for this constant because of the approximations inherent in it. Correcting the true constant from -23° to +20° using an energy of 6000 calories, we get 3.9 as the monomer-dimer constant at room temperature, with a large error possible due mainly to the lack of precise knowledge of the energy of the bond.

If one could measure the association by non-spectroscopic means at room temperature, one could obtain information about the energy quantities, and also have results that would be directly comparable with spectroscopic observations. A method is being developed to accomplish this by measuring deviations from Henry's law, but so far no results have been obtained.

It is to be expected that for aliphatic alcohols, association as measured by physico-chemical and by spectroscopic methods should be identical. For phenols, however, this might not necessarily be the case, since other types of association than by hydrogen bonds might occur.

2. Calculations on Quantitative Spectroscopic Measurements and Their Interpretation.

Perhaps the most direct and useful way to study the energy relations of hydrogen bonds is that of infra-red spectroscopy. In order to obtain reliable data by this method, it is necessary to be able to make accurate quantitative intensity measurements, to have good resolving power if narrow bands are being measured, and to go down to very low concentrations. Such measurements should give equilibrium constants at one temperature, and if carried out over a temperature range, should yield the energies of formation of the bonds. Only a very few papers have appeared in which many of these conditions are fulfilled. The lower aliphatic acids in the vapor phase have been studied over a temperature range by Hofstadter, Herman and co-workers[15], and the monomer-dimer energies determined.

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(15) Herman, J. Chem. Phys., 8, 252 (1940).

On solutions, there have appeared papers on ethyl alcohol[14], phenol[16,17,18] and benzyl alcohol[19], all in carbon tetrachloride.

Comparison of Freezing Point and Spectroscopic Data.

In default of being able to make exact absorption intensity measurements on ethyl alcohol in carbon tetrachloride to compare with the freezing point data, some of the published transmission curves of Errera, Gaspart and Sack[14] in the 3 μ region have been used for this purpose. These curves seem adequate for a rough quantitative treatment, although they were not so used by the authors. They cover the frequency range 3100 to 3750 cm.$^{-1}$, and concentration range from .125 to 8 volume per cent. They show the usual narrow band at 3640 cm.$^{-1}$ which is attributed to free hydroxyl groups and the very broad band extending from 3100 to 3600 cm.$^{-1}$ which is characteristic of the hydrogen bonded hydroxyl. In dilute solutions the narrow band is stronger, while in concentrated ones it is weaker than the broad association band.

The calculations presented below are on the narrow 3640 cm.$^{-1}$ band in dilute solutions at 20°C. The change of this band with concentration is compared with association data derived in the last

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(16) Fox and Martin, Proc. Roy. Soc. (London), A162, 419 (1937).
(17) Kempter and Mecke, Naturwiss., 27, 583 (1939).
(18) Wulf and Jones, J. Chem. Phys., 8, 745 (1940).
(19) Fox and Martin, Trans. Faraday Soc., 36, 897 (1940).

section. The spectral slit width was about one third of the half-width of the band, so that there should not be much falsification of the value of minimum transmission. The measurements made from the curves are given in Table V. The transmission coefficients for several frequencies were taken, and the formal absorption coefficients α calculated from the usual relation

$$\alpha = -\frac{1}{Q\ell} \log_{10} \frac{I}{I_o} ,$$

where Q is as before the formal concentration and ℓ is the path length in centimeters. The absorption coefficients were plotted, and small background corrections estimated. Since the shape of this band does not change noticeably with concentration, it is sufficient to take the maximum absorption coefficient minus the background correction as a measure of the strength of absorption, rather than the integrated area under the whole band. Fox and Martin[19] have investigated this procedure in detail for the sharp benzyl alcohol band, and found it to be valid. The values of corrected $\alpha_{max.}$ so calculated are given in the next to last column of Table V.

Errera et al. gave two sets of curves covering the concentration range of interest here: one set using a 1 mm. cell for the more concentrated solutions, and one set using a 5 mm. cell for the dilute solutions. One solution, .5 volume per cent, was run in both cells and there is a discrepancy between the two values of $\alpha_{max.}$ which is too large to be accounted for by errors in transmission measurements. It is in all probability due to errors in measuring

Table V. Calculation of absorption coefficients of maximum of 3640 cm.$^{-1}$ band, ethyl alcohol in carbon tetrachloride (from transmission curves of Errera, Gaspart and Sack, J. Chem. Phys., 8, 63 (1940).)

volume percent	formal conc. $\mathcal{Q}$	transmission $T = I/I_0$	ℓ	α	α*	α**
.125	.0214	.238	.5	58.2	56	56
.25	.0427	.110	.5	44.8	43	43
.5	.0854	.0275	.5	36.5	34.5	34.5
.5	.0854	.425	.1	43.5	41.5	34.5
.75	.1282	.321	.1	38.5	36.5	30.5
1.0	.1709	.276	.1	32.7	30.5	25.5

* Corrected for background

** Corrected for cell discrepancy

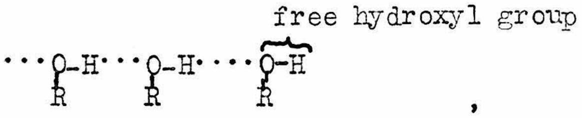
the cell lengths; indeed, correcting the $\alpha_{\text{max.}}$ values for the 1 mm. cell by a multiplicative factor so that the .5 volume per cent solutions match makes all the $\alpha_{\text{max.}}$ values fall on a fairly smooth curve (see last column of Table V).

The $\alpha_{\text{max.}}$ so calculated is not constant, as it would be for substances which do not associate, but is related to the concentration of absorbing groups, C_a, thus:

$$\alpha_{\text{max.}} = \frac{C_a}{Q}\,\alpha_o \qquad , \tag{2}$$

where α_o is the true absorption coefficient of absorbing groups, and is a constant independent of concentration (assuming the Lambert-Beer law, of course).

As to the identification of the absorbing groups, two ways of interpreting the 3640 cm.$^{-1}$ band have been suggested. Either it is due to all the hydroxyl groups which have not acted as the donor of a hydrogen bond (free hydroxyl groups), of which there are one per polymer irrespective of size:



$$\cdots\underset{R}{O}\text{-H}\cdots\underset{R}{O}\text{-H}\cdots\overbrace{\underset{R}{O}\text{-H}}^{\text{free hydroxyl group}} \quad ,$$

or else it is due to the monomers only, the frequency of the free hydroxyl groups on the polymers being changed simply because the oxygen has become the acceptor of a hydrogen bond. In the first case, the quantity C_a in (2) is N, the total concentration of all polymers; in the second case, C_a is C_1, the monomer concentration.

Now by choosing an appropriate value for α_0 and knowing the dependence of N and C_1 on Q from the freezing point data, we can match the spectroscopic data. In figure 6 are plotted the five spectroscopically measured points that fall in the concentration range covered by the freezing point measurements. There are also shown calculated curves, which were constructed from the curves mentioned on p. 27 giving the dependence of C_1 and N on Q assuming the two values for ΔE. An α_0 was chosen in each case to give the best fit. Two of the curves shown are on the assumption that only monomers absorb, and two that all polymers absorb. It is seen that no one of the curves fits well, although the 6000 calorie one fits best; the inaccuracy in the spectroscopic points is one or two units of α, so too good a fit is not to be expected. It seems reasonably clear, however, that the assumption that all polymers absorb gives too flat a curve to fit the points; i.e., the rate of falling off of absorbing groups with increase in concentration is too slow if we assume all polymers absorb. Hence we can conclude that the narrow 3640 cm.$^{-1}$ band is due to monomers only.

In all three papers on phenol referred to above[16,17,18], the authors made the assumption of regarding the absorption at the narrow band as due to monomers only, and fitted their data fairly well by choosing appropriate equilibrium constants and absorption coefficients. The procedure described above, however, which uses equili-

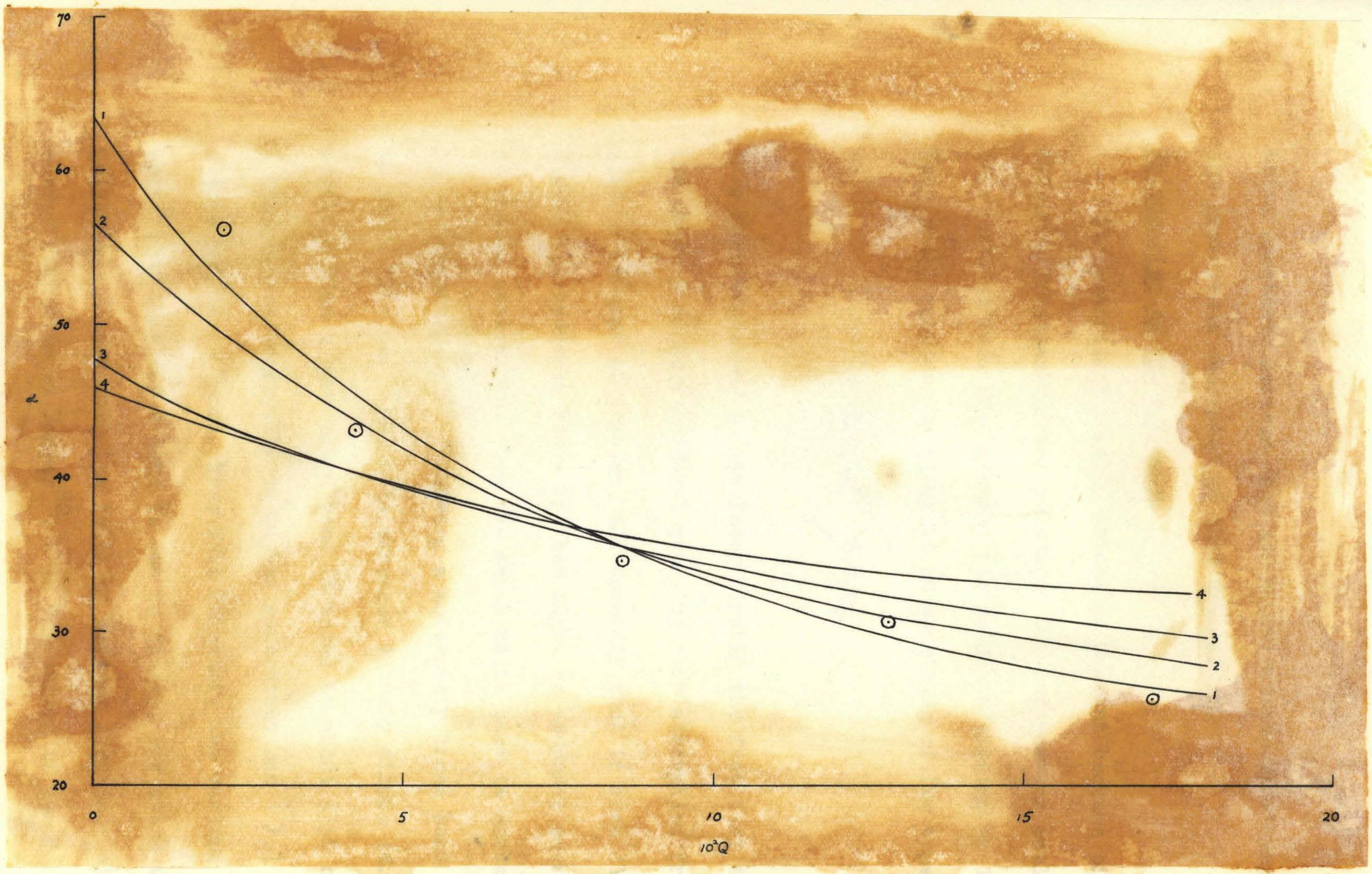


Figure 6. Formal absorption coefficient vs. concentration, ethyl alcohol in CCl_4.

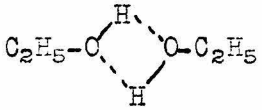
⊙ - experimental
1 - calculated, absorption by monomers, $\Delta E = 6000$ cal.
2 - " " " " $\Delta E = 7000$ cal.
3 - " " " polymers, $\Delta E = 6000$ cal.
4 - " " " " $\Delta E = 7000$ cal.

brium constants derived from non-spectroscopic measurements, removes the gratuitous character of this assumption.

Frequencies of the Polymers.

The question naturally arises as to what becomes of the free hydroxyl frequency of the polymer. One explanation would be that there are no such free groups, the polymers closing up in rings. This would require the dimer to be something of the type,

(3)



This hypothesis has in its favor firstly the fact that it explains the absence of free hydroxyl group polymer absorption from the region of monomer absorption, and secondly that if such dimers as (3) occur, the hydrogen bonds in them might be somewhat weaker because of steric conditions. Now the association band is actually found to be composite,[15,16,19] having a moderately broad band (A band) at about 3500 cm.$^{-1}$ which is stronger in very dilute ($<$.1 molar) solution than a very broad band (B band) at about 3350 cm.$^{-1}$. The B band increases rapidly in higher concentrations ($>$.1 molar), and swamps out the A band. From this behavior, the various authors have postulated that the A band is due to dimers, and the B to higher polymers. If one uses the relation between frequency shift and energy suggested by Badger[20], then the energy of the dimer bond would

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(20) Badger, J. Chem. Phys., 8, 288 (1940).

	monomer band	association A	bands B
Ethyl alcohol (Errera, Gaspart and Sack	3640 cm.$^{-1}$	3525	3325
Phenol (Fox and Martin)	3610	3470	3370
Benzyl alcohol (Fox and Martin)	3620 3640	3490	3350

be less by a factor of about one-half than that for higher polymers, as would be expected for the weaker bonds of a dimer such as (3). The presence of two such bonds per dimer would, however, make the total energy of dimerization about the same as that of an ordinary bond, i.e., about 6000 cal. Regarding this hypothesis of the cyclization of polymers, however, one is a little inclined to question the stability of such complexes as (3), and, on grounds of entropy, the stability of larger cyclic polymers. However, some apparently very strong evidence in favor of dimers of the form of (3) can be adduced from dipole moment calculations made by Wilson[21] on ethyl alcohol in n-hexane solution, from the data of Smythe and Stoops[22]. It is found that when μ^2/μ_g^2 is plotted against concentration, where μ/μ_g is the ratio of dipole moments in solution and in vapor, the curve first decreases, going down from unity at zero concentration

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(21) Wilson, Chem. Rev., 25, 400 (1939).
(22) Smythe and Stoops, J. Am. Chem. Soc., 51, 3312 (1929).

to 0.6 at 0.4 molar, and then rises uniformly to the very high values characteristic of the large polymers. The initial decrease indicates that the dimers have a smaller electric moment than the monomers. If one assumes that the monomer moment is identical with that of the vapor and the dimer moment is zero (as Wilson suggested), and uses the equilibrium constant 3.9 of monomer-dimer association of ethyl alcohol in carbon tetrachloride, then a curve of μ^2/μ_g^2 can be calculated which fits the Wilson curve fairly well in the region of small concentration, where trimers and higher polymers are unimportant. The deviations from perfect fit are such that if one used a larger constant, as would be anticipated in passing from carbon tetrachloride, which bonds slightly to the hydroxyl group, to hexane, which has very little interaction with the alcohol, then the fit would be better.

There are other possible explanations for the A and B bands, however. For instance, the A band might be the shifted free hydroxyl frequency of the polymers, assuming they do not form rings, while the B band is due to the hydrogen bonded hydroxyls in the polymer. A priori, we would expect these free hydroxyls of the polymers, if they have their frequency shifted at all, to have it shifted to lower frequency[23]. This explanation of the A and B bands suffers from

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(23) The band in aliphatic alcohol and acid liquids and concentrated solutions at ca. 9100 Å (to the high frequency side of the third harmonic monomer band) found by Badger and Bauer, J. Chem. Phys., 5, 839 (1937), must be attributed to some sort of an overtone in the higher polymers and is not the shifted free hydroxyl frequency as assumed by Pauling, "Nature of the Chemical Bond," p. 307. No such band has been reported in the fundamental or second harmonic regions.

the disadvantage that from the great deal of work that has been done on intra-molecular hydrogen bonds it is known that the acceptor oxygen does not have its hydroxyl frequency changed[24]. This might conceivably be due to some difference between inter- and intra-molecular bonds.

In any case, it should be possible to distinguish experimentally between these two hypotheses, since the A band is in the first case due to dimers, and in the second to all polymers. Careful spectroscopic measurements might decide whether it increases with concentration as the dimer does, or as all the polymers. None of the work so far published is adequate to make a decision in this manner, however.

It seems most probable that the true state of affairs is between the two extremes of complete cyclization or none. The explanation of the A band as due to the dimer in the form (3) seems to fit all the facts and does not contradict the evidence from intra-molecular bonds, as an open dimer would. In the higher polymers, there are probably both chain and ring configurations, with the number of free hydroxyls from polymers comparatively small so that in dilute solution they are negligible compared to the monomer.

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(24) e.g., compare the curves for catechol and phenol given by Wulf and Liddel, J. Am. Chem. Soc., 57, 1464 (1935).

Free Energy of Hydrogen Bond Formation.

It is of interest to compare the known equilibrium constants of monomer-dimer association.

Wulf and Jones[18] obtained a value of 1.7 for the association constant of the phenol reaction,

$$2C_6H_5OH \rightleftarrows (C_6H_5OH)_2 \ ,$$

at 25°C. Correcting this to 20°, using an energy of 6000 calories, we obtain 2.0. Kempter and Mecke[17] found this constant to be 2.3 at an unspecified room temperature.

From Fox and Martin's work on benzyl alcohol[19], the constant for this monomer-dimer equilibrium has been calculated from the published values of $\alpha_{max.}$ of the A band. Using this band as a measure of dimer concentration, which is valid in dilute solution regardless of whether this band has contributions from higher polymers at higher concentrations or not, the equilibrium constant can be obtained from the limiting first and second derivatives of the formal absorption intensity $\alpha_{max.}$ with respect to concentration. The relations are,

$$\left(\frac{d\alpha_{max.}}{dQ}\right)_{Q=0} = \alpha_o K$$

$$\left(\frac{d^2\alpha_{max.}}{dQ^2}\right)_{Q=0} = 8\ \alpha_o K^2$$

where a_0 is the true absorption coefficient of the dimer at the maximum of the A band, and K is as usual the constant for the association,

$$K = \frac{C_2}{C_1^2} .$$

The value obtained in this manner for benzyl alcohol is .46.

Tabulating the values (for monomer-dimer constants in carbon tetrachloride) that have been obtained so far:

	K(CCl_4 solution)	ΔF° of association
Ethyl alcohol	3.9	-800 cal.
Phenol	2.0	-410
Benzyl alcohol	.46	+450

The inaccuracies in the constants are not believed great enough to change the order. If the energies of the bonds are about the same in the three cases, then the free energies follow the order one would expect from the relative entropies: the larger the radical, the greater the probability of dissociating the dimer.

3. Widths of Association Bands.

One of the most striking features of the infra-red absorption band associated with the hydrogen bond is its great width as compared with other vibrational bands. The band of methyl alcohol in liquid or concentrated solution in the third harmonic, for example, has a half-width (width at half of maximum intensity) of around 700 $cm.^{-1}$.

Two rough empirical generalizations concerning the width of association bands have become evident from some studies made by the author and from absorption curves published by others. One of these is that the width of the association band formed by a given molecule bonding itself to various other molecules is roughly proportional to the frequency shift. Figure 7 illustrates this on methyl alcohol in the third harmonic region. Methyl alcohol monomers form weak hydrogen bonds with carbon tetrachloride, as mentioned previously; this is indicated by a shift of the monomer frequency of 25 cm.$^{-1}$ in this solvent from its frequency in the relatively inert solvent petroleum ether[25]. This shift is accompanied by a slight broadening, as indicated in figure 7. Furthermore, dilute methyl alcohol solutions in benzene show the hydroxyl band to be shifted very considerably and correspondingly broadened. This rather large effect is undoubtedly due to the high polarizability of the aromatic ring. These two cases together with the liquid alcohol band are shown in figure 7, and indicate the trend of the width with the frequency shift.

A second generalization which can be made regarding the width of association bands is that the width increases by a factor of two or more in the second harmonic and of three or more in the third

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(25) This frequency shift might be explained in other words as due to the increased electrostatic interaction of the hydroxyl dipole with the more polarizable chlorine over the less polarizable hydrocarbon molecules. This is just what we understand as a hydrogen bond in cases where the interaction is more pronounced, however, so it seems not unjustified to call this a weak hydrogen bond.

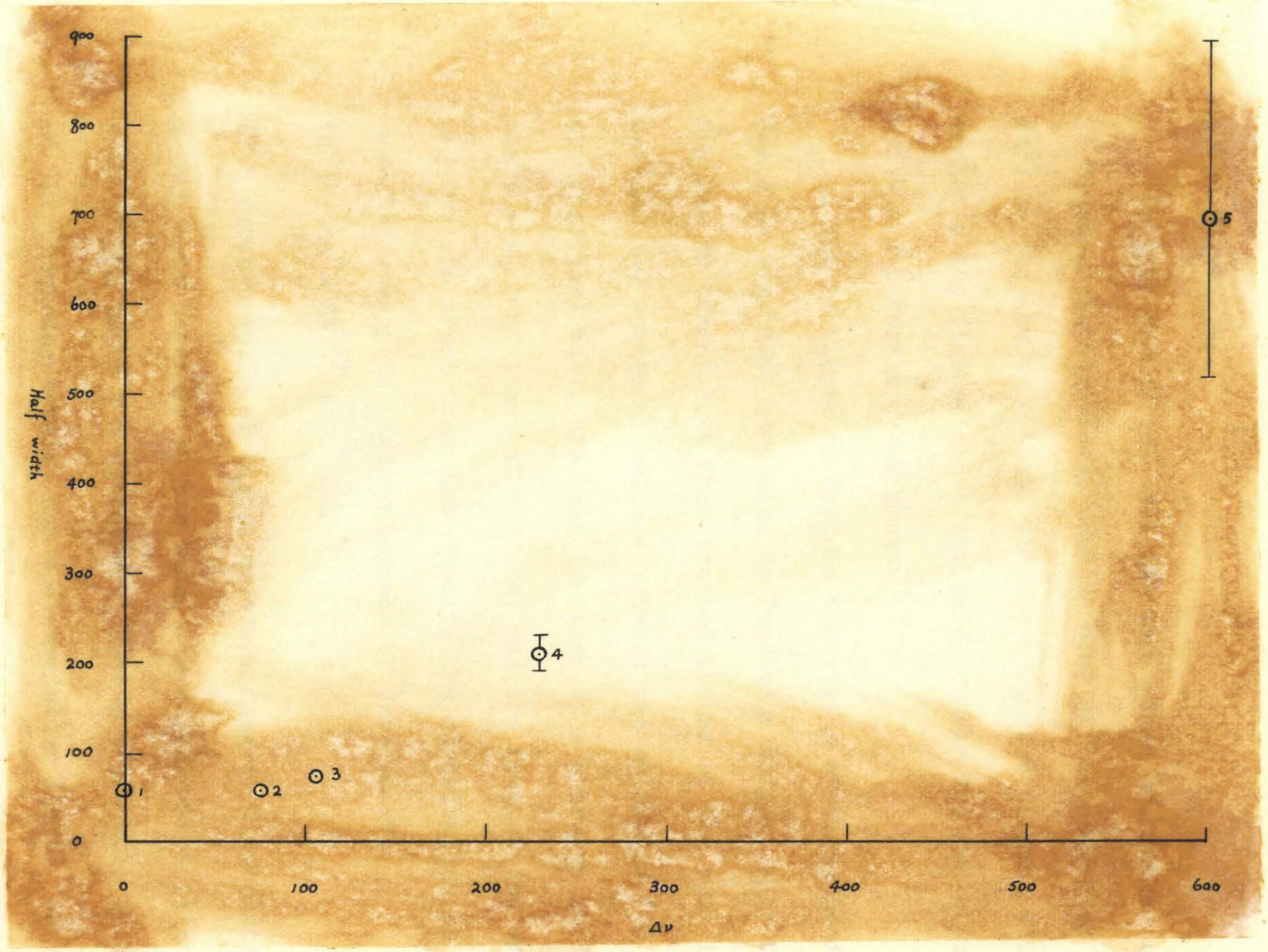

Figure 7. Half-widths of CH_3OH third harmonic OH band vs. frequency shift.

1. vapor
2. petroleum ether solution
3. CCl_4 solution
4. benzene, solution
5. liquid methyl alcohol

over that in the fundamental. Table VI shows the available data on a few molecules.

It will be noticed that the data given are rather meager; this is because the dispersion used in most of the published hydrogen bond work is too low to obtain reliable estimates of band widths. Nevertheless, the figures given indicate roughly the relation between width and harmonic given above.

A simple theory to explain the widths of these bands can be based on the idea, suggested by Professor Badger, that the bands are due to transitions from excited states of the very low frequency bending and torsional motions between two molecules (or clusters of molecules) which are held together by a hydrogen bond. Assuming there are m of these vibrations, and the frequencies are so low that we can treat them classically, the distribution of the systems over the energy in these m degrees of freedom is,

$$(4) \qquad dn = CE^{m-1}\, e^{-\frac{E}{kt}}\, dE.$$

At a certain value of energy corresponding to dissociation of the groups held together by the bond, the distribution is cut off. For each of the upper O-H vibrational levels there will be a similar set of low frequency levels, and a dissociation limit. An energy level diagram would appear as shown in figure 8. An association band is now to be understood as due to transitions from the whole group of lower levels to a group of upper ones. If we neglect any variation

Table VI. Half-widths of some association bands
(half-widths in $cm.^{-1}$)

	Fundamental	2nd harmonic	3rd harmonic
Methyl alcohol	180[a]		700[b]
Ethyl alcohol	200[c]	500[d]	700[b]
Phenol	310[e]		
Benzyl Alcohol	220[f]		

[a] Buswell, Deitz and Rodebush, J. Chem. Phys., 5, 501 (1937).

[b] Badger and Bauer, J. Chem. Phys., 5, 839 (1937).

[c] Errera, Gaspart and Sack, J. Chem. Phys., 8, 63 (1940).

[d] Errera and Sack, Trans. Faraday Soc., 34, 728 (1938).

[e] Fox and Martin, Proc. Roy. Soc. (London), A162, 419 (1937).

[f] Fox and Martin, Trans. Faraday Soc., 36, 897 (1940).

in transition probability among the group of lower levels, then the band intensity distribution will be entirely determined by the population distribution in the lower group. To discuss the transitions, it is necessary to know how the two sets of levels interact, i.e., how a level corresponding to a certain set of quantum members of the low frequency vibrations changes as we change the O-H vibrational quantum number. From the fact that the bands do get wider as we go to successively higher harmonics, we can say that the low frequency levels must spread apart in the upper O-H vibrational states, the more so the higher the state.

This is illustrated by the transitions shown in figure 8. Because of the spreading apart of the levels in the third O-H vibrational level, the absorption arising from molecules in the energy regions indicated at the bottom of the transition arrows occurs at different frequencies; hence the association band is broad, since it includes contributions from the whole lower group of levels. The main part of the intensity will undoubtedly come from transitions in which the low frequency vibration quantum numbers do not change; contributions to the intensity from transitions in which these change also will not affect the main argument, but will result in some additional broadening.

This spreading apart of the levels must increase with harmonic, as remarked above, to explain the increase in width with harmonic. In order to make rough numerical calculations, it will be necessary

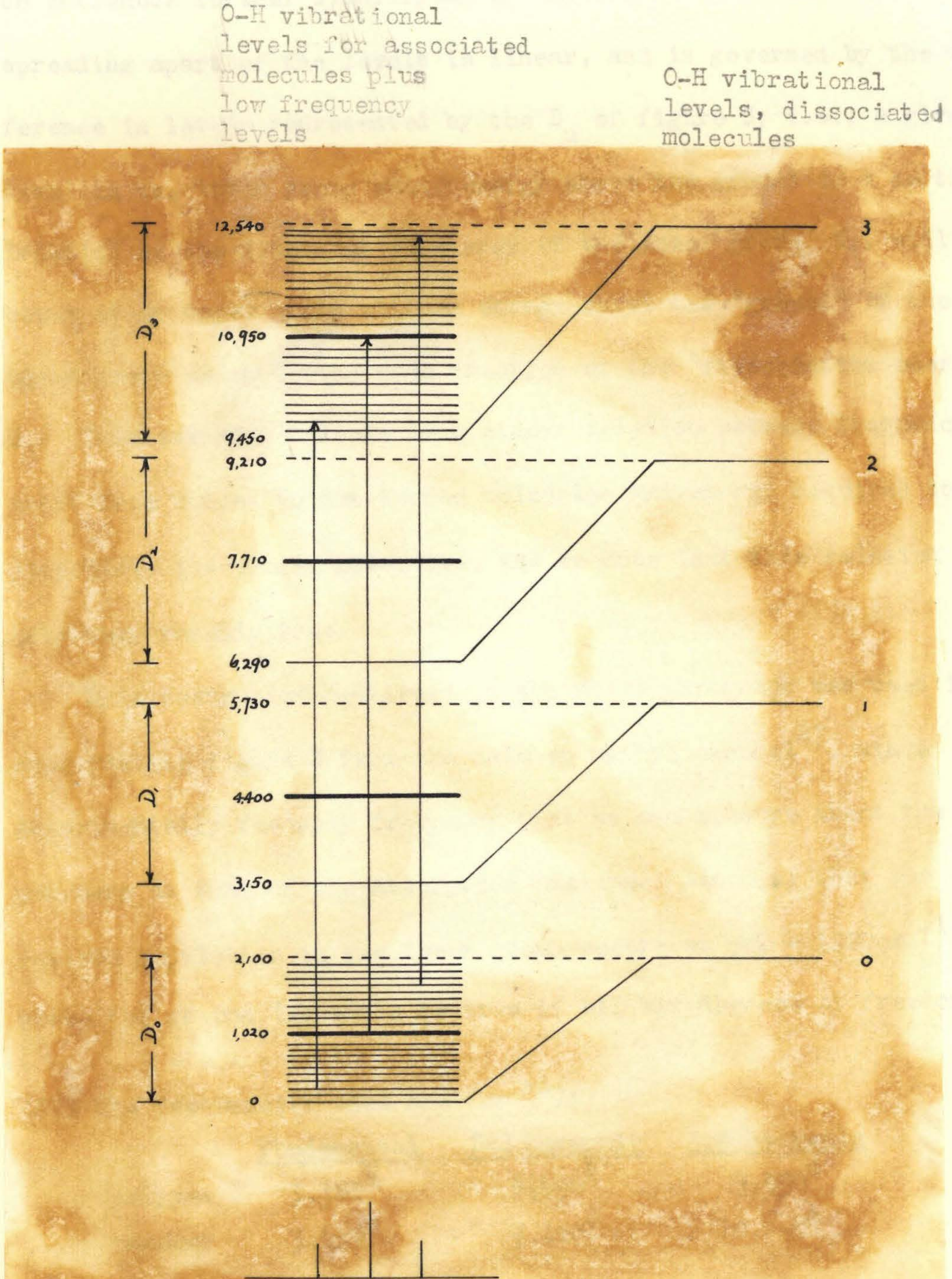

Figure 8. Energy level diagram for association of methyl alcohol.

to introduce further simplifying assumptions. We assume that the spreading apart of the levels is linear, and is governed by the difference in levels represented by the D_n of figure 8; i.e., a given level in the lower group whose energy above the ground is a certain fraction of the dissociation energy of the lower group, D_0, will occur in an upper group with an energy above the "ground" of the upper group which is the same fraction of the "dissociation energy", D_n. This assumption leads to a linear relation between frequency shift from bonded to non-bonded molecules and energy required to dissociate the bonded molecules, and we know that this relation is only very roughly true.

This assumption mentioned in the above paragraph was used in constructing figure 8 from the data on methyl alcohol[27], since experimentally the only frequency that we can measure about the polymers is that of the absorption maximum. Assuming that the maximum population in the lower group occurs at $5kT = 1020 \text{cm.}^{-1}$ above the ground (as would be true if all six degrees of freedom

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(27) The frequencies used are (cm.^{-1}):

	fundamental	2nd harmonic	3rd harmonic
polymer	3,380[a]	6,690[b]	9,930[d]
monomer	3,630[a]	7,110[c]	10,440[d]

[a] Buswell, Deitz and Rodebush, J. Chem. Phys., 5, 501 (1937).
[b] Calculated from quadratic term value expression
[c] Wulf and Liddel, J. Am. Chem. Soc., 57, 1464 (1935).
[d] Badger and Bauer, J. Chem. Phys., 5, 839 (1937).

in the bond were of low enough frequency to be classically excited), and taking the dissociation energy in the ground state as 6000 cal. = 2100 cm.$^{-1}$, we can construct the polymer levels combining with the level of maximum population in the lower group from the known polymer frequencies. These are the levels 4400, 7710, and 10,950 cm.$^{-1}$ The "ground" of each upper group is then calculated from the relative positions in the lowest group.

Now if we assume, as mentioned before, that molecules in levels of energy E in the lowest group make transitions principally to levels in the upper groups of the same low frequency vibration quantum members, then the principal absorption for these molecules will occur at a frequency,

(5) $\nu = 3150 + \frac{D_1 - D_o}{D_o} E$ in the fundamental,

$\nu = 6290 + \frac{D_2 - D_o}{D_o} E$ in the second harmonic, etc. Furthermore, molecules in the lower group which are separated by an energy ΔE give rise to absorption frequencies to an upper group which are separated by a frequency difference,

$$\frac{D_n - D_o}{D_o} \Delta E \quad .$$

Since we assume intensity is governed only by the lower group population, this means that the quantity, $\frac{D_n - D_o}{D_o}$, which we obtain from frequency data only, should be a measure of the relative widths of the harmonics. The calculated relative widths turn out to be,

fundamental	480
2nd harmonic	820
3rd harmonic	890 .

Comparing this with Table VI , it is seen to give an increase of only two from the third harmonic to the fundamental, against the experimental factor of more than three. The fact that a large change is predicted is satisfying; considering the assumptions made, not much better agreement could be expected.

The theory also accounts qualitatively for the relation between frequency shift of one type of molecule bonding to various other types, and width of band. In terms of figure 8, this means that the intervals between levels of the dissociated molecules remain constant from one bond acceptor to another, but those of the associated molecules move closer together the stronger the bond formed, causing the quantities D_n to become large, and consequently produce a wide band.

Another effect which the theory accounts for roughly is that of the increase of frequency of maximum absorption of the association band with temperature. According to the picture given above, this is due to the change in population distribution in the lowest group of levels. The frequency of maximum absorption in the third harmonic is given, according to (5), by,

$$\nu = 9450 + \frac{D_3 - D_0}{D_0} E_{max.}$$

We have taken $E_{max.}$ to be 5kT, so that

$$\frac{d\nu}{dT} = \frac{D_3 - D_0}{D_0} 5kT = 1.5 \frac{cm.^{-1}}{degree} .$$

This can be compared with the experimental value of 1 cm.$^{-1}$ per degree, obtained from photographs taken in this laboratory over a temperature range of -80° to +71° C. Again, considering the assumptions, the agreement seems to be satisfactory.

An attempt has been made[26] to explain the breadth of association bands as due simply to a superposition of combination bands from low-lying states of low frequency vibrations to an upper group of such states. The breadth is presumably due to the combination frequencies only; this however, does not explain the change in width with harmonic, or the temperature shift. The necessary thing is the interaction between the O-H vibrational levels and the low frequency levels, so that the ~~different~~ spacings in the lower and upper groups of levels is different and thus accounts for the breadth.

In conclusion, it might be worthwhile to summarize the present status of our knowledge regarding hydrogen bonds. For the compounds that have been studied most exhaustively, namely the hydroxyl-

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(26) Davies and Sutherland, J. Chem. Phys., 8, 755 (1938).

containing molecules, a rather good qualitative idea can be had of the process of hydrogen bond formation and the spectroscopic changes associated with it. Precise quantitative data are, however, noticeably lacking. Knowledge about bonds formed by other than hydroxyl groups is still in a rather empirical stage; in the case of bonding by amino groups, which is of prime importance, this is due to the increased complexity introduced by the presence of two N-H bonds.

PART III. THE RAMAN SPECTRA OF $CCl_2F-CClF_2$ AND $CClF_2-CClF_2$.

THE RAMAN SPECTRA OF $CCl_2F - CClF_2$ AND $CClF_2 - CClF_2$.

In connection with the question of the configuration of ethane-like molecules, some information might be expected to come from the Raman spectra of halogen substituted ethanes. Several of these spectra have been published[28]. Fluorine derivatives have not been studied so extensively, because of their unavailability until rather lately. The spectra of $CH_3 - CF_3$[29] and $CCl_2F - CCl_2F$[30] have appeared. This series has now been further extended by the author and Mr. R. A. Spurr to include $CCl_2F - CClF_2$ and $CClF_2 - CClF_2$. The compounds were obtained through the courtesy of Dr. A. F. Benning of the DuPont de Nemours Company. They were used without any further purification. The boiling points are 47.7° and 3.55° respectively. For the high-boiling compound, the liquid was poured into the Raman tube, in which it was kept from evaporating simply by a cork. The low-boiling one was distilled into the Raman tube, and the tube sealed off.

The spectrometer used had a dispersion of 7 mm. between the 4046 and 4358 Å. mercury lines. The mercury arc was of glass, and water cooled. Eastman D-C ortho plates were used. Exposure times

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(28) See the bibliography given by Hibben, "The Raman Effect and its Chemical Applications," Am. Chem. Soc. Monograph Series, Reinhold (1939).
(29) Yost and Hatcher, J. Chem. Phys., 5, 992 (1937).
(30) Glockler and Sage, J. Chem. Phys., 8, 291 (1940).

were of the order of 18 to 24 hours. The spectra were calibrated from an iron arc reference spectrum, employing a quadratic dispersion equation and a correction chart. Wave lengths are accurate to better than one Ångstrom.

For the $CCl_2F - CClF_2$, no filters were used; this was the first compound run and showed no decomposition on exposure. Scattering was measured from all three mercury lines, 4046, 4077, and 4358 Å. Some subsequent compounds, however, were decomposed, so on the $CClF_2 - CClF_2$ a saturated sodium nitrite solution was used as filter. This cut out nearly all of the 4046 and 4077 Å. mercury lines, so that the only scattering line used was the 4358. The plates showed very little background.

The observed frequencies are given in Table VII.

We have available several other fluorine and mixed chlorine-fluorine derivatives of ethane, which will be done in the future. So far no analysis has been made of the spectra obtained.

Table VII. Raman frequencies of $CCl_2F - CClF_2$ and $CClF_2 - CClF_2$.

$CCl_2F - CClF_2$

ν (cm.$^{-1}$)	intensity	exciting lines
171	vwb	a', c
208	vvw	a', c
248	w	a, a', b, c, c'
290	w	a, a', c, c'
318	w	a, a', b, c
352	vw	a, c
394	vw	a, b, c
443	m	a, b
461	m	a, b
508	w	a, b, c
532	w	a, b, c
654	s	a, b, c
902	wb	a, b, c
1048	w	a, b, c
1102	vvw	a, c
1112	vw	a, b
1211	w	a, c

$CClF_2 - CClF_2$ (all excited by 4358)

170	w	
255	m	anti
314	m	anti
327	m	
359	vvw	
403	vvw	
443	s	anti
500	m	
547	w	
679	s	
702	s	
1058	w	
1117	w	
1170	m	
1250	m	

Abbreviations: b (under intensity) = broad
a scattered from 4048 Å.
b scattered from 4077 Å.
c scattered from 4358 Å.
prime - anti-Stokes line measured.
anti- anti-Stokes line measured.

SUMMARY OF THESIS

In Part I, the absorption of formaldehyde and difluoro-methane in the photographic infra-red region is described and discussed, and the third harmonic C-H band of formic acid under high dispersion is described and partially analyzed, yielding the small moment of inertia and the band origin.

In Part II, a study of the association of ethyl alcohol in carbon tetrachloride solution by the freezing point method is presented. The results are compared with published spectroscopic work, and conclusions drawn as to the interpretation of the spectra. Equilibrium constants of monomer-dimer association are presented and compared. Widths of association bands and the temperature shift of these bands are described and interpreted.

Part III gives the Raman spectra of $CCl_2F-CClF_2$ and $CClF_2-CClF_2$.

ACKNOWLEDGEMENTS

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Propositions.

1. Dry gelatin saturated with heavy water will exchange its hydrogen for deuterium in a period of 48 hours at room temperature. This leads to doubt about the interpretation of infra-red bands of gelatin +D_2O given by Ellis and Bath, J. Chem. Phys., 6, 727 (1938).

2. 3N solutions of KCl, KNO_3 and KCNS in water do not have any effect measurable by photographic methods on the frequency or intensity of the water band at 9700 Å. This behavior is different from that reported for some other bands.

3. A possible way of making correlations between force constants and internuclear distances for diatomic molecules might be to assume a simple potential function with only a few constants, to calculate these constants for a large number of known molecules, and to look for regularities in the way the constants change with the constituent atoms. Such constants would have more physical significance than the constants of empirical relations such as Badger's rule, and might lend themselves more readily to use with polyatomic molecules.

4. The theory of symmetry groups can be used to obtain rather simply some of the infra-red rotational selection rules for molecular spectra. For example, it indicates the absence of a Q branch in parallel vibrations of linear molecules.

5. Laue photographs of phenol crystals show that they are monoclinic, and not orthorhombic, as stated by Groth, "Chemische Krystallographie," W. Engelmann, Leipzig (1917), Vol. 4, p. 72. In view

of the fact that no monohydroxy alcohols have been done, this crystal should have its complete structure worked out. The results will have an important bearing on the theories of hydrogen bonding, on the explanation of dielectric properties of alcohols, and on entropy calculations on alcohols from calorimetric data.

6. The vapor absorption spectrum of trimethylene glycol ($CH_2OH-CH_2-CH_2OH$) in the photographic infra-red shows that it does not form an intra-molecular hydrogen bond, whereas ethylene glycol (CH_2OH-CH_2OH) does.

7. A great deal of evidence has accumulated showing that molecules with permanent dipoles, or even molecules with no permanent dipole but with high polarizability, interact strongly and form complexes with aromatic rings. Therefore the continued use of benzene as a solvent in association studies, spectroscopic work, kinetics studies, etc., seems ill considered, since it makes the problem of theoretical interpretation more difficult. Carbon tetrachloride, or better a saturated hydrocarbon, is preferable.

8. Some confusion has existed in the literature regarding the definition of the energy of a hydrogen bond (e.g., see Fox and Martin, Trans, Faraday Soc., 36, 908 (1940).). This is unwarranted, since the energy is naturally defined as that required to pull two bonded molecules apart from their position of minimum energy to infinity; the relation of this energy to other energy quantities of the system

is clearly shown if an energy surface is drawn, using as coordinates the distance of the hydrogen from the atom to which it is chemically bonded, and its distance from the atom to which it is hydrogen bonded.

9. A simple theory of hydrogen bond formation can be based on the assumption that the attractive potential between a hydrogen atom on one molecule and a polarizable group on another molecule follows an R^{-4} law (which is the law for a free charge and a polarizable body). The dependence of the frequency shift $\Delta\nu$ on the bond energy E then comes out,

$$\Delta\nu = kE^{\frac{3}{2}} ,$$

for bonds to atoms of the same polarizability. This is very closely the shape of the empirical curve given by Badger, J. Chem. Phys., 8, 288 (1940).

10. In the scheme of correlation of statistical and thermodynamic quantities proposed by Tolman, "The Principles of Statistical Mechanics," Oxford (1938), ch. XIV, the three correlations made are,

statistical	thermodynamic
$E_{avg.}$	E
ψ	A
Θ	kT

where $E_{avg.}$, ψ, and Θ are the statistical quantities of a Gibbs canonical ensemble; E, A, and T are the thermodynamic internal energy, work function and temperature respectively; and k is the Boltzmann constant. It is sufficient, however, only to make the first two.

It then follows that,

θ = CT, where C is a function of volume satisfying a certain differential equation. C = k is a particular solution of this equation.